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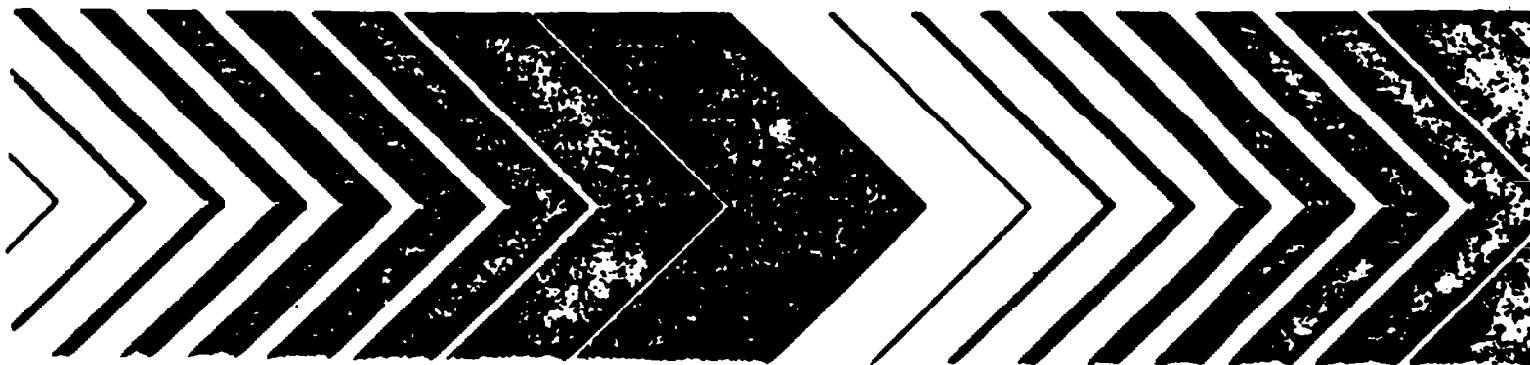
Water Quality Assessment:

A Screening Procedure for Toxic and Conventional Pollutants in Surface and Ground Water—Part I (Revised—1985)

WATER QUALITY ASSESSMENT:
A Screening Procedure for Toxic
and Conventional Pollutants
in Surface and Ground Water

(Revised 1985)
Part 1

by

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ABSTRACT

New technical developments in the field of water quality assessment and a reordering of water quality priorities prompted a revision of the first two editions of this manual. The utility of the revised manual is enhanced by the inclusion of methods to predict the transport and fate of toxic chemicals in ground water, and by methods to predict the fate of metals in rivers. In addition, major revisions were completed on Chapter 2 (organic toxicants), Chapter 3 (waste loadings), and Chapter 5 (impoundments) that reflect recent advancements in these fields.

Applying the manual's simple techniques, the user is now capable of assessing the loading and fate of conventional pollutants (temperature, biochemical oxygen demand-dissolved oxygen, nutrients, and sediments) and toxic pollutants (from the U.S. EPA list of priority pollutants) in streams, impoundments, estuaries, and ground waters. The techniques are readily programmed on hand-held calculators or microcomputers. Most of the data required for using these procedures are contained in the manual.

Because of its size, the manual has been divided into two parts. Part I contains the introduction and chapters on the aquatic fate of toxic organic substances, waste loading calculations, and the assessment of water quality parameters in rivers and streams. Part II continues with chapters on the assessment of impoundments, estuaries, and ground water and appendices E, H, I, and J. Appendices D, F, and G are provided on microfiche in the EPA-printed manual. Appendices A, B, and C, which appeared in the first two editions, are now out of date and have been deleted.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

In 1977, the United States Environmental Protection Agency published Water Quality Assessment: A Screening Method for Nondesignated 208 Areas (Zison, et al., 1977). This document was intended as a simplified methodology that water quality planners in nondesignated 208 areas could use to perform preliminary assessments of surface water quality. The methods addressed both point and nonpoint sources of pollutants including nutrients, sediments, dissolved oxygen deficits, temperature, salinity, and coliforms in rivers, lakes, and estuaries. The methodology was applied to the Sandusky River in northern Ohio, to the Ware, Patuxent, and Chester Rivers in Virginia and Maryland, and to the Occoquan Reservoir in Virginia. Test results were favorable (Dean et al., 1981). and some urban pollutants in streams, lakes and estuaries.

In 1982 the screening methods were revised and updated to include toxic organic chemicals in surface waters (Mills et al., 1982). The methods were demonstrated for a formaldehyde spill in the Russian River, California (Mills and Porcella, 1983), and for synfuel contamination of rivers (Mills and Porcella, 1984).

1.2 PURPOSE AND SCOPE

Due to increased emphasis on contaminant transport in ground waters and on contamination by heavy metals in all natural waters, the screening methods have been expanded to address these issues. This report contains a simplified methodology which can be used by planners or engineers to perform preliminary assessments of toxic and conventional pollutants in surface and ground waters. Conventional pollutants include suspended sediments, nitrogen, phosphorus, coliform bacteria, BOD, temperature, and dissolved oxygen deficits. The 129 EPA priority pollutants are included in the sections on toxic chemicals. Much data are supplied by figures and tables in the text and appendices. An additional source of data for many rate constants used in this manual is Bowie et al., 1985. All the algorithms are intended to be used on desk-top calculators, or on microcomputers. Many of the environmental chemistry, ground water, and river algorithms have been put on microcomputer (Mills et al., 1985).

Where instructive, introductory material has preceded the actual presentation of water quality assessment methodologies. This is done to orient the planner toward pertinent background material, as well as to clearly state limitations of the methodologies due to assumptions and simplifications. Further, example calculations are included to illustrate the ideas being presented. These examples are designed to unify the theory that has preceded it, as well as in some cases to introduce new but related ideas.

The units most commonly used in this report are those that historically appear in the literature. Often, the units are not metric. Consequently an English-metric-conversion appendix is included at the end of this report. Many equations are presented with both English and metric constants.

The report is divided into six major chapters (two through seven). A brief description of the content of each chapter is presented in the following paragraphs:

- Chapter 2 deals with the environmental chemistry of toxic organic chemicals. Processes considered include photolysis, hydrolysis, volatilization, biodegradation and adsorption. The purpose of the chapter is to provide an understanding of the processes and to provide procedures for estimating associated rate and equilibrium constants.

- Chapter 3 addresses methods to estimate pollutant loads from nonpoint and point sources for both toxic and conventional pollutants. Procedures include load estimation for single events and annual loads from agricultural, forested, and urban areas.

- In Chapter 4, impacts of point and nonpoint sources of conventional and toxic pollutants in rivers are addressed. Conventional pollutants include BOD-DO, temperature, coliform bacteria, nutrients, and sediment transport. Fate of toxic organic chemicals is assessed with consideration being given to the importance of volatilization, sorption and first order degradation. Metals are also assessed, and emphasis is given to nine priority metals. MINEQL is used to predict aqueous solubility and speciation of the metals in natural waters around the country. Methods are also presented to handle large spills of toxic chemicals having density the same as or different from the receiving waters.

- Chapter 5 contains methods for assessing water quality in impoundments. The topics covered are sediment accumulation, thermal stratification, BOD-DO interactions, eutrophication, and fate of toxic materials. The physical/chemical processes governing the fate of toxicants as well as biological uptake and bioconcentration are considered.

- In Chapter 6, methods are presented for estuary classification, flushing time prediction, and transport of conservative and non-conservative pollutants and dissolved oxygen in well-mixed estuaries. For stratified estuaries, Pritchard's box model is used to determine the distribution of conservative materials. Additionally, methods are presented to calculate initial dilution from a waste water discharge and pollution distribution at the completion of and subsequent to initial dilution.

- Chapter 7 presents the methodology necessary to predict the transport and fate of ground water contamination from typical sources. Sets of

tables are provided to give representative values and methods of measurement for the required ground water hydrology and transport parameters. In addition, five analytical models are presented with worked out examples to show how contaminant sources such as solute injection wells, leaky ponds, landfills, and spills can be handled.

1.3 METHODOLOGY APPLICATION

For each category in the methodology, the six conceptual steps shown below can be followed to screen a river basin:

- Obtain necessary tools and data to make calculations
- Identify problems that are obvious from inspection of the data base
- Determine the state variables which will be screened
- Apply procedures and compare where possible to observed data
- Consider consequences of errors
- Reevaluate and make recommendations for further analyses or remedial actions.

The techniques in the screening procedure are designed to interact which makes them ideal for use as an analytical tool for river basin surface waters which may include rivers, lakes, and/or estuaries. Although the procedures may interact, they can be applied individually and with identified data sets for specific case studies.

1.3.1 Base Maps

The first step in the screening process can be to obtain large scale topographic maps of the study area. These can be used to determine which water bodies are to be examined and to establish an order of study. Once this has been done, selected small scale (7 1/2-minute or 15-minute series) topographic sheets can be obtained. On these, the planner can locate and mark point source discharges, regions of specific kinds of land use, population centers, and industrial complexes. Use of overlays or push pins may be helpful in preparing these displays.

1.4 LIMITATIONS

The processes which govern the fate of pollutants in the environment are complex. Any methodology, particularly one designed for hand calculation or microcomputer applications, cannot be inclusive of all of these processes. An attempt has been made in each chapter to cover the assumptions under which algorithms are developed. Users should be aware of the assumptions, potential errors, and limitations of the tools presented. When deficiencies are noted or the methods deemed inappropriate, the user should be prepared to use a higher level analytical tool.

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CHAPTER 2

AQUATIC FATE OF TOXIC ORGANIC SUBSTANCES

2.1 INTRODUCTION

2.1.1 Background

Today's technological society generates enormous quantities of chemicals both as products for consumption and as waste. As the volume and number of chemicals has increased, numerous unintended adverse effects of these chemicals have been observed in the environment. Because of the potential hazard that exposure to these compounds poses to biota, the levels of toxic and carcinogenic substances in the environment have become important criteria for evaluating environmental quality.

The level, or concentration, of a toxic compound in the environment depends on the quantity added to the environment and the processes which influence its fate. "Transport" processes tend to distribute chemicals between the atmospheric, aquatic, and soil environments depending on the affinity of the compound for each phase. "Transformation" processes within each phase chemically alter pollutants to forms of lesser, equivalent, or sometimes greater toxicity. These processes occur at rates which are specific to each chemical and to each environmental compartment. The sum of these processes and their interactions, as Figure II-1 illustrates, determines the environmental fate and consequent exposure of biota to a toxic pollutant. The fate of toxic substances in the aquatic environment is the concern of this chapter. The algorithms presented in this chapter have recently been programmed on microcomputers (Mills et al., 1985).

2.1.2 Comparison of Conventional and Toxic Pollutants

Toxic substances frequently exhibit properties which are quite different from the properties of conventional aquatic pollutants. It is worthwhile to compare these differences in order to better appreciate the problems of analyzing impacts of toxicants in surface water systems. Table II-1 shows some of the more important differences.

Typically, one to two dozen pollutants and water quality parameters are classified as "conventional". Until the past several years, these parameters (e.g. BOD, nutrients) have received most of the attention of water quality planners. In contrast to the small number of conventional pollutants there are thousands of toxicants and many more synthetic chemicals are continually being developed. Potentially, any of these toxicants could enter the environment.

Even though there are relatively few types of conventional pollutants, numerous sources combine to routinely discharge large quantities. However, because many surface water bodies have a capacity to assimilate conventional pollutants (e.g. BOD) without apparent adverse effects, this practice is, within limits, both acceptable and pragmatic. Toxic substances, on the other hand, can cause adverse effects

AIR

CHEMICAL

WATER

SOIL SEDIMENT

BIOTA
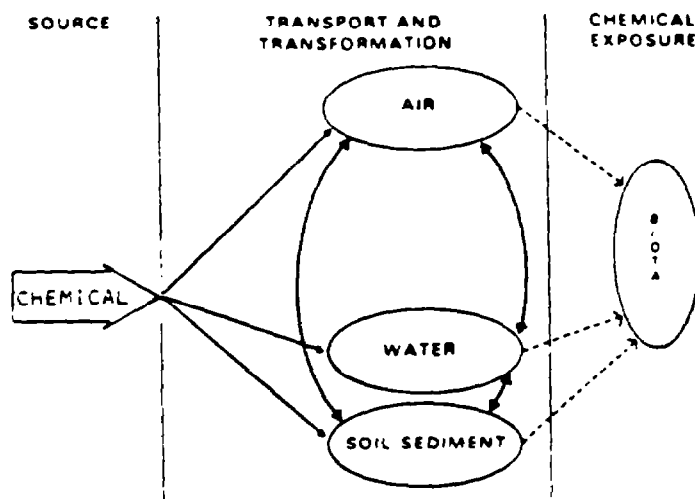
FIGURE II-1   ENVIRONMENTAL FATE OF A TOXIC
POLLUTANT (AFTER HAQUE, 1980)

TABLE II-1

BRIEF COMPARISON OF CONVENTIONAL AND TOXIC POLLUTANTS

Conventional	Toxic
One to two dozen pollutants fall into this category	Thousands fall into this category; many more being synthesized
Often large quantities required to produce impact (e.g. thousands lbs/day)	Small quantities can produce impact (e.g. few lbs/day)
Concentrations often expressed as ppm (mg/1)	Concentrations often expressed as ppb (μg/1), or in smaller units
Often travel in dissolved form	May be highly sorbed to suspended and bedded sediments
Mean residence time within water bodies often equal to or less than the mean residence time of moving waters	Can reside in bedded sediments for years
Many biodegrade into harmless substances	Many are transformed to chemicals which are also toxic; others are resistant to degradation and bioconcentrate

even at low discharge rates.

Concentrations of conventional pollutants are most often expressed in units of ppm (or mg/l). Because of the small quantities of toxicants which are typically released, concentrations are often expressed in the ppb (or μg/l) range, or in even smaller units. This represents at least a thousandfold difference relative to concentrations of conventional pollutants. However, because toxic substances present in small amounts can adversely impact the environment, these small concentrations can not always be ignored.

Many conventional pollutants are transported in dissolved form. The mean residence times of dissolved, conservative pollutants in a system is equivalent to the mean residence time of water in the system, which is:

- The hydraulic detention time for freshwater lakes
- The travel time for freshwater rivers
- The flushing time for estuaries.

Many toxic chemicals strongly sorb to suspended and bedded sediments and consequently can become a part of the immobile sediments in the bed. The residence time of such chemicals can be on the order of years. Therefore, depending on the properties of the toxicant the period of impact can greatly exceed the period of discharge (e.g., a PCB spill may occur in a few minutes, but quantities of the PCB may remain in immobile, bedded, sediments for years). Consequently the recovery period of a system can be years.

2.1.3 Water Quality Criteria

As previously indicated, toxicants are presented in the environment in quantities which are often measured in the ppb range. Such small concentrations are often foreign to many workers in the field. When data or model predictions contain concentrations in the ppb range, the significance of the toxicant level is not always obvious (i.e., there is no "feel" as to whether the concentration is large or small). Proposed criteria for toxic substances can serve as a basis to gauge the significance of observed or predicted levels. Table II-2 shows proposed criteria for numerous toxicants. Since proposed criteria evolve over time the criteria shown in the table are not necessarily the most current. Nevertheless, their function remains: to provide a comparison with levels observed or predicted in real systems. The data in these tables come from the "Red Book" (U.S. EPA, 1976) and the Federal Register, March 15, 1979; July 25, 1979; October 1, 1979; and November 28, 1980. Criteria designed to protect human health, for levels of toxicants in domestic water supplies, are available from these same sources as well.

2.1.4 Frequency of Discharge of Toxic Substances from Industries

Numerous organizations, including the U.S. Department of Transportation and the U.S. Environmental Protection Agency, continually collect and analyze data on the

TABLE II-2

PROPOSED CRITERIA FOR TOXIC SUBSTANCES DESIGNATED

TO PROTECT AQUATIC LIFE

	Freshwater			Saline Water		
	24 Hour Average µg/l	Maximum µg/l	"Red Book" µg/l	24 Hour Average µg/l	Maximum µg/l	"Red Book" µg/l
Acenaphthene	LD[a]	1700[b]		710[c]	970[b]	
Acrolein	21[c]	68[b]		LD	55[b]	
Acrylonitrile	2600[c]	7550[b]		LD	LD	
Aldrin/Dieldrin	0.0019	2.5	0.003	0.0019	0.71	0.003
Antimony	1600	9000		LD	LD	
Arsenic	40[c]	440[b]		LD	508[b]	
Asbestos	LD	LD		LD	LD	
Benzene	LD	5300[b]		700[c]	5100[b]	
Benzidine	LD	2500		LD	LD	
Beryllium	5.3[c]	130[b]	11.-1100	LD	LD	
Cadmium	d	e	0.4-1.2[f] 4.0-12.0[g]	4.5	59	5.0
Carbon Tetrachloride	620	1400		2000	4000	
Chlordane	0.0043	2.4	0.01	0.0040	0.09	0.004
Chlorinated benzenes						
Chlorobenzene	1500[h]	3500[h]		120[h]	280[h]	
1,2,4 - Trichlorobenzene	210[h]	470[h]		3.4[h]	7.8[h]	
1,2,3,5 - Tetrachlorobenzene	170[h]	390[h]		2.6[h]	5.9[h]	
1,2,4,5 - Tetrachlorobenzene	97[h]	220[h]		9.6	26	
Pentachlorobenzene	16[h]	36[h]		1.3[h]	2.9[h]	

TABLE II-2

(Continued)

	Freshwater			Saline Water		
	24 Hour Average μg/l	Maximum μg/l	"Red Book" μg/l	24 Hour Average μg/l	Maximum μg/l	"Red Book" μg/l
Chlorinated Ethanes						
1,2 - Dichloroethane	3900^h	8000^h		880^h	2000^h	
1,1,1 - Trichloroethane	5300^h	12000^h		240^h	540^h	
1,1,2 - Trichloroethane	310^h	710^h		LD	LD	
1,1,1,2 - Tetrachloroethane	420^h	960^h		LD	LD.	
1,1,2,2 - Tetrachloroethane	170^h	380^h		70^h	160^h	
Pentachloroethane	440^h	1000^h		38	87	
Hexachloroethane	62^h	140^h		7.0^h	16^h	
Chlorinated Naphthalenes	29	67		2.8	6.4	
Chlorinated Phenols						
4 - Chlorophenol	45	180		LD	LD	
2,4,6 - Trichlorophenol	52	150		LD	LD	
Chloroalkyl Ethers	LD	LD		LD	LD	
Chloroform	500	1200		620^h	1400^h	
2 - Chlorophenol	60	180		LD	LD	
Chromium (Hexavalent)	0.29	21	100	18	1260	
Copper	5.6	1	j	4.0	23	j
Cyanide	3.5	52	5.0	LD	LD	5.0
DDT	0.00023	0.41	.001	0.0067^h	0.021^h	.001

TABLE II-2

(Continued)

	Freshwater			Saline Water		
	24 Hour Average μg/l	Maximum μg/l	"Red Book" μg/l	24 Hour Average μg/l	Maximum μg/l	"Red Book" μg/l
Dichlorobenzenes						
1,2 - Dichlorobenzene	44	99		15[h]	34[h]	
1,3 - Dichlorobenzene	310[h]	700[h]		22[h]	49[h]	
1,4 - Dichlorobenzene	190[h]	440[h]		15[h]	34[h]	
3,3' - Dichlorobenzidine	LD	LD		LD	LD	
Dichloroethylenes						
1,1 - Dichloroethylene		11600		224000		
1,2 - Dichloroethylene		11600		224000		
2,4 - Dichlorophenol	0.4	110		LD	LD	
Dichloropropanes and Dichloropropenes						
1,1 - Dichloropropane	410	930		LD	LD	
1,2 - Dichloropropane	920	2100		400[h]	910[h]	
1,3 - Dichloropropane	4800	11000		79	180	
1,3 - Dichloropropene	18	250		5.5[h]	14[h]	
2,4 - Dimethylphenol	38	86		LD	LD	
Dinitrotoluenes						
2,3 - Dinitrotoluene	12	27		4.4[h]	10[h]	
2,4 - Dinitrotoluene	620	1400		LD	LD	
1,2 - Diphenylhydrazine	17	38		LD	LD	
Endosulfan	0.042	0.49	0.003	LD	LD	0.001

TABLE II-2

(Continued)

	Freshwater			Saline Water		
	24 Hour Average μg/l	Maximum μg/l	"Red Book" μg/l	24 Hour Average μg/l	Maximum μg/l	"Red Book" μg/l
Endrin	0.0023	0.18	0.004	0.0023	0.037	0.004
Enthylbenzene	LD	LD		LD	LD	
Fluoranthene	250[h]	560[h]		0.30	0.69	
Haloethers						
4 - bromophenylphenly ether	6.2	14		LD	LD	
Halomethanes						
Chloromethane	7000	16000		3700[h]	8400[h]	
Bromomethane	140	320		170[h]	380[h]	
Dichloromethane	4000[h]	9000[h]		1900[h]	4400[h]	
Tribromomethane	840[h]	1900[h]		180	420	
Heptachlor	0.0038	0.52	0.001	0.0036	0.053	0.001
Hexachlorobutadiene	LD	LD		LD	LD	
Hexachlorocyclohexane						
Lindane	0.080	2.0		LD	0.16	
Other isomers	LD	LD		LD	LD	
Hexachlorocyclopentadiene	0.39	7.0		LD	LD	
Isophorone	2100	4700		97	220	
Lead	k	l	m	25[b]	668[b]	
Mercury (total)	0.2	4.1	0.05	0.10	3.7	0.10

TABLE II-2

(Continued)

	Freshwater			Saline Water		
	24 Hour Average $\mu g/l$	Maximum $\mu g/l$	"Red Book" $\mu g/l$	24 Hour Average $\mu g/l$	Maximum $\mu g/l$	"Red Book" $\mu g/l$
Naphthalene	LD	LD		LD	LD	
Nickel	n	o	p	7.1	140	p
Nitrobenzene	480	1100		53	120	
Nitrophenols						
2 - Nitrophenol	2700[h]	6200[h]		LD	LD	
4 - Nitrophenol	240[h]	550[h]		53	120	
2,4 - Dinitrophenol	79[h]	180[h]		37[h]	84[h]	
2,4 - Dinitro-6-methylphenol	57[h]	140[h]		LD	LD	
2,4,6 - Trinitrophenol	1500[h]	3400[h]		150[h]	340[h]	
N-Nitrosodiphenylamine	LD	LD		LD	LD	
Pentachlorophenol	6.2	14		3.7	8.5	
Phenol	600	3400		LD	LD	
Phthalate esters	LD	LD	3.0	LD	LD	
Polychlorinated biphenyls	0.014	2.0[b]	0.001	0.030	10[b]	0.001
Polynuclear aromatic hydrocarbons	LD	LD		LD	LD	
Selenium	35	260	p	54	410	p
Silver	0.0090	1.9	p	0.26	2.3	p
2,3,7,8 - Tetrachlorodibenzo-p-dioxin	LD	LD				
Tetrachloroethene	310	700		79	180	

TABLE II-2

(Continued)

	Freshwater			Saline Water		
	24 Hour Average $\mu g/l$	Maximum $\mu g/l$	"Red Book" $\mu g/l$	24 Hour Average $\mu g/l$	Maximum $\mu g/l$	"Red Book" $\mu g/l$
Thallium	LD	LD		LD	LD	
Toluene	2300[h]	5200[h]		100	230	
Toxaphene	0.013	1.6	0.005	LD	0.07	0.005
Trichloroethene	1500	3400		LD	LD	
Vinyl chloride	LD	LD		LD	LD	
Zinc	47	q	p	58	170	

Source: The criteria in this Table are from the following sources:

- "Red Book" (U.S. EPA 1976)

- Federal Register on these dates:

    March 15, 1979 - July 25, 1979 - October 1, 1979 - November 28, 1980

[a]LD denotes lack of data.

[b]Acute toxicity level.

[c]Chronic toxicity level.

[d]The value in $\mu g/l$ should not exceed exp [1.05 ln (hardness) -8.53] where hardness is expressed in mg/l as $CaCO_3$.

[e]The value in $\mu g/l$ should not exceed exp [1.05 ln (hardness) -3.73] where hardness is expressed in mg/l as $CaCO_3$.

[f]0.4 mg - 1.2 mg/l for cladocerans and salmonid fishes.

[g]4.0 mg - 12.0 mg/l for other, less sensitive aquatic life.

[h]Values derived using procedures other than the guideline.

TABLE II-2

(Continued)

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[i]The value in μg/l should not exceed exp [0.94 ln (hardness) -1.23], where hardness is expressed in mg/l as $CaCO_3$.

[j]For freshwater and marine aquatic life, 0.1 times a 96 hr LC_{50} as determined through nonaerated bioassay using a sensitive aquatic resident species.

[k]The value in μg/l should not exceed exp [2.35 ln (hardness) -9.48] where hardness is expressed in mg/l as $CaCO_3$.

[l]The value in μg/l should not exceed exp [1.22 ln (hardness)-0.47] where hardness is expressed in mg/l as $CaCO_3$.

[m]0.01 times the 96 hour LC_{50} value, using the receiving or comparable water as the diluent and soluble lead measurements (using an 0.45 micron filter) for sensitive freshwater resident species.

[n]The value in μg/l should not exceed exp [0.76 ln (hardness) +1.06] where hardness is expressed in mg/l as $CaCO_3$.

[o]The value in μg/l should not exceed exp [0.76 ln (hardness) +4.02] where hardness is expressed in mg/l as $CaCO_3$.

[p]For marine and/or fresh water aquatic life, 0.01 of the 96 hour LC_{50} as determined through bioassay using a sensitive resident species.

[q]The value in μg/l should not exceed exp [0.83 ln (hardness) + 1.95] where hardness is expressed in mg/l as $CaCO_3$.

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discharge of toxic substances. Table II-3 summarizes the results of a study reported by Keith and Telliard (1979) which shows the frequency of detection of the 129 priority pollutants in industrial wastewaters. A total of 32 industrial categories were analyzed for organics and 28 for metals. The number of samples ranged from 2532 to 2988. Table II-4 summarizes the most commonly discharged priority pollutants. Table III-53, shown in the next chapter, provides a breakdown by industry of the occurrence of priority pollutants in industrial effluent.

It is common in this country for numerous industrial plants to release their effluents into a single water body. Because of this situation a question that naturally arises is: Based on the number and type of industries located on the water body, what kinds of toxic chemicals are likely to be discharged there? If the industrial categories of each plant are known, the probability that a particular pollutant is discharged from at least one of the plants is:

$$P_j = 1 - \prod_{i=1}^{n} \left(1 - \frac{f_{ij}}{100}\right) \quad j = 1, M \quad (II-1)$$

where

f_{ij} = relative frequency of discharge of pollutant type j from plant type i, expressed as a percent

P_j = probability that pollutant type j is discharged from at least one of the n plants located on the water body

M = number of toxic substances being analyzed.

If the industrial categories of the plants are not known, then the probability that a particular pollutant is discharged can be estimated using Table II-3 together with the following formula:

$$P_j = 1 - \left(1 - \frac{g_j}{100}\right)^n \quad j = 1, M \quad (II-2)$$

where

g_j = percent of samples containing pollutant j

P_j = probability that pollutant j is detected in at least one of the n discharges.

Equation II-1 is obviously the more accurate of the two formulae, because it is based on a knowledge of the types of industries which discharge. Although the above equations provide information on the likelihood that different chemicals ar discharged into the environment, and thus can be used to prioritize investigative efforts, they do not predict quantities of pollutants which are discharged. Chapter III can be used to generate that type of information.

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TABLE II-3

EPA LIST OF 129 PRIORITY POLLUTANTS AND THE RELATIVE FREQUENCY OF THESE MATERIALS IN INDUSTRIAL WASTEWATERS
(After Keith and Telliard, 1979)

Purgeable Organics

Percent of Samples[a]	Number of Industrial Categories[b]		Percent of Samples[a]	Number of Industrial Categories[b]	
1.2	5	Acrolein	2.1	5	1,2-Dichloropropane
2.7	10	Acrylonitrile	1.0	5	1,3-Dichloropropene
29.1	25	Benzene	34.2	25	Methylene chloride
29.3	28	Toluene	1.9	6	Methyl chloride
16.7	24	Ethylbenzene	0.1	1	Methyl bromide
7.7	14	Carbon tetrachloride	1.9	12	Bromoform
5.0	10	Chlorobenzene	4.3	17	Dichlorobromomethane
6.5	16	1,2-Dichloroethane	6.8	11	Trichlorofluoromethane
10.2	25	1,1,1-Trichloroethane	0.3	4	Dichlorodifluoromethane
1.4	8	1,1-Dichloroethane	2.5	15	Chlorodibromomethane
7.7	17	1,1-Dichloroethylene	10.2	19	Tetrachloroethylene
1.9	12	1,1,2-Trichloroethane	10.5	21	Trichloroethylene
4.2	13	1,1,2,2-Tetrachloroethane	0.2	2	Vinyl chloride
0.4	2	Chloroethane	7.7	18	1,2-trans-Dichloroethylene
1.5	1	2-Chloroethyl vinyl ether	0.1	2	bis(Chloromethyl)ether
40.2	28	Chloroform			

Base/Neutral Extractable Organic Compounds

Percent of Samples[a]	Number of Industrial Categories[b]		Percent of Samples[a]	Number of Industrial Categories[b]	
6.0	9	1,2-Dichlorobenzene / 1,3-Dichlorobenzene / 1,4-Dichlorobenzene	5.7	11	Fluorene
			7.2	12	Fluoranthene
			5.1	9	Chrysene
0.5	5	Hexachloroethane	7.8	14	Pyrene
0.2	1	Hexachlorobutadiene	10.6	16	Phenanthrene / Anthracene
1.1	7	Hexachlorobenzene			
1.0	8	1,2,4-Trichlorobenzene	2.3	6	Benzo(a)anthracene
0.4	3	bis(2-Chloroethoxy)methane	1.6	6	Benzo(b)fluoranthene
10.6	18	Naphthalene	1.8	6	Benzo(k)fluoranthene
0.9	9	2-Chloronaphthalene	3.2	8	Benzo(a)pyrene
1.5	13	Isophorone	0.8	4	Indeno(1,2,3-c,d)pyrene
1.8	9	Nitrobenzene	0.2	4	Dibenzo(a,h)anthracene
1.1	3	2,4-Dinitrotoluene	0.6	7	Benzo(g,h,i)perylene
1.5	9	2,6-Dinitrotoluene	0.1	2	4-Chlorophenyl phenyl ether
0.04	1	4-Bromophenyl phenyl ether	0	0	3,3'-Dichlorobenzidine
41.9	29	bis(2-Ethylhexyl)phthalate	0.2	4	Benzidine
6.4	12	Di-n-octyl phthalate	1.1	4	bis(2-Chloroethyl)ether
5.8	15	Dimethyl phthalate	0.8	7	1,2-Diphenylhydrazine
7.6	20	Diethyl phthalate	0.1	1	Hexachlorocyclopentadiene
18.9	23	Di-n-butyl phthalate	1.2	5	N-Nitrosodiphenylamine
4.5	12	Acenaphthylene	0.1	1	N-Nitrosodimethylamine
4.2	14	Acenaphthene	0.1	2	N-Nitrosodi-n-propylamine
8.5	13	Butyl benzyl phthalate	1.4	6	bis(2-Chloroisopropyl)ether

Acid Extractable Organic Compounds

Percent of Samples[a]	Number of Industrial Categories[b]		Percent of Samples[a]	Number of Industrial Categories[b]	
26.1	25	Phenol	1.9	8	p-Chloro-m-cresol
2.3	11	2-Nitrophenol	2.3	10	2-Chlorophenol
2.2	9	4-Nitrophenol	3.3	12	2,4-Dichlorophenol
1.6	6	2,4-Dinitrophenol	4.6	12	2,4,6-Trichlorophenol
1.1	6	4,6-Dinitro-o-cresol	5.2	15	2,4-Dimethylphenol
6.5	18	Pentachlorophenol			

Pesticides/PCB's

Percent of Samples[a]	Number of Industrial Categories[b]		Percent of Samples[a]	Number of Industrial Categories[b]	
0.3	3	a-Endosulfan	0.3	3	Heptachlor
0.4	4	b-Endosulfan	0.1	1	Heptachlor epoxide
0.2	2	Endosulfan sulfate	0.2	4	Chlordane
0.6	4	a-BHC	0.2	2	Toxaphene
0.8	6	b-BHC	0.6	2	Aroclor 1016
0.2	4	d-BHC	0.5	1	Aroclor 1221
0.5	3	g-BHC	0.9	2	Aroclor 1232
0.5	5	Aldrin	0.8	3	Aroclor 1242
0.1	3	Dieldrin	0.6	2	Aroclor 1248
0.04	1	4,4'-DDE	0.6	3	Aroclor 1254
0.1	2	4,4'-DDD	0.5	1	Aroclor 1260
0.2	2	4,4'-DDT	-	-	2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)
0.2	3	Endrin			
0.2	2	Endrin aldehyde			

Percent of Samples[a]	Number of Industrial Categories[b]		Percent of Samples[a]	Number of Industrial Categories[b]	
		Metals			
18.2	20	Antimony	16.5	20	Mercury
19.9	19	Arsenic	34.7	27	Nickel
14.1	18	Beryllium	18.9	21	Selenium
30.7	25	Cadmium	22.9	25	Silver
53.7	28	Chromium	19.2	19	Thallium
55.5	28	Copper	54.6	28	Zinc
43.8	27	Lead			
		Miscellaneous			
33.4	19	Total cyanides	Not available		Asbestos (fibrous)
			Not available		Total phenols

[a] The percent of samples represents the number of times this compound was found in all samples in which it was analyzed for divided by the total as of 31 August 1978. Numbers of samples ranged from 2532 to 2998 with the average being 2617.

[b] A total of 32 industrial categories and subcategories were analyzed for organics and 28 for metals as of 31 August 1978.

TABLE II-4

MOST COMMONLY DISCHARGED PRIORITY POLLUTANTS

Pollutant	Percent of Samples	Percent of Industries
Non-Metals		
Bis (2-Ethylhexyl) Phthalate	41.9	91
Chloroform	40.2	88
Methylene Chloride	34.2	78
Total Cyanides	33.4	59
Toluene	29.3	88
Benzene	29.1	78
Phenol	29.1	78
Di-*n*-Butyl Phthalate	18.9	72
Ethylbenzene	16.7	75
Naphthalene	10.6	56
Phenanthrene and Anthracene	10.6	50
Metals		
Copper	55.5	100
Zinc	54.6	100
Chromium	53.7	100
Lead	43.8	96
Nickel	34.7	96

2.1.5 Physical and Chemical Characteristics of Toxic Organic Compounds

The most intensively investigated toxic pollutants, as a group, are the priority pollutants. Because of the greater availability of data on priority pollutants from such sources as Callahan et al. (1979), Dilling et al. (1975) and Mackay and Leinonen (1975), data are presented for organic priority pollutants in the following categories:

- Halogenated Aliphatic Hydrocarbons (Table II-5)
- Pesticides (Table II-6)
- Polychlorinated Biphenyls (Table II-7)
- Monocyclic Aromatic Hydrocarbons (Table II-8)
- Polycyclic Aromatic Hydrocarbons (Table II-9).

The properties of the pollutants tabulated in Tables II-5 through II-9 are:

- Vapor pressure, Torr (1 Torr = 1 mm-Hg)
- Solubility
- Octanol-water partition coefficient (K_{ow})
- Volatilization half-life
- Qualitative statement of the importance of sorption.

Specific information is included in the tables for volatilization and sorption because of the demonstrated importance of these processes in governing the fate of many pollutants. In particular, for the approximately 103 organic priority pollutants:

- Sorption processes are important for 60
- Sorption is not important for 28
- It is not certain if sorption is important for the remaining 15
- Volatilization is important for 52
- Volatilization is not important for 44
- It is uncertain if volatilization is important for the remaining 7.

The volatilization half-lives presented in the tables were typically measured under a specific set of laboratory conditions, and consequently are shorter than in most natural systems. Other useful properties such as molecular weight and specific gravity are available in standard references such as Perry and Chilton (1973).

2.1.6 Scope and Organization of Chapter

The complexity of the transport and transformation processes which influence the fate of toxicants require additional analytical tools beyond those required for conventional pollutants. This chapter develops these analytical tools in a general way that is applicable to rivers, lakes, and estuaries. Individual chapters on the various surface water types refine these tools further and provide a framework within which to use them. When used together, the various chapters in this document should help the user to both understand and quantitatively represent the processes influencing the aquatic fate of a pollutant.

This chapter presents both a general overview of the screening approach for

TABLE II-5
SELECTED CHARACTERISTICS OF VARIOUS ALIPHATIC HYDROCARBONS

Halogenated Aliphatic Hydrocarbons	Vapor Pressure (Torr) at 20°C	Solubility	K_{ow}	Volatilization Half-Life	Sorption Important?
Chloromethane	3700	6450-7250 mg/l at 20°C	8	27 minutes[a]	No
Dichloromethane	362	13000-20000 mg/l at 25°C	20	21 minutes[a]	Probably Not
Trichloromethane (chloroform)	150	8200 mg/l at 20°C	93	21 minutes[a]	Probably Not
Tetrachloromethane (carbon tetrachloride)	90	785 mg/l at 20°C	400	29 minutes[a]	Uncertain
Chloroethane	1000	5740 mg/l at 20°C	35	21 minutes[a]	Probably Not
1,1-Dichloroethane	180	5500 mg/l at 20°C	60	22 minutes[a]	Probably Not
1,2-Dichloroethane	61	8690 mg/l at 20°C	30	29 minutes[a]	Probably Not
1,1,1-Trichloroethane	96	440-4400 mg/l at 20°C	150	20 minutes[a]	Probably Not
1,1,2-Trichloroethane	19	4500 mg/l at 20°C	150	21 minutes[a]	Uncertain
1,1,2,2-Tetrachloroethane	5	2900 mg/l at 20°C	360	56 minutes[a]	Uncertain
Hexachloroethane	0.4	50 mg/l at 22°C	2200	45 minutes[a]	Uncertain
Chloroethene (vinyl chloride)	2660	60 mg/l at 10°C	4	26 minutes[a]	Probably Not
1,1-Dichloroethene	591	400 mg/l at 20°C	30	22 minutes[a]	Probably Not
1,2-trans-Dichloroethene	200	600 mg/l at 20°C	30	22 minutes[a]	Probably Not
Trichloroethene	57.9	1100 mg/l at 20°C	200	21 minutes[a]	Probably Not
Tetrachloroethene	14	150-200 mg/l	760	28 minutes[a]	Probably Not
1,2-Dichloropropane	42	2700 mg/l	190	<50 minutes[a]	Probably
1,3-Dichloropropene	25	2700 mg/l	95	31 minutes[a]	Uncertain
Hexachlorobutadiene	0.15	2	5500	-	Probably
Hexachlorocyclopentadiene	0.081 at 25°C	0.8 mg/l	10^4	-	Probably
Bromomethane	1420	900 mg/l	10	~30 minutes	Probably Not
Bromodichloromethane	50	-	75	-	Uncertain
Dibromochloromethane	15	-	120	-	Uncertain
Tribromomethane	10	3000 mg/l	200	-	Uncertain
Dichlorodifluoromethane	4300	280 mg/l	145	few minutes	Probably
Trichlorofluoromethane	667	1100 mg/l	3400	few minutes	Uncertain

a Stirring in an open container of depth 65 mm at 200 RPM (Dilling et al., 1975)

TABLE II-6

VARIOUS CHARACTERISTICS OF SELECTED PESTICIDES

Pesticide	Vapor Pressure (Torr)	Solubility	K_{ow}	Volatilization Half-life [a]	Sorption Important?
Acrolein	220 at 20°C 330 at 30°C	20.8% at 20°C	0.8	Uncertain	No
Aldrin	2.3×10^{-5} at 20°C 6×10^{-6} at 25°C	17-180 ppb at 25°C	~410	Few hours to few days	Yes
Chlordane	1×10^{-5} at 25°C	0.056-1.85 ppm	600	Several weeks	Probably
DDD	$10.2-18.9 \times 10^{-7}$ at 30°C	20-100 ppb at 25°C	10^6	1 day to 1 month	Yes
DDE	$6.2-6.5 \times 10^{-6}$ at 20°C	1.2-140 ppb at 20°C	5×10^5	1 to 10 hours	Yes
DDT	1.5×10^{-7} at 20°C 1.9×10^{-7} at 25°C	2-85 ppb	10^4-10^6	4 hours-1 week	Yes
Dieldrin	1.8×10^{-7} to 2.9×10^{-7} at 20°C	186-200 ppb at 25°C	-	Few hours to few days	Probably
Endosulfan	1×10^{-5} at 25°C	100-260 ppb at 20°C	4×10^3	11 days-1 year	Yes
Endrin	2×10^{-7}	220 ppb at 25°C	4×10^5	-	Uncertain
Heptachlor	3×10^{-4}	56-180 ppb at 25°C	-	-	Probably
Heptachlor Epoxide	-	200-350 ppb at 25°C	-	-	Probably
Hexachlorocyclohexane	$10^{-5}-10^{-7}$	0.70-21.3 ppm at 25°C	10^4	-	Probably
Lindane	$10^{-4}-10^{-6}$	5-12 ppm at 25°C	5×10^3	100-200 days	Probably
Isophorone	0.38	12000 ppm	50	Probably great	No
TCDD	-	0.2 ppb	-	-	Yes
Toxaphene	0.2-0.4	0.7-3. ppm	2000	-	Yes

[a] Conditions described in Callahan et al. (1979).

TABLE 11-7

SELECTED CHARACTERISTICS OF POLYCHLORINATED BIPHENYLS AND RELATED COMPOUNDS

PCBs and Related Compounds	Percent Chlorine	Density (gm/cm^3)	Vapor Pressure at 25 C°(Torr)	Solubility mg/l	K_{ow}	Volatilization	
						Half-Lives in laboratory (hrs)[a]	Loss in Natural Systems[b]
Aroclor 1016	41	1.33	4×10^{-4}	0.42	$2 \times 10^4 - 3 \times 10^5$	9.9	3.6% after 24 hours
Aroclor 1221	21	1.15	6.7×10^{-3}	15.	$600 - 10^4$	-	4.2% after 24 hours
Aroclor 1232	32	1.24	4×10^{-3}	1.45	$1.5 \times 10^3 - 3 \times 10^4$	-	-
Aroclor 1242	42	1.35	4×10^{-4}	0.1-0.3	$10^4 - 4 \times 10^5$	12.1	-
Aroclor 1248	48	1.41	4.9×10^{-4}	0.054	$\sim 10^6$	9.5	-
Aroclor 1254	54	1.50	7.7×10^{-5}	0.01-0.06	$\sim 10^6$	10.3	-
Aroclor 1260	60	1.58	4×10^{-5}	0.0027	$> 10^6$	10.2	34%-67% after 12 weeks
2-chloronaphthalene	-	-	0.017	6.47	10^4	-	

[a] At 25°C in 1 m^3 of water, 1 m deep (MacKay and Leinonen, 1975).

[b] Conditions described in Callahan et al. (1979).

TABLE 11-8

SELECTED CHARACTERISTICS OF MONOCYCLIC AROMATIC HYDROCARBONS

Monocyclic Aromatics	Vapor Pressure (Torr)	Solubility	K_{ow}	Volatilization Half-life	Sorption Important?
Benzene	95. at 25°C	1800 mg/l at 25°C	100	4.8 hrs at 25°C[a]	Uncertain
Chlorobenzene	~10 at 20°C	~500 mg/l	700	0.5-9 hrs	Probably
1,2-Dichlorobenzene	1.5 at 25°C	145 mg/l	2400	8-9 hours[a]	Probably
Hexachlorobenzene	10^{-5} at 20°C	~20 µg/l	~10^6	8 hours[a]	Yes
Ethylbenzene	7	152 mg/l	1400	5-6 hours[a]	Probably
Toluene	29 at 25°C	535 mg/l	500	5 hours[a]	Probably
2,4-Dinitrotoluene	0.001 at 59°C	270 mg/l at 22°C	100	~100 days	Yes
2,6-Dinitrotoluene	low	~300 mg/l	100	~100 days	Yes
Pentachlorophenol	0.0001	14 mg/l	10^5	>100 days	Yes
2-Nitrophenol	1.0 at 49°C	2100 mg/l at 20°C	60	-	Yes
4-Nitrophenol	2.2 at 146°C	16000 mg/l at 25°C	80	-	Yes
2,4-Dinitrophenol	-	5600 mg/l	34	-	Yes
4,6-Dinitro-o-cresol	-	-	700	-	Yes

[a] Mackay and Leinonen (1975). Calculated based on water depth of 1 m, and using mass transfer coefficients of 20 cm/hr and 3000 cm/hr for the liquid and gas transfer phases, respectively.

TABLE II-9

SELECTED CHARACTERISTICS OF VARIOUS POLYCYCLIC AROMATIC HYDROCARBONS

Polycyclic Aromatics	Vapor Pressure (Torr)	Solubility	K_{OW}	Volatilization Important?	Sorption Important?
Acenaphthene	10^{-3}-10^{-2} at 20°C	3.4 mg/l at 25°C	21,000	Less than sorption	Yes
Acenaphthylene	10^{-3}-10^{-2} at 20°C	3.93 mg/l	12,000	Less than sorption	Yes
Fluorene	10^{-3}-10^{-2} at 20°C	1.9 mg/l	15,000	Less than sorption	Yes
Naphthalene	.0492	32. mg/l	2,300	Less than sorption	Yes
Anthracene	2×10^{-4} at 20°C	0.05-0.07 mg/l at 25°C	28,000	Probably	Yes
Fluoranthene	10^{-6} to 10^{-4} at 20°C	0.26 mg/l at 25°C	340,000	Probably Not	Yes
Phenanthrene	6.8×10^{-4} at 20°C	1.0-1.3 mg/l at 25°C	29,000	Probably Not	Yes
Benzo[a]anthracene	5×10^{-9} at 20°C	0.01 mg/l at 25°C	4×10^{5}	No	Yes
Benzo[b]fluoranthene	11^{-11} to 10^{-6} at 20°C	-	4×10^{6}	Probably Not	Yes
Benzo[k]fluoranthene	9.6×10^{-11} at 20°C	-	7×10^{6}	Probably Not	Yes
Chrysene	10^{-11} to 10^{-6} at 20°C	0.002 mg/l at 25°C	4×10^{5}	Probably Not	Yes
Pyrene	6.9×10^{-7} at 20°C	0.14 mg/l at 25°C	2×10^{5}	Probably Not	Yes
Benzo[ghi]perylene	$\sim 10^{-10}$	0.00026 mg/l at 25°C	10^{7}	Probably Not	Yes
Benzo[a]pyrene	5×10^{-9}	0.0038 mg/l at 25°C	10^{6}	Probably Not	Yes
Dibenzo[a]anthracene	$\sim 10^{-10}$	0.0005 mg/l at 25°C	10^{6}	Probably Not	Yes
Indeno[1,2,3-cd]pyrene	$\sim 10^{-10}$	-	5×10^{7}	Probably Not	Yes

toxicants and a detailed description of the processes included in the screening methodology. The various topics are organized as follows:

Screening methods for toxic organic substances

Speciation processes

1) Acid-base effects

2) Sorption

Transport processes

1) Solubility limits

2) Volatilization

Transformation processes

1) Biodegradation

2) Photolysis

3) Hydrolysis.

Lyman et al. (1982) and Mabey et al. (1984) provide additional information that can be used to evaluate the importance of these processes.

2.2 SCREENING METHODS FOR TOXIC ORGANIC COMPOUNDS

2.2.1 Modeling the Fate of Toxic Organics

The goal of this screening methodology for toxic pollutants is to help the user identify surface water bodies where toxicants could reach hazardous levels. Multiple approaches for identifying pollution problems are possible, e.g. extensive field measurements, statistical correlations of discharges and pollutants detected in rivers, computer simulation models, etc. The approach taken here is to present simple methods for assessing the fate of toxicants.

The application of any method necessitates the use of judgment on the part of those applying it. In almost every case, the user must estimate many of the methods' input parameters on the basis of limited data. Consequently, even the projections of detailed computer models such as EXAMS (Burns, et al., 1981) and PEST (Park, et al., 1980) are only as good as the accuracy of the assumptions made by their developers and users. Thus, the goal of the materials presented herein is twofold: to present simple methods and to provide the background necessary to make knowledgeable judgments.

Predicting aquatic fate of pollutants involves several steps. The steps described in the remainder of this section include:

- Determination of Fate-Influencing Processes
- Delineation of Environmental Compartments
- Representation of Hydrologic Flow
- Mathematical Representation of Speciation Processes
- Mathematical Representation of Transport and Transformation Processes
- Determination of Pollutant Load and Mode of Entry into the Aquatic Environment.
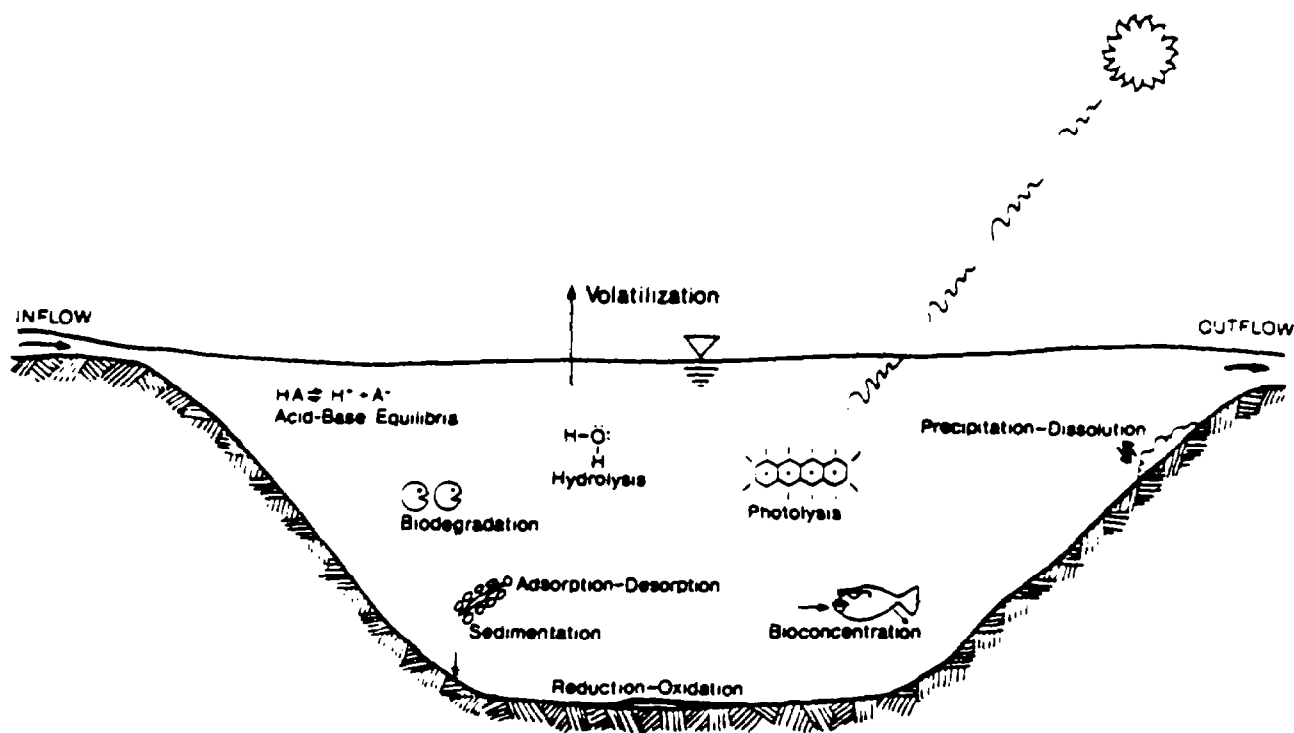
FIGURE II-2 SPECIATION, TRANSPORT AND TRANSFORMATION PROCESSES IN THE AQUATIC
ENVIRONMENT

Prediction of the fate of toxic pollutants requires the user to know which
processes act on the toxicant. Figure II-2 illustrates the transport and transforma-
tion processes which are of potential importance in a lake or other surface water
body. The processes fall into four categories as follows:

Loading Processes.

The rates at which waste discharges, atmospheric deposition, and land
runoff introduce toxicants into natural waters influence resulting
pollutant levels.

Speciation Processes

Acid-Base Equilibria. The pH of a natural water determines the fraction
of an organic acid or base in neutral or ionic states, and therefore
influences volatility.

Sorption. Hydrophobic organic compounds sorb to suspended matter;
their subsequent fate is influenced by the fate of the suspended
matter.

Transport Processes

Precipitation-Dissolution. Solubility limits of both organic and
inorganic pollutants can cause a pure pollutant phase to form restrict-
ing its availability to transport and transformation processes or
substantially changing the transport route.

-25-

Advection. Hydraulic flows transport pollutants which are dissolved or
sorbed on suspended sediments into and out of particular aquatic
habitats.

Volatilization. Organic pollutants may enter the atmosphere from
a water body, thereby reducing aquatic concentrations.

Sedimentation. Deposition of suspended sediments containing sorbed
pollutants, as well as direct sorption onto or desorption from bottom
sediments can alter pollutant concentrations.

Transformation Processes

Biodegradation. Microbial organisms metabolize pollutants, altering
their toxicity in the process.

Photolysis. The absorption of sunlight by pollutants causes chemical
reactions which affect their toxicity.

Hydrolysis. The reaction of a compound with water frequently produces
smaller, simpler organic products.

Reduction-Oxidation. Reactions of organic pollutants and metals
which involve the subtraction or addition of electrons strongly
influence their environmental properties. For organics, nearly
all significant redox reactions are microbially mediated.

Bioaccumulation

Bioconcentration. Uptake of toxic pollutants into biota via passive
means, e.g. absorption through fish gills.

Biomagnification. Uptake of toxicants into biota via consumption
of contaminated food.

Once the pertinent processes have been identified, the physical compartments of
the environment between which the transport processes act must be delineated. For
most water bodies, compartments representing the atmosphere, bottom sediments, and
one or more water elements are sufficient. These methods are capable of representing
transport of pollutants between the atmosphere and a water body. But rather than
calculating atmospheric concentrations of a pollutant, these methods generally assume
them to be close to zero unless available data indicate otherwise. Bottom sediments,
however, frequently accumulate high levels of organic pollutants. Because of the
difficulty of modeling the behavior of toxicants in sediments, usually assumptions
which approximate only the removal or addition of a pollutant to the water column are
made. These approximations are presented in the individual chapters on each water
body.

The next step in assessing the aquatic fate of toxic pollutants is to represent
the advection or flow of water. Figure II-3 illustrates a representation of rivers
as a segregated flow system and lake layers as completely mixed flow systems.
Although these models are simple, they serve as adequate first-approximations of real

COMPLETELY MIXED FLOW

NATURAL SYSTEM:
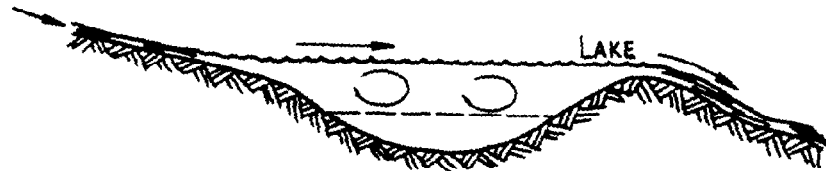
IDEALIZATION:
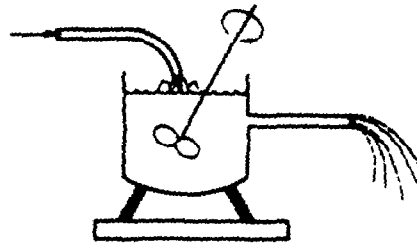
MIXED FLOW

SEGREGATED FLOW

NATURAL SYSTEM:

RIVER

IDEALIZATIONS:

PLUG FLOW

FLOW WITH
AXIAL DISPERSION
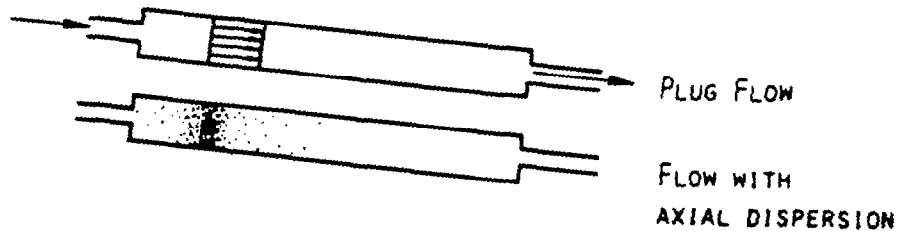
FIGURE II-3 FLOW SYSTEM REPRESENTATIONS

systems. Refinements and limitations of these flow system models are considered in
the individual chapters on rivers, lakes, and estuaries.

The transport and transformation processes responsible for the removal of a
pollutant from the water column are considered next. First-order rate expressions
adequately represent all of the processes considered here. The first-order decay of

a pollutant by a process is represented as follows:

$$\text{Rate of Pollutant Removal} = k_i \cdot C_T \qquad (II\text{-}3)$$

where

k_i = first-order rate constant for process i

C_T = total concentration of pollutant.

The rate constant for a process is specific to both the chemical it acts upon and the local environment in which it acts.

When all the first-order processes acts independently, the total rate of pollutant removal is:

$$\text{Total Rate of Removal} = k_T \cdot C_T \qquad (II\text{-}4)$$

where

$$k_T = k_{vm} + k_S + k_B + k_P + k_H \qquad (II\text{-}5)$$

and

k_{vm} = specific mixed-body volatilization rate constant

k_S = specific rate constant for removal to bottom sediment

k_B = specific rate constant for biodegradation

k_P = specific rate constant for photolysis

k_H = specific rate constant for hydrolysis.

The additivity of processes which are first-order with respect to pollutant concentration is particularly convenient for analysis.

Many of the decay processes are influenced by the chemical state of the toxicant. For example, sorbed pollutants cannot volatilize. Mathematical representations of equilibria between two species of a chemical can be reduced to the following type of equation. This type of equation serves well at the low solute concentrations encountered in waste waters and natural waters:

$$C_i = k_{ij} C_j \qquad (II\text{-}6)$$

where

C_i = concentration of form i

K_{ij} = equilibrium constant

C_j = concentration of form j.

It is also convenient to know the fraction of the total pollutant concentration which is in a given state:

$$\alpha_i = \frac{C_i}{C_T} \qquad (II\text{-}7)$$

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where

C_i = concentration in state i

C_T = $C + C_S$

C = total dissolved phase pollutant concentration

C_S = total sorbed phase pollutant concentration.

To complete the assessment of the aquatic fate of a pollutant the mode of entry into the aquatic environment must be considered. Many pollutants enter in dissolved or sorbed form from a point source. In this case, a simple mixing computation is sufficient to determine the initial concentration of a pollutant in the water body. Other cases include spills, non-point sources, and desorption from sediments. Chapter 4 presents methods for dealing with these cases.

The user may now reckon the concentration of a pollutant in a given water body. The equations which yield the desired results are specific to each surface water type and are developed in the individual chapters on lakes, rivers, and estuaries. An equation representative of those in each chapter is presented in Table II-10. The individual chapters go into greater detail about factors influencing rate processes and interactions with other important phenomena in each water body (See Sections 4.9, 5.6, 6.4.3, and 6.4.5).

2.2.2 Use of Assessment Techniques as Screening Tools

2.2.2.1 Making Conservative Assumptions

With the computational methods presented in this document, the user could produce a relatively complete analysis of the aquatic fate of a pollutant. The goal of this screening method, however, is to determine--with a minimum of effort--whether toxicants are likely to reach problem levels in surface water bodies for either existing or projected loading rates. The user can minimize the effort expended in screening a pollutant by starting with a simple approach which incorporates conservative assumptions about the fate of a pollutant. Conservative assumptions are designed to yield higher calculated environmental concentrations than probably exist in the real system. If these higher concentrations are below the water quality criterion under consideration, a violation of the standard is unlikely. If the initial predictions are higher than the standard, the user may successively refine the approach until it becomes apparent that either the standard will be met or that a more detailed study is necessary.

Three levels of refinement in assessing the aquatic fate of a pollutant are considered here. In order of increasing complexity, they are:

   1) Treating the pollutant as a conservative substance

   2) Considering transport and speciation processes

   3) Considering transformation, transport, and speciation processes.

Each approach has advantages and limitations which the user should consider. By

TABLE II-10

EXPRESSIONS FOR TOXIC POLLUTANT LEVELS
IN VARIOUS WATER BODIES

Water Body	Expression for Steady-State Pollutant Concentration
Rivers (Chapter IV)	$$C = C_0 \exp \left[\frac{-K_v' - \sum K_i}{1 + K_p S} \cdot \frac{x}{U} \right] \quad (IV-115)$$ where x = distance downstream U = river velocity C = total dissolved phase concentration
Impoundments (Chapter V)	$$C = C_{in}/(1 + T_w \times k) \quad (V-47)$$ where T_w = hydraulic residence time C = total dissolved and sediment phase concentration
Estuaries	$$C_i = C_{i-1} \frac{f_i}{f_{i-1}} B_i \quad (VI-33)$$ $$B_i = \frac{r_i}{1-(1-r_i)e^{-kt}} \quad (VI-34)$$ where C_i = concentration in segment i f_i = fraction of fresh water in segment i r_i = segment i exchange ratio t = time expressed in tidal cycles

following this sequence of refinements, the user should be able to eliminate cases where water quality problems are unlikely with a minimum of time and effort.

2.2.2.2 Treating the Pollutant as a Conservative Substance

The simplest approach to estimating the concentration of a toxic pollutant is to assume it behaves conservatively (i.e. does not undergo reaction):

$$k_T = 0$$

Unless an internal source of the pollutant exists, this approach will yield the highest possible pollutant levels since pollutant decay and removal processes are neglected. The obvious advantage of this approach is that it requires no chemical or environmental data to evaluate rate and equilibrium constants. The only data needed are pollutant loads and hydrological parameters. Its major drawback is that it neglects the possibility of a compound accumulating in another environmental compart-

ment, especially bedded sediments. This could result in the underestimation of the duration of the exposure of an aquatic habitat to a chemical. Although the duration of exposure may be underestimated, water column concentrations would not exceed the upper limits predicted by this approach at any time during the exposure period. The fate of conservative pollutants in rivers, impoundments, and estuaries is discussed in Sections 4.1.9, 5.6.1, and 6.4.

2.2.2.3 Considering Transport and Speciation Processes

This refinement incorporates those processes which influence pollutant transport out of the aquatic environment but neglects those processes which chemically alter the compound. Transport processes strongly depend upon chemical speciation, which therefore must be included. The rate constant for first-order pollutant attenuation in this approach is:

$$k_T = k_S + k_{vm} \qquad\qquad (II-8)$$

where

k_S = specific rate constant for removal to bottom sediment

k_{vm} = specific mixed body volatilization rate constant.

This approach requires more information on the properties of the toxicant and the environment than when the pollutant is assumed to behave conservatively, but the necessary data are much more readily available than those required to characterize transformation processes. Nearly all the chemical data necessary to characterize acid-base equilibria, sediment sorption, solubility limitations, and volatilization for the organic priority pollutants are presented in tables in Sections 2.1.5, 2.3.1, and 2.4.2. The necessary environmental data can usually be obtained or estimated with a minimal amount of effort. Because of the demonstrated importance of transport processes and the relative simplicity of assessing them, this is a good intermediate step between the simplest and most complicated approaches.

Transport and speciation processes are applied specifically to rivers, impoundments, and estuaries in Sections 4.9, 5.6, 6.4.3, and 6.4.5.

2.2.2.4 Considering Transformation, Transport, and Speciation Processes

The most complex model which the user can employ using these screening methods includes consideration of transformation, transport, and speciation processes. With this approach, the rate constant for first-order attenuation of a pollutant is:

$$k_T = k_S + k_{vm} + k_B + k_p + k_H \qquad\qquad (II-9)$$

where

k_B = specific rate constant for biodegradation

k_P = specific rate constant for photolysis

k_H = specific rate constant for hydrolysis.

The inclusion of the degradative processes (i.e. biodegradation, photolysis, and hydrolysis), considerably increases the chemical and environmental data required to model a compound's fate. Rather than accurately determining all the constants for speciation, transport, and transformation, the user should first ascertain which processes are the most significant for a compound. As a first step the user should obtain data on the properties of the chemical which influence its aquatic fate from this document or other sources. From compound specific data, it is usually possible to eliminate some processes from consideration. For organic priority pollutants, consulting the ratings of the relative importance of aquatic processes for the fate of each compound, Table II-11, may aid the user in eliminating unimportant processes. Once the most significant processes have been identified, the user should collect the environmental data necessary to determine site specific constants. These site specific constants are then applied in the appropriate equation for each water body type to obtain the best estimate of the actual pollutant concentrations in the environment that these methods are capable of making. (See Sections 4.9, 5.6, 6.4.3, and 6.4.5).

Frequently, kinetic and equilibrium constants will depend on the values of parameters which the user must estimate (e.g., pH). In such cases, assuming conservative values is the best policy. However, calculations using a range of values may identify processes for which a more careful determination of the key environmental and chemical parameters is warranted.

Example II-1 is an overall example for this chapter. It demonstrates the initial steps a user would take in applying these methods to assess the fate of a particular organic pollutant. The example follows the three level analysis described above and also draws upon some of the procedures for specific environmental processes which are developed later in this chapter. This example can serve as a guide to evaluating the importance of the various fate influencing processes for a particular pollutant.

TABLE II-11

RELATIVE IMPORTANCE OF PROCESSES INFLUENCING
AQUATIC FATE OF ORGANIC PRIORITY POLLUTANTS (After Callahan et al., 1979)

Compound	Process					
	Sorption	Volatilization	Biodegradation	Photolysis-Direct	Hydrolysis	Bioaccumulation
PESTICIDES						
Acrolein	-	+	+	+	-	-
Aldrin	+	+	?	-	-	+
Chlordane	+	+	?	-	-	+
DDD	+	+	-	-	-	+
DDE	+	+	-	+	-	+
DDT	+	+	-	-	+	+
Dieldrin	+	+	-	+	-	+
Endosulfan and Endosulfan Sulfate	+	+	+	?	+	-
Endrin and Endrin Aldehyde	?	?	?	+	-	+
Heptachlor	+	+	-	?	++	+
Heptachlor Epoxide	+	-	?	?	-	+
Hexachlorocyclohexane (α,β,δ isomers)	+	?	+	-	-	-
-Hexachlorocyclohexane (Lindane)	+	-	+	-	-	-
Isophorone	-	-	?	+	-	-
TCDD	+	-	-	?	-	+
Toxaphene	+	+	+	-	-	+
PCBs and RELATED COMPOUNDS						
Polychlorinated Biphenyls	+	+	+[a]	?	-	+
2-Chloronaphthalene	-	?	+	+	-	-
HALOGENATED ALIPHATIC HYDROCARBONS						
Chloromethane (methyl chloride)	-	+	-	-	-	-
Dichloromethane (methylene chloride)	-	+	?	-	-	-
Trichloromethane (chloroform)	-	+	?	-	-	-
Tetrachloromethane (carbon tetrachloride)	?	+	-	-	-	?
Chloroethane (ethyl chloride)	-	+	?	-	+	-
1,1-Dichloroethane (ethylidene chloride)	-	+	?	-	-	-
1,2-Dichloroethane (ethylene dichloride)	-	+	?	-	-	-
1,1,1-Trichloroethane (methyl chloroform)	-	+	-	-	-	-
1,1,2-Trichloroethane	?	+	-	-	-	?
1,1,2,2-Tetrachloroethane	?	+	-	-	-	?
Hexachloroethane	?	?	?	?	?	+
Chloroethene (vinyl chloride)	+	-	-	-	-	-
1,1-Dichloroethene (vinylidene chloride)	?	+	?	-	-	?
1,2-trans-Dichloroethene	-	+	?	-	-	-
Trichloroethene	-	+	?	-	-	-
Tetrachloroethene (perchloroethylene)	-	+	+	-	-	-
1,2-Dichloropropane	?	+	-	?	+	?
1,3-Dichloropropene	?	+	-	?	+	-
Hexachlorobutadiene	+	+	?	-	?	+
Hexachlorocyclopentadiene	+	+	-	+	+	+
Bromomethane (methyl bromide)	-	+	-	-	+	-

TABLE II-11 (continued)

Compound	Sorption	Volatilization	Biodegradation	Photolysis-Direct	Hydrolysis	Bioaccumulation
Bromodichloromethane	?	?	?	?	-	+
Dibromochloromethane	?	+	?	?	-	+
Tribromomethane (bromoform)	?	+	?	?	-	+
Dichlorodifluoromethane	?	+	-	?	-	?
Trichlorofluoromethane	?	+	-	-	-	?
HALOGENATED ETHERS						
Bis(choromethyl) ether	-	-	?	-	++	-
Bis(2-chloroethyl) ether	-	+	-	-	-	?
Bis(2-chloroisopropyl) ether	-	+	-	-	-	?
2-Chloroethyl vinyl ether	-	+	?	-	+	-
4-Chlorophenyl phenyl ether	+	?	?	+	-	+
4-Bromophenyl phenyl ether	+	?	?	+	-	+
Bis(2-chloroethoxy) methane	-	-	?	-	+	?
MONOCYCLIC AROMATICS						
Benzene	+	+	-	-	-	-
Chlorobenzene	+	+	-	-	-	+
1,2-Dichlorobenzene (o-dichlorobenzene)	+	+	-	?	-	+
1,3-Dichlorobenzene (m-dichlorobenzene)	+	+	?	?	?	+
1,4-Dichlorobenzene (p-dichlorobenzene)	+	+	-	?	-	+
1,2,4-Trichlorobenzene	+	+	-	?	-	+
Hexachlorobenzene	+	-	-	-	-	-
Ethylbenzene	?	+	?	-	-	-
Nitrobenzene	+	-	-	+	-	-
Toluene	+	+	?	-	-	-
2,4-Dinitrotoluene	+	-	-	+	-	?
2,6-Dinitrotoluene	+	-	-	+	?	?
Phenol	-	+	+	-	-	-
2-Chlorophenol	-	-	?	+	-	-
2,4-Dichlorophenol	-	-	++	-	-	-
2,4,6-Trichlorophenol	?	-	?	?	-	-
Pentachlorophenol	+	-	+	+	-	+
2-Nitrophenol	-	-	-	++[b]	-	-
4-Nitrophenol	+	-	-	++	-	-
2,4-Dinitrophenol	+	-	-	++[b]	-	-
2,4-Dimethyl phenol (2,4-xylenol)	-	-	?	+	-	-
p-chloro-m-cresol	-	-	?	++	-	-
4,6-Dinitro-o-cresol	+	-	-	++	?	?
PHTHALATE ESTERS						
Dimethyl phthalate	+	-	+	-	-	+
Diethyl phthalate	+	-	+	-	-	+
Di-n-butyl phthalate	+	-	+	-	-	+
Di-n-octyl phthalate	+	-	+	-	-	+
Bis(2-ethylhexyl) phthalate	+	-	+	-	-	+
Butyl benzy phthalate	+	-	+	-	-	+

TABLE II-11 (continued)

Compound	Process					
	Sorption	Volatilization	Biodegradation	Photolysis-Direct	Hydrolysis	Bioaccumulation
POLYCYCLIC AROMATIC HYDROCARBONS						
Acenaphthene[c]	+	-	+	+	-	-
Acenaphthylene[c]	+	-	+	+	-	-
Fluorene[c]	+	-	+	+	-	-
Naphthalene	+	-	+	+	-	-
Anthracene	+	+	+	+	-	-
Fluoranthene[c]	+	+	+	+	-	-
Phenanthrene[c]	+	+	+	+	-	-
Benzo(a)anthracene	+	+	+	+	-	-
Benzo(b)fluoranthene[c]	+	-	+	+	-	-
Benzo(k)fluoranthene[c]	+	-	+	+	-	-
Chrysene[c]	+	-	+	+	-	-
Pyrene[c]	+	-	+	+	-	-
Benzo(ghi)perylene[c]	+	-	+	+	-	-
Benzo(a)pyrene	+	+	+	+	-	-
Dibenzo(a,h)anthracene[c]	+	-	+	+	-	-
Indeno(1,2,3-cd)pyrene[c]	+	-	+	+	-	-
NITROSAMINES AND MISC. COMPOUNDS						
Dimethylnitrosamine	-	-	-	++	-	-
Diphenylnitrosamine	+	-	?	+	-	?
Di-n-propyl nitrosamine	-	-	-	++	-	-
Benzidine	+	-	?	+	-	-
3,3'-Dichlorobenzidine	++	-	-	+	-	-
1,2-Diphenylhydrazine (Hydrazobenzene)	+	-	?	+	-	+
Acrylonitrile	-	+	?	-	-	+

Key to Symbols:

++ Predominate fate determining process   - Not likely to be an important process

 + Could be an important fate process   ? Importance of process uncertain or not known

Notes

a Biodegradation is the only process known to transform polychlorinated biphenyls under environmental conditions, and only the lighter compounds are measurably biodegraded. There is experimental evidence that the heavier polychlorinated biphenyls (five chlorine atoms or more per molecule) can be photolyzed by ultraviolet light, but there are no data to indicate that this process is operative in the environment.

b Based on information for 4-nitrophenol.

c Based on information for PAH's as a group. Little or no information for these compounds exists.

————————— EXAMPLE II-1 —————————

Pentachlorophenol in the Aurum Mirth Watershed

Pentachlorophenol enters the Aurum Mirth River from a continuous point source. The river is the sole tributary to Lake Castile. After mixing at the point of entry, the concentration of pentachlorophenol in the river is 20 μg/l. The travel time from the point of contamination with pentachlorophenol to Lake Castile is about 6 days. The mean hydraulic residence time in Lake Castile is 10 days.

Use the screening methods to determine which chemical and environmental parameters are of the greatest importance for predicting the fate of pentachlorophenol in the watershed's surface waters.

1) TREATING PENTACHLOROPHENOL AS A CONSERVATIVE SUBSTANCE

The first step in the screening method is to assess the fate of pentachlorophenol treating it as a conservative substance. Sections 4.1.9, 5.6.1, and 6.4 discuss the fate of conservative pollutants in rivers, lakes, and estuaries. In this case, we assume no further dilution of the pentachlorophenol occurs in either the lake or the river. Consequently, the conservative pollutant approach predicts a mean concentration in the river and lake of 20 μg/l.

Table II-2 lists a proposed water quality standard for pentachlorophenol. The 24 hour mean concentration must be less than 6.2 μg/l. Since 20 μg/l exceeds this standard, a second level assessment is in order.

Prior to applying the next two levels of analysis it is worthwhile to check Table II-11 for the relative importance of the different transformation and transport processes. Table II-11 summarizes the influence of the aquatic processes on pentachlorophenol as follows:

- Sorption - Important process
- Volatilization - Not an important process
- Biodegradation - Important process
- Direct Photolysis - Important process
- Hydrolysis - Not an important process
- Bioaccumulation - Important process.

It will be instructive to compare these statements to the results of the screening methodology.

2) CONSIDERING TRANSPORT AND SPECIATION PROCESSES

To analyze transport and speciation processes, first examine each process for its potential influence on the fate of pentachlorophenol.

Speciation Processes

Acid-Base Effects (Section 2.3.1). The chemical and environmental parameters governing acid-base effects are:

- Chemical Parameters:

    pK_a or pK_b - Acid or base equilibrium constants

- Environmental Parameters:

    pH - Hydrogen ion concentrations.

The pK_a of pentachlorophenol is 4.74, as shown in Table II-13. According to Table II-12, at least 90 percent of the pentachlorophenol will be in the anionic state at pH's greater than 5.74. As long as the pH in the Aurum Mirth River and Lake Castile remain above 5.74, the properties of pentachlorophenol as measured for neutral waters will remain unaffected. But, because pH's below 5.74 could significantly alter the behavior of the compound, it is important to determine actual surface water pH values.

Sorption (Section 2.3.2) The key environmental and chemical parameters which influence sorption are:

- Chemical parameters:

    K_{ow} - Octanol-water coefficient

    S_w - solubility in water

- Environmental Properties:

    Suspended sediment concentration

    Organic carbon content of the suspended sediment.

Table II-8 lists the solubility and octanol-water coefficient of pentachlorophenol as:

$$S = 14 \text{ mg/l}$$
$$K_{ow} = 10^5$$

Assuming an organic carbon content of 2 percent for the suspended sediments, calculate K_p using Equations II-18 and II-16:

$$K_p = (.02) (.63) (10^5) = 1300$$

According to Table II-16, greater than 10 percent of the pentachlorophenol will be in the sorbed state at suspended sediment concentrations exceeding 100 mg/l. The relatively strong sorption of pentachlorophenol dictates that the suspended sediment concentration in the Aurum Mirth River and the sediment trapping efficiency of Lake Castile be investigated further. Sorption of pentachlorophenol potentially affects both its speciation and its transport rates.

Transport Processes

Solubility Limitations (Section 2.4.1). The most important chemical

and environmental factors which influence solubility of a compound are:

- Chemical Parameters:

    S_w - Aqueous equilibrium solubility

- Environmental Parameters:

    T - Temperature

    Salinity.

Table II-8 lists the solubility limit for pentachlorophenol as 14 mg/l (14000 μg/l). At no point in the Aurum Mirth watershed should the solubility of pentachlorophenol restrict the ability of the aqueous phase to transport it.

Volatilization (Section 2.4.2). The most significant chemical and environmental properties which influence volatilization are:

- Chemical Parameters:

    K_H - Henry's Law Constant

- Environmental Parameters:

    k_a - Reaeration constant

    V - Wind speed

    Z - Mixed depth of water body.

It is possible to estimate the Henry's Law Constant for pentachlorophenol from its vapor pressure and aqueous solubility using Equation II-32. However, it is simpler to rule out volatilization as a significant transport process on the basis of the volatilization half-life of 100 days given in Table II-8. Because laboratory volatilization half-lives are shorter than the true environmental values, it is safe to assume the environmental half-life will be much greater than 100 days. Given a total system mean hydraulic residence time of only 16 days (6 + 10), volatilization can be safely neglected.

Summary

Acid-base equilibria and sorption significantly influence the transport and speciation of pentachlorophenol in the aquatic environment. Acid-base effects do not influence the near-neutral volatilization and photolysis rate constants presented in this document as long as pH's remain above 5.7. Sorption is a potentially important speciation process. Consequently, the pH values and suspended sediment concentrations should be determined in order to accurately evaluate these processes.

The strong tendency of pentachlorophenol to sorb on sediments may result in sedimentation serving as a significant removal process in Lake Castile. The absence of net sediment deposition in the river implies that transport processes do not reduce pentachlorophenol concentrations in the Aurum Mirth. Thus, the second level analysis predicts a total concentration of 20 μg/l of pentachlorophenol in the Aurum Mirth River with lower levels possible in the lake. Because the

predicted river concentrations exceed the standard, the third level model is
necessary.

3) CONSIDERING TRANSFORMATION, TRANSPORT, AND SPECIATION PROCESSES

To consider transformation, transport, and speciation processes, the trans-
formation processes which were neglected in the level two analysis must be examined
for their potential importance in influencing the rate of pentachlorophenol
degradation.

Transformation Processes

Biodegradation (Section 2.5.1). The key chemical and environmental variables
which influence biodegradation are:

Chemical Parameters:

Metabolic Pathway (growth or co-metabolism)

k_B - Biodegradation rate constant

Environmental Parameters:

Bacterial population size

State of adaptation

Inorganic nutrient concentrations - Phosphorus

Dissolved oxygen

Temperature

Pollutant concentration.

According to Table II-26, pentachlorophenol is potentially biodegradable,
although adaptation may be slow. The reported specific rate constant values, 0.1
to 1.0 per day, in Table II-27 are in the same range as the 0.05 to 0.5 per day
values suggested in Table II-26. Although both rate constants were determined
under laboratory rather than environmental conditions, they do indicate that
pentachlorophenol can degrade very rapidly.

Table II-27 also indicates that pentachlorophenol is used by bacteria as a
growth substrate. Thus, the time required for adaptation is of primary concern.
The most important environmental factors for determining whether microorganisms in
the Aurum Mirth watershed will adapt to degrade pentachlorophenol are previous
exposure, time, and the actual concentrations of pentachlorophenol in the surface
waters (too low--no enzyme induction; too high--may have toxic effect on microbiota).

Photolysis (Section 2.5.2). The key chemical and environmental characteris-
tics influencing the rate of photolysis are:

● Chemical Properties:

k_{do} - Near-surface rate constant

$\epsilon(\lambda)$ - Light absorption coefficient of pollutant

ϕ - Quantum yield

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- Environmental Properties:
    - I - Solar radiant flux
    - Z - Mixed depth of water body
    - K - Diffuse light attenuation coefficient
        - a) Z_{sd} - Secchi disc depth
        - b) C_{ss} - Suspended sediment concentration
        - C_{DOC} - Dissolved organic carbon concentration
        - C_a - Chlorophyll pigment concentration.

According to Table II-32, the near-surface photolysis rate constant for pentachlorophenol is .46/day. The size of the rate constant implies that photolysis would be an important factor if the water bodies are not too deep or too turbid. Thus, it is important to gather information on the water depths, and to estimate the light attenuation coefficients and the solar radiant flux in the Aurum Mirth watershed.

Hydrolysis (Section 2.5.3). The important parameters influencing the rate of hydrolysis are:

Chemical Parameters:

k_a, k_n, k_b - Acid, neutral, and base catalyzed hydrolysis rate constants

Environmental Properties:

pH - Concentration of hydrogen ion in the water bodies.

Table II-40 gives acid and base hydrolysis rate constants for pentachlorophenol of 1.1×10^4 and 3.3 liter mole^{-1} day^{-1}. The neutral rate constant is 5.8×10^{-3} per day. The same table lists a half life of 100 days at pH = 7. Because the acid catalyzed rate constant is large, significantly higher rates could occur at lower pH's. Using Equation II-85, the rate constant for pH = 5 is:

$$k_H = 1.1 \times 10^4 \, (10^{-5}) + 5.8 \times 10^{-3} + 3.3 \, (10^{-9})$$
$$= .23 \text{ day}^{-1}$$

At this lower pH, degradation by abiotic hydrolysis would be very rapid. Thus, determining the pH in the Aurum Mirth River and Lake Castile is very important.

Summary

The consideration given to transformation, transport, and speciation processes indicates the following processes are of potential importance to the fate of pentachlorophenol in the Aurum Mirth watershed:

- Acid-base effects
- Sorption
- Biodegradation
- Photolysis
- Hydrolysis.

Since the three transformation processes are potentially important, there is
a good possibility that the initial pentachlorophenol concentration of 20 µg/l
will be reduced below the 6.2 µg/l standard. Therefore further analysis as
presented in the specific water body sections is warranted.

The results of this example agree with the summary of rate processes given in
Table II-11 except for the case of hydrolysis. This demonstrates that the process
summary table can serve as a useful guide but should be supplemented with actual
data whenever possible.

——————————————————— END OF EXAMPLE II-1 ————————————————————————

2.3 SPECIATION PROCESSES

2.3.1 Acid-Base Effects

The fate of toxic organics which are either acids or bases can be strongly
affected by the concentration of hydrogen ions in a water body. It is therefore
necessary to have a means for estimating this influence. This section will first
present a brief review of acid-base equilibria and then will give a technique for
quantifying the influence of hydrogen ion concentration on the behavior of toxicants.

2.3.1.1 Acid-Base Equilibria

Acids by definition donate hydrogen ions, H^+, to solution. Bases, by
definition, accept hydrogen ions from solution. 2-Nitrophenol, one of the 129
priority pollutants, is an acid and donates hydrogen ions as shown by the following
reaction:

2-nitrophenol	2-nitrophenolate	+ hydrogen ion
(HP)	(P⁻)	(H⁺)
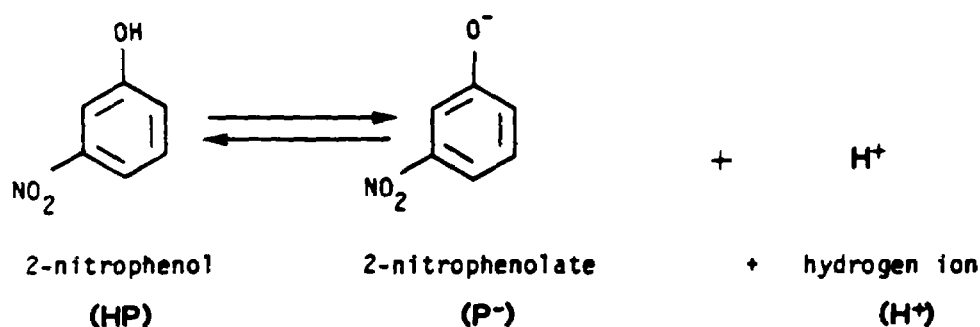
Acid-base reactions are extremely fast and can be represented by equilibrium
expressions. For the above reaction the expression would be:

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$$\frac{[H^+] \ [P^-]}{[HP]} = K_a \qquad\qquad\qquad (II\text{-}10)$$

where

[H^+] = concentration of hydrogen ions, moles/liter

[P^-] = concentration of nitrophenolate ions, moles/liter

[HP] = concentration of undissociated nitrophenol, moles/liter

[K_a] = an equilibrium constant for acid dissociation (also called an acidity constant).

The extent to which any acid will donate hydrogen ions to the solution depends on how many hydrogen ions are in solution (the concentration of hydrogen ions) and on the strength of the acid.

The concentration of free hydrogen ions in natural waters can range from about 10^{-4} to 10^{-10} moles per liter. Hydrogen ion concentrations are normally expressed in pH units. In dilute solutions, such as natural waters, pH is defined as the negative logarithm of the molar hydrogen ion concentration (pH = $-\log_{10}$ [H^+]). For the above two concentrations the pH values are 4 and 10.

The strength of an acid is quantified by the equilibrium constant, K_a. For very strong acids (those which most readily donate hydrogen ions) the value of this constant is greater than unity. Included in this group are strong acids such as hydrochloric and nitric acid. Toxic organic acids, though, are generally weak acids and have K_a values between 10^{-3} and 10^{-9}. K_a values are typically expressed in terms of negative base ten logarithms. When this approach is used the equilibrium constants are called "pK_a" (pK_a = $-\log_{10} K_a$).

When the pH of a solution is the same as the pK_a value of an acid (i.e., pH = pK_a), 50 percent of the acid will have donated its hydrogen ions to the solution and will exist as a charged anionic species. For pH values greater than the pK_a value by one or more units, the acid will have donated essentially all of its hydrogen ions to the solution and will exist in the anionic form (i.e., P^-).

The extent to which any base will extract hydrogen ions from solution depends upon the concentration of hydrogen ions in solution (pH) and on the strength of the base. The strength of a base is quantified by an equilibrium constant, K_b. For very strong bases (those that most readily extract hydrogen ions from solution) the value of K_b is of the order of 1. Toxic organic bases are generally weak and have K_b values between 10^{-3} and 10^{-10}. In a manner similar to acids, K_b is typically expressed in terms of negative base ten logarithms and is called "pK_b" (pK_b = $-\log_{10} K_b$).

Water itself can behave as a weak acid or a weak base:

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{(acidic behavior)}$$

$$H_2O + H^+ \rightleftharpoons H_3O^+ \quad \text{(basic behavior)}$$
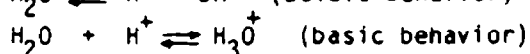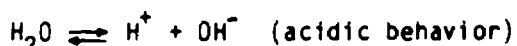
Note that $[H^+] \cdot [OH^-] = K_w$

where $[OH^-]$ = the concentration of hydroxide ion, moles/l

$K_w \approx 10^{-14}$, at 20°C

$pK_w \approx 14$, at 20°C.

When the pH of a solution equals the value $(pK_w - pK_b)$ of a base, 50 percent of the base has accepted hydrogen ions and will exist as a charged cationic species. For pH values greater than one unit above the value of $(pK_w - pK_b)$, essentially all of the base will exist in electrically neutral form (e.g. NH_3). For pH values less than the value of $(pK_w - pK_b)$ by 1 or more units, the base will essentially exist in the electrically charged cationic form (e.g., NH_4^+).

Table II-12 summarizes the behavior described above for acids and bases. Values for pK_a and pK_b for selected toxic organic acids and bases and values of pK_w are given in Table II-13. Additional pK_a values can be found in Donigian et al. (1983).

Since toxic organics almost always exist in very low concentrations and are at best only weak acids or weak bases, they will have little influence, if any, on the pH values of the water. The hydrogen ion concentration of the water will, however, determine whether acids or bases exist in neutral or ionic forms.

Values of pH for natural waters can be obtained from the USGS, the U.S. EPA, and state and local agencies. Waters with low alkalinities (e.g., $\leq$ 50 mg/l as $CaCO_3$, or 1 milliequivalent/liter) are quite susceptible to changes in pH due to natural processes such as photosynthesis and respiration and even to relatively small additions of strong acid or base. Selection of representative pH values for such waters will require more data than for systems with higher alkalinities where less change in pH can be anticipated.

2.3.1.2 Quantifying the Influence of pH on Toxicant Volatilization

Only electrically neutral species are directly volatile. Volatilization rate expressions must therefore use as the concentration of toxicant only that fraction which is electrically neutral (non-ionic). The fraction of an acid or base which is in the non-ionic form can be determined by use of the expressions given below:

For organic acids:

$$\alpha_{Ao} = \frac{Ao}{A} = \frac{1}{1 + 10^{(pH-pK_A)}} \tag{II-11}$$

TABLE II-12

OCCURRENCE OF ACIDS AND BASES IN NEUTRAL AND CHARGED
FORMS AS A FUNCTION OF pH, pK_a, AND pK_b

Acids			Bases		
Definition: Hydrogen ion donors			Definition: Hydrogen ion acceptors		

Example:

$$HNO_3 \longrightarrow H^+ + NO_3^-$$

Example:

$$NH_3 + H^+ \longrightarrow NH_4^+$$

General Reaction:

$$HP \longrightarrow H^+ + P^-$$

General Reaction:

$$B + H^+ \longrightarrow BH^+$$

Speciation:

Speciation:

pH	Fraction in Neutral Form	Fraction in Ionic Form	pH	Fraction in Neutral Form	Fraction in Ionic Form
pK_a+3	0.001	0.999	pK_w-pK_b+3	0.999	0.001
pK_a+2	0.01	0.99	pK_w-pK_b+2	0.99	0.01
pK_a+1	0.09	0.91	pK_w-pK_b+1	0.91	0.09
pK_a	0.5	0.5	pK_w-pK_b	0.5	0.5
pK_a-1	0.91	0.09	pK_w-pK_b-1	0.09	0.91
pK_a-2	0.99	0.01	pK_w-pK_b-2	0.01	0.99
pK_a-3	0.999	0.001	pK_w-pK_b-3	0.001	0.999

For organic bases:

$$\alpha_{Bo} = \frac{Bo}{B} = \frac{1}{1 + 10^{(pK_w-pK_B-pH)}} \qquad (II-12)$$

where

α_{Ao} = the decimal fraction of the organic acid which is in the electrically neutral (non-ionic) form

α_{Bo} = the decimal fraction of the organic base which is in the electrically neutral (non-ionic) form

A = the total dissolved concentrations of the toxic organic acid (e.g., $HP+P^-$), also called the analytical concentration of A

B = the total dissolved concentration of the toxic organic base (e.g., $BH^+ + B$), also called the analytical concentration of B.

The rate expressions then become in general form:

TABLE II-13

pK_a AND pK_b VALUES FOR SELECTED TOXIC ORGANIC
ACIDS AND BASES AND VALUES OF pK_w FOR WATER

Acids	pK_a [a]
Phenol	10.0
2-Chlorophenol	8.52
2,4-Dichlorophenol	7.85
2,4,6-Trichlorophenol	5.99
Pentachlorophenol	4.74
2-Nitrophenol	7.21
4-Nitrophenol	7.15
2,4-Dinitrophenol	4.09
2,4-Dimethylphenol	10.6
4,6-Dinitro-o-cresol	4.35
Bases	**pK_b [b]**
Benzidine	9.34, 10.43
Water	**pK_w [c]**
Freshwater	14.63 at 5°C
	14.53 at 10°C
	14.35 at 15°C
	14.17 at 20°C
	14.00 at 25°C
	13.82 at 30°C
Seawater	14.03 at 5°C
	13.81 at 10°C
	13.60 at 15°C
	13.40 at 20°C
	13.20 at 25°C
	13.00 at 30°C

Notes:

[a] All pK_a values from Callahan et al (1979).

[b] All pK_b values from Weast and Astle (1980).

[c] pK_w values from Stumm and Morgan (1981) and from Dickson and Riley (1979).

$$R = k_v \alpha_A A_0 \quad (II\text{-}13a)$$

and

$$R = k_v \alpha_B B_0 \quad (II\text{-}13b)$$

where

R = rate of volatilization

k_v = specific rate constants for volatilization.

Table II-14 summarizes the procedure.

```
┌────────────────────────── EXAMPLE II-2 ──────────────────────────┐
│                                                                   │
│     2-nitrophenol has been detected in the Alehandra Estuary,     │
│  which has a pH of 8, at concentrations of 20 µg/l (total         │
│  dissolved form). Determine the volatilization flux on a per      │
│  unit area basis. Assume the volatilization rate constant, $k_v$, │
│  is 2 cm/hr.                                                      │
│                                                                   │
│     From Table II-13, the $pK_a$ of 2-nitrophenol is 7.21. The    │
│  fraction present in the electrically neutral (non-ionic) form    │
│  is:                                                              │
│                                                                   │
│         $\alpha_{Ao} = \dfrac{1}{1 + 10^{(pH-pK_a)}}$             │
│                                                                   │
│              $= \dfrac{1}{1 + 10^{(8.0-7.2)}}$                    │
│                                                                   │
│              $= 0.14$                                             │
│                                                                   │
│  From Equation II-13 the volatilization flux is:                  │
│                                                                   │
│   $R_v = 2 \text{ cm/hr } (0.14) \left(\frac{20 \mu g}{1}\right)$ │
│   $\left(\frac{1000\ 1}{m^3}\right) \left(\frac{1\ m}{100\ cm}\right)$ │
│   $= 56 \ \mu g \cdot hr^{-1} m^{-2}$                             │
│                                                                   │
└────────────────────────── END OF EXAMPLE II-2 ───────────────────┘
```

2.3.2 Sorption on Suspended Sediments

2.3.2.1 Introduction

Sorption refers to the accumulation of a chemical in the boundary region of a solid-liquid interface. Sorption occurs when the net sorbate-sorbent attraction overcomes the solute-solvent attraction, where solute and sorbate refer to the sorbing species in solution and sorbed at the interface, respectively.

Sorption of chemicals in the natural environment is significant because the

TABLE II-14

PROCEDURE FOR CALCULATING FRACTION OF A COMPOUND
WHICH IS IN THE NEUTRAL (NON-CHARGED) FORM

1. Decimal fraction of a compound which is in the
   neutral (non-charged) form:

   For Organic Acids $\qquad \alpha_{A_0} = \dfrac{A_0}{A} = \dfrac{1}{1 + 10^{(pH-pK_A)}}$ $\qquad$ (1)

   For Organic Bases $\qquad \alpha_{B_0} = \dfrac{B_0}{B} = \dfrac{1}{1 + 10^{(pK_W-pK_B-pH)}}$ $\qquad$ (2)

2. Procedure

   a) Find the pH value of the water, pH = _____.

   a) For an organic acid, use Table II-13 to find the
      pK_A value of the organic acid, pK_A = _____.

   c) For an organic base, use Table II-13 to find the
      pK_B value of the organic base, pK_B = _____.

   d) Also use Table II-13 to find the pK_W value for water,
      pK_W = _____.

3. Substitute: For organic acids substitute pH and
   pK_A into equation 1. α_{A_0} = _____.

   For organic bases substitute
   pH, pK_B, and pK_W into equation 2. α_{B_0} = _____.

   Note: 10^0 = 1 (any number to the zero power equals 1)

4. For approximations of the decimal fraction of a compound
   which is in the neutral form use Table II-12.

fates of sorbates and solutes can be significantly different. Sorbates are trans-
ported along with sediments, and can be deposited in river or lake beds to remain
indefinitely. Sorbates are in many ways protected from transformation processes
which would otherwise affect the solute. For example:

- Microbial degradation rates can be reduced. Steen et al. (1978) performed tests which showed that sorption of toxicants to suspended sediments renders some compounds unavailable for biodegradation in the adsorbed state.

- Volatilization is diminished. Since volatilization of a chemical occurs from the dissolved phase, the sorbate is not directly available for volatilization. Rather, the sorbate first desorbs before it volatilizes. Example II-4 will show the significant influence of sorption on volatilization.

- Direct photolysis of pollutants adsorbed on suspended particles is inhibited in some cases. Further, suspended solids deposited on the bed of a river, lake, or estuary, receive very little radiation for photolytic reactions.

The net interaction between the surface of a solid and sorbate can result from a variety of forces, including coulombic attraction, Van der Waals forces, orientation energy, induction forces, hydrogen bonding, and chemical forces (Reinbold et al., 1979). In the case of many organic compounds, the solute-solvent interaction is often weak so that even a weak sorbate-sorbent attraction can result in sorption. This type of sorption is referred to as hydrophobic sorption because of the importance of the weak solute-solvent attraction. Hydrophobic sorption will be the topic of much of the following discussion, but it is preceded by brief discussions of equilibrium isotherms and sorption kinetics.

2.3.2.2 Adsorption Isotherms

Adsorption isotherms describe the relationship between the amount of chemical sorbed and the equilibrium solution concentration. The most commonly used isotherms are:

- **Langmuir Adsorption Isotherm.** This equation was originally developed to describe adsorption of a gas to a solid surface, but has been used to describe solid-liquid sorption.

- **Freundlich Adsorption Isotherm.** This empirical equation is based on surface-free energy and monolayer capacity.

- **Linear Adsorption Isotherm.** This equation assumes that there is a linear relationship between the concentrations of solute and sorbate at equilibrium. It is valid for dilute solutions.

Figure II-4 shows example comparisons between the three isotherms, and includes the equations which describe each isotherm. The quantity X is the amount of sorbed chemical per mass of sediment, and C_w is the amount of dissolved chemical per
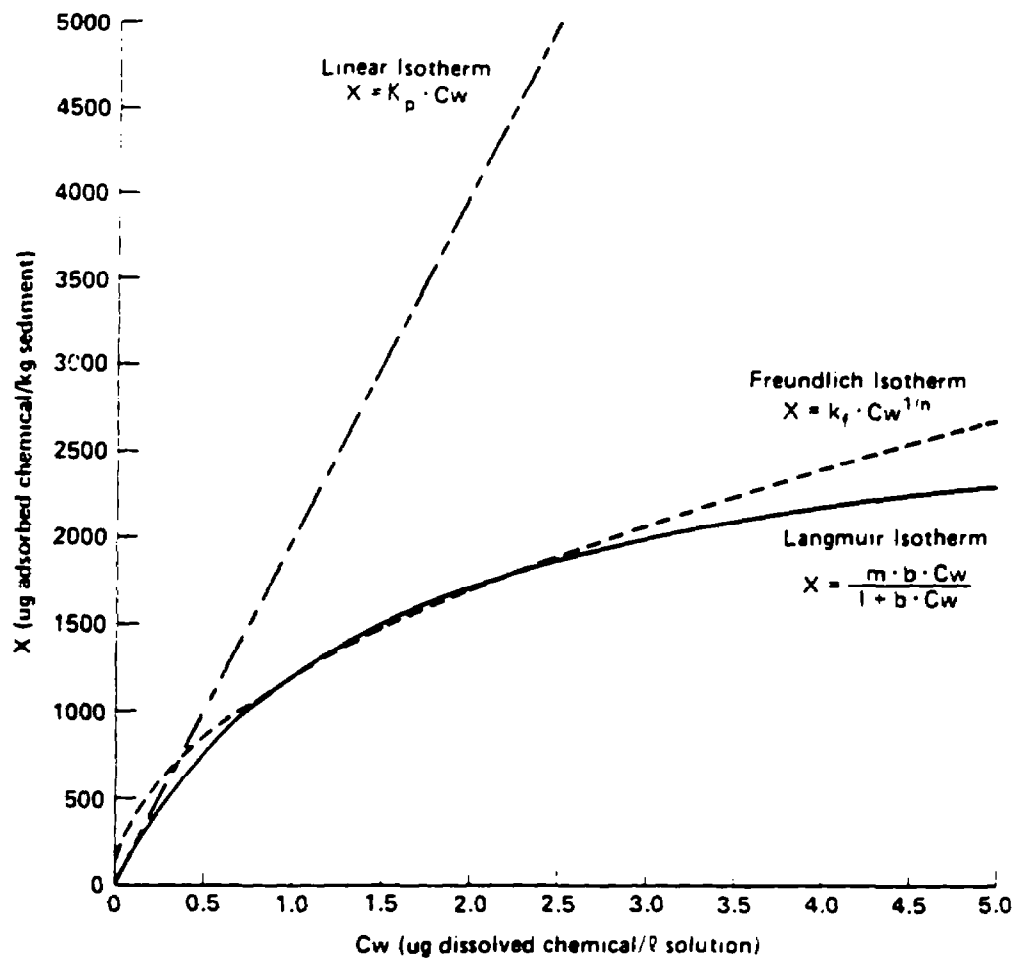
FIGURE II-4   ISOTHERMS FOR ADSORPTION OF A HYDROPHOBIC POLLUTANT
ON SEDIMENTS

volume of solution. The remaining variables are unknown parameters required to
define the relationship between X and C_w. The linear isotherm has one unknown
parameter (K_p), while both the Freundlich and Langmuir isotherms have two unknown
parameters (k_f,n and m,b, respectively).

For the purposes of this document, analyses will mostly deal with dilute
aqueous solution in the range where the linear isotherm is generally valid. This
approach has the advantage of requiring that one unknown parameter (K_p) be
evaluated, rather than two, and of being easier to manipulate mathematically.
Section 2.3.2.4 will present methods of predicting the unknown parameter K_p.

2.3.2.3 Kinetics of Adsorption

Sorption of organic pollutants is often treated as a process which achieves
rapid equilibrium so that expressions of kinetics are not needed. The equilibrium
approach will be used in the remaining chapters of this document. However, a brief

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introduction will be given of sorption kinetics.

Studies of sorption kinetics are apparently few, with the result that parameters required in rate expressions are ill defined and applicable only under a specific set of conditions. Under these constraints, kinetics expressions become less attractive unless the user can determine values of the rate constants which apply to the specific system being investigated.

Most typically, kinetics expressions for sorption and desorption are chosen to be first order. Specifically:

$$\frac{\partial C_w}{\partial t} = -k_a C_w \qquad (II-14)$$

expresses the kinetic expression for the solute and

$$S \frac{\partial X}{\partial t} = -k_d X \qquad (II-15)$$

for the sorbate. The concentrations X and C_w are not necessarily equilibrium concentrations. In these two equations, the rate constant for adsorption is k_a and for desorption is k_d. When the rates of adsorption and desorption are equal, Equations II-14 and II-15 can be equated, with the result that $X = K_p C_w$, where $K_p = k_a/k_d$.

Karickhoff (1979) investigated the sorption and desorption of organic pollutants and found that a very rapid component of adsorption preceded a much slower component of adsorption, and that first order kinetics were obeyed during each of the two periods. For the fast process, the time constant was found to range from 4 to 30 per hour, while for the slow process the time constant ranged from 0.06 to 1.5 per hour. Approximately half of the sorptive equilibrium was realized within minutes, while the slower component required days or weeks to complete. The slower second period was visualized as diffusive transfer to sorption sites that were inaccessible directly to the bulk water. Thus, equilibrium conditions are more likely to be rapidly attained when the number of easily accessible surface sites exceeds the amount of available sorbate, e.g. when suspended sediment concentrations are high.

2.3.2.4 Partition Coefficients for Organic Chemicals Obeying Linear Isotherms

The single unknown parameter, K_p, which relates the sorbate and solute for linear isotherms is called the partition coefficient. A number of studies have been completed which develop empirical relationships for partition coefficients in natural sediments. Several of these studies will be summarized here. Theoretically based methods of estimating partition coefficients exist, such as a thermodynamic approach described in Pavlou (1979); however, these will not be discussed here.

Karickhoff et al. (1979) examined the sorption of aromatic hydrocarbons and chlorinated hydrocarbons on natural sediments. They found it convenient to relate the partition coefficient directly to organic carbon content of the sediments as follows:

$$K_p = K_{oc} x_{oc} \qquad (II-16)$$

where

K_{oc} = partition coefficient expressed on an organic carbon basis

x_{oc} = mass fraction of organic carbon in sediment.

These workers were able to expand this relationship to segregate the influence of particle size as follows:

$$K_p = K_{oc} [0.2(1-f)x_{oc}^s + fx_{oc}^f] \qquad (II-17)$$

where

f = mass fraction of fine sediments (d < 50 µm)

x_{oc}^s = organic carbon content of coarse sediment fraction

x_{oc}^f = organic carbon content of fine sediment fraction.

Karickhoff et al. (1979) were able to relate K_{oc} to the octanol-water partition coefficient and to the water solubility by the following relationships:

$$K_{oc} = 0.63 K_{ow} \qquad (II-18)$$

where

K_{ow} = octanol-water partition coefficient (concentration of chemical in octanol divided by concentration of chemical in water, at equilibrium)

and

$$K_{oc} = -0.54 \log S_w + 0.44 \qquad (II-19)$$

where

S_w = water solubility of sorbate, expressed as a mole fraction.

The water solubilities of the compounds examined ranged from 1 ppb to 1000 ppm.

Hassett et al. (1980) found a similar relationship between K_{oc} and K_{ow} for organic energy-related pollutants. Figure II-5 shows the relationship. Data from Karickhoff et al. are included in the plot for comparison.

Prior to the work of Karickhoff et al., Chiou et al. (1977) investigated the relationship between octanol-water partitioning and aqueous solubilities for a wide variety of chemicals including aliphatic and aromatic hydrocarbons, aromatic
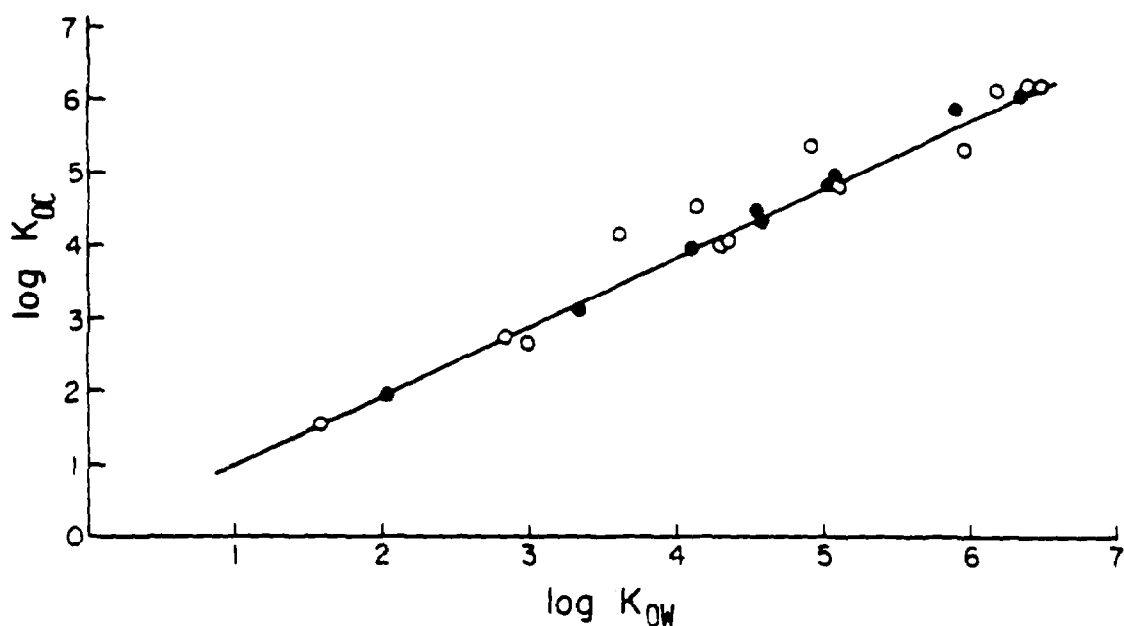
REFERENCE: HASSETT ET AL. (1980)

FIGURE II-5 RELATIONSHIP BETWEEN K_{OC} AND OCTANOL-WATER PARTITION
COEFFICIENT (K_{OW}) OF ENERGY-RELATED ORGANIC POLLUTANTS

acids, organochlorine and organophosphate pesticides, and polychlorinated biphenyls. Their results, shown in Figure II-6, cover more than eight orders of magnitude in solubility and six orders of magnitude in the octanol-water partition coefficient. The regression equation based on this figure is:

$$\log K_{OW} = 5.00 - 0.670 \log S_w \tag{II-20}$$

where

S_w = solubility, in μmol/l.

Bowman and Sans (1983) report additional K_{OW} versus S_w relationships. Leo et al. (1971) have tabulated K_{OW} values for thousands of organics. Subsequent to their work in 1971, they have determined K_{OW} values for many additional compounds.

Brown and Flagg (1981) have extended the work of Karickhoff et al. by developing an empirical relationship between K_{OW} and K_{OC} for nine chloro-s-triazine and dinitroaniline compounds. They plotted their results, along with those of Karickhoff et al., as shown in Figure II-7. The combined data set produces the following correlation:

FIGURE II-6 CORRELATION OF AQUEOUS SOLUBILITY
WITH OCTANOL-WATER PARTITION COEFFICIENT

$$\log K_{OC} = 0.937 \log K_{OW} - 0.006 \qquad\qquad (II-21)$$

The linear correlation between K_{OC} and K_{OW} for the compounds studied by Brown and Flagg has a larger factor of uncertainty than those studied by Karickhoff et al. Other relationships between K_{OC} and K_{OW} for specific groups of compounds are reported in Karickhoff (1984).

The previous paragraphs have shown how the partition coefficient K_p can be predicted for organic hydrophobic compounds which obey a linear isotherm relationship. First, K_{OC} is predicted based on either water solubility or the octanol-water partition coefficient. Tables II-5 through II-9 shown earlier contain K_{OW} values for a number of compounds. Then based on an estimate of organic carbon fraction in the fine and coarse sediments, K_p can be estimated from Equation II-17. This procedure is summarized in Table II-15.

2.3.2.5 Solute and Sorbate Fractions

The relative amount of pollutant sorbed and dissolved depends on both the suspended sediment concentration and the partition coefficient, and at equilibrium is given by:

$$\alpha_w \equiv \frac{C_w}{C_T} = \frac{1}{1+K_p S} \qquad\qquad (II-22)$$

Note: The actual error bands for this figure are probably
greater than indicated here due to error in the
measurement of K_{OW}.

FIGURE II-7 RELATIONSHIP BETWEEN K_{OC} AND K_{OW} FOR COARSE SILT

where

C_W = total dissolved phase concentration

C_T = C_W + C_S

C_S = XS

K_p = partition coefficient

S = suspended sediment concentration, on a part per part basis

X = mass of sorbed pollutant per mass of suspended sediment.

Equation II-22 can be illustrated more vividly by tabulating ranges of K_p
and S values. Table II-16 shows this information. Partition coefficients and
suspended sediment concentrations range from 10^0 to 10^4. For the lowest
value of the partition coefficient nearly all of the pollutant is present in the
dissolved form, regardless of the suspended sediment concentration. Also, for low
suspended sediment concentrations, nearly all of the pollutant is dissolved, unless
the partition coefficient is extremely large. When relatively high partition
coefficients and sediment concentrations occur simultaneously, then most of the

TABLE II-15

PROCEDURE FOR CALCULATING PARTITION COEFFICIENT

1. **Partition Coefficient**

$$K_p = K_{OC} \left[0.2 \ (1-f) \ x_{OC}^s + f \ x_{OC}^f \right]$$ (1)

2. **Procedure**

   a. Find K_{OW} (octanol-water partition coefficient)

      (1) Use Tables II-5 through II-9 for priority pollutants. K_{OW} = [____]

          OR, if the value is not tabulated

      (2) Estimate K_{OW} by:

          $\log K_{OW} = 5.00 - 0.670 \log S_w$ = [____]

          where S_w = solubility, μmole/l

          $$S_w \ (\mu mole/l) = \frac{S_w \ (mg/l)}{molecular \ weight} \times 10^3$$

          Use Tables II-5 through II-9 to find S_w (mg/l)

   b. Find K_{OC}:

      $K_{OC} = 0.63 \ K_{OW}$ = ____ (2)

   c. **Estimate:**

      (1) f (mass fraction of silt or clay) = ____, $(0 \leq f \leq 1;$

          f = 1, if all suspended solids are silts and clays

          f = 0, if all suspended solids are sands)

      (2) x_{OC}^s (organic carbon content of sand, 0.00 - 0.05 typically) = ____

      (3) x_{OC}^f (organic carbon content of silt-clay, 0.03 - 0.10 typically) = ____

3. **Substitute:** K_{OC}, f, x_{OC}^f, x_{OC}^s into Equation (1).

   K_p = ____

4. **Typical Value for** $K_p = 0.01 \ K_{OW}$

   Maximum Value for $K_p = 0.065 \ K_{OW}$

TABLE II-16

RELATIONSHIP OF DISSOLVED AND SORBED PHASE POLLUTANT CONCENTRATIONS TO PARTITION COEFFICIENT AND SEDIMENT CONCENTRATION

K_p	S (ppm)	C_w/C_T	If $C_T = 100$ ppb $C_w =$	X =	$C_S =$
10^0	1	1.0	100.	100.	0.0
	10	1.0	100.	100.	0.0
	100	1.0	100.	100.	0.0
	1000	1.0	100.	100.	0.0
	10000	1.0	99.	99.	1.0
10^1	1	1.0	100.	1×10^3	0.0
	10	1.0	100.	1×10^3	0.0
	100	1.0	99.9	999.	0.1
	1000	1.0	99.0	990.	1.0
	10000	0.9	90.9	909.	9.1
10^2	1	1.0	100.	1×10^4	0.0
	10	1.0	99.9	1×10^4	0.1
	100	1.0	99.0	9.9×10^3	1.0
	1000	0.9	90.9	9.1×10^3	9.1
	10000	0.5	50.	5×10^3	50.
10^3	1	1.0	99.9	1×10^5	0.1
	10	1.0	99.0	9.9×10^4	1.0
	100	0.9	90.9	9.1×10^4	9.1
	1000	0.5	50.	5×10^4	50.
	10000	0.1	9.1	9×10^3	90.9
10^4	1	1.0	99.0	9.9×10^5	1.0
	10	0.9	90.9	9.1×10^5	9.1
	100	0.5	50.	5×10^5	50.
	1000	0.1	9.1	9.1×10^4	90.9
	10000	0.0	1.0	9.9×10^3	99.0

pollutant present exists as sorbate. For all the cases shown, X is high which indicates that the mass sorbed per unit mass of sediment present can be high while C_s is simultaneously low.

— EXAMPLE II-3 —

Determine the fraction of benzo(a)pyrene that is dissolved in a system containing 300 ppm suspended solids. The suspended sediments are 70 percent fines (d < 5⁻ μm) and the weight fraction of organic carbon is 10 percent of the fines and 5 percent of the sand fraction.

From Table II-9, the solubility of benzo(a)pyrene is 0.0038 mg/l, and the octanol-water partition coefficient is 10^6. If, for the moment, the octanol-water partition coefficient is ignored, Equation II-20 can be used to predict K_{ow} based on solubility. The solubility of 0.0038 mg/l must be converted to mole/l:

$$S_w = (0.0038 \text{ mg/l}) \ (10^{-3} \text{ g/mg}) \ (\frac{1}{252} \frac{mole}{gm}) \ (10^6 \ \frac{\mu mole}{mole})$$

$$= 0.015 \ \mu mole/l$$

From Equation II-20, the predicted octanol-water partition coefficient is:

$$\log K_{ow} = 5.00 - 0.670 \log (.015)$$

$$= 6.22$$

so $K_{ow} = 10^{6.22}$, which is acceptably close to the tabulated value of 10^6. Using the tabulated K_{ow}, K_{oc} is computed from Equation II-18:

$$K_{oc} = 0.63 \times 10^6$$

$$= 630,000$$

From Equation II-17, the partition coefficient becomes:

$$K_p = 630,000 \ [0.2 \ (1-.7) \ (.05) + 0.7 \ (.10)]$$

$$= 46,000$$

The suspended sediment concentration for the system is 300 ppm, or $300 \cdot 10^{-6}$ parts per part. Using Equation II-22, the fraction of benzo(a)-pyrene which is dissolved is:

$$\frac{C_w}{C_T} = \frac{1}{1 + 300 \cdot 10^{-6} \cdot 46,000}$$

$$= 0.067 \text{ or about 7 percent}$$

Consequently, most of the benzo(a)pyrene is present as sorbate.

2.4 TRANSPORT PROCESSES

2.4.1 Solubility Limits

The concentration of a compound in a natural water, and therefore the rate of transport by that water, can be limited by its equilibrium solubility. The aqueous solubility of organic compounds ranges widely:

Compound	Aqueous Solubility at 25°C (mass which will dissolve in 1 liter of water) (in milligrams)
Sucrose	2,000,000
Benzene	2,000
Toxaphene	2
Chrysene	0.002

Non-polar compounds have limited solubilities in polar solvents such as water. The solubility of toxic organic compounds is generally much lower than for inorganic salts. Equilibrium solubilities for toxic organic compounds are given in Tables II-5 through II-9. Solubility increases with temperature for most organic compounds, typically by a factor of about 3 from 0°C to 30°C.

Organics are generally less soluble in sea water than in fresh water as can be seen in the tabulations below (Rossi and Thomas, 1981):

Compound	Solubility at 25°C Distilled Water (mg/l)	Sea Water (mg/l)
Toluene	507	419
Acenapthene	2.41	1.84
Pyrene	0.13	0.09

In the absence of colloids or micelles, the maximum amount of a toxic organic substance which can be held in the water column under equilibrium conditions is just the aqueous equilibrium solubility S_w, plus the equilibrium amount of solute sorbed on suspended matter:

$$C_T = S_w + f_s (S_w) \qquad (II-23)$$

where

C_T = total amount of compound which can be held in a natural water at equilibrium conditions, μg liter^{-1}

S_w = equilibrium aqueous solubility, μg liter^{-1}

$f_s(S_w)$ = equilibrium amount of sorbate on suspended matter; a function of S_w. f_s is the sorption isotherm function.

If a linear sorption isotherm is used, as is commonly the case for trace constituents (see Section 2.3.2), the above expression becomes:

$$C_T \leq S_w (1 + K_p S) \qquad \qquad (II-24)$$

where

K_p = linear partition coefficient (see Section 2.3.2.4), liter Kg^{-1}

S = the "concentration" of suspended matter (sorbent), Kg $liter^{-1}$

The inequality results in the above equation because at high solute concentrations linear isotherms overpredict the amount of solute sorbed. The use of linear sorption isotherms (a common practice for trace constituents) is adequate at pollutant concentrations which are equal to, or less than, one half of the equilibrium solubility. When linear sorption isotherms are used, e.g. those with the simple partition coefficient approach (K_p) presented in Section 2.3.2, one must then check to insure that the aqueous pollutant concentration is less than or equal to one-half of its equilibrium solubility.

2.4.2 Volatilization

2.4.2.1 Introduction

Volatilization is defined as the transfer of matter from the dissolved to the gaseous phase. A considerable number of toxic substances volatilize in the natural environment. Volatilization rates depend on the properties of the toxicant and on the characteristics of the water body. If a toxicant is "highly volatile", then obviously volatilization is an important process affecting the fate of the toxicant. However, even for toxicants which are considerably less volatile, volatilization cannot always be ignored. This is because the fate of a toxicant is governed by a variety of processes. If volatilization proceeds as fast as other competing mechanisms, even though all the rates might be slow, then volatilization will influence the fate of the toxicant.

Methods will be provided in this section to predict the volatilization rate for toxic organic substances, which volatilize according to the following relationship:

$$\frac{\partial C}{\partial t} = \frac{-k_v}{Z} (C - \frac{P}{K_H}) = -k_v' (C - \frac{P}{K_H}) \qquad (II-25)$$

where

C = concentration of toxicant in dissolved phase (concentration of solute)

k_v = volatilization rate constant in units of length/time

k_v' = volatilization rate constant in mixed water body in units of $time^{-1}$

Z = mixed depth of water body

P = partial pressure of toxicant in atmosphere above the water body being investigated

K_H = Henry's Law constant.

For many applications the partial pressure of the compound in the atmosphere is zero, so that Equation II-25 simplifies to:

$$\frac{\partial C}{\partial t} = -k_v' C \qquad (II-26)$$

An alternate form of Equation II-26 is in terms of the total pollutant concentration, C_T, and the site specific volatilization rate constant, k_{vm}:

$$\frac{\partial C_T}{\partial t} = -k_{vm} C_T \qquad (II-27)$$

where

$$k_{vm} = \frac{k_v \alpha_w}{Z} \qquad (II-28)$$

where

α_w = fraction of toxicant present in dissolved phase.

The following sections will illustrate how to predict the volatilization rate for toxicants of either low or high volatility. But first, a brief discussion of Henry's Law is required.

2.4.2.2 Henry's Law

Henry's Law is an expression which relates the concentration of a chemical dissolved in the aqueous phase to the concentration (or pressure) of the chemical in the gaseous phase when the two phases are at equilibrium with each other. One common method of expressing Henry's Law is:

$$P = K_H C_w \qquad (II-29)$$

where

P = equilibrium partial pressure of pollutant in atmosphere above the water, atm

C_w = equilibrium concentration of pollutant in the water, $mole/m^3$

K_H = Henry's Law constant, $atm\ m^3/mole$.

Henry's Law in this form is valid for pollutants present in concentrations up to 0.02 expressed as a mole fraction. For compounds with molecular weights greater than 50 g/mole, a mole fraction of 0.02 represents a concentration of at least 55,000 mg/l.

Typically toxic pollutants in the environment are present at levels far below this concentration.

Table II-17 contains values of Henry's Law constants for a number of selected hydrocarbons. In the table, Henry's Law constant is expressed in units of atm m^3/mole. However, in the literature Henry's Law constant can be defined in numerous ways. A second, widely used method of defining Henry's Law constant is:

$$K_H^- = \frac{C_a}{C_w} \qquad (II-30)$$

where

C_a = molar concentration in air, mole/m^3

K_H^- = alternate form of Henry's Law constant, dimensionless.

Equations II-29 and II-30 are related as follows:

$$K_H^- = \frac{K_H}{R_u T_k} = \frac{K_H}{8.2 \times 10^{-5} \, T} = 41.6 \, K_H \text{ at } 20°C \qquad (II-31)$$

where

T_k = temperature of water, $°K$.

R_u = universal gas constant.

This relationship is based on the ideal gas law. Equation II-31 is useful because of the frequent necessity to convert literature data from one set of units to another.

Henry's Law constant can be estimated for slightly soluble compounds (mole fraction $\leq$ 0.02) by the following expression:

$$K_H \text{ (atm·m}^3\text{/mole)} = \frac{P_s \times MW}{760 \times S_w} \qquad (II-32)$$

where

P_s = saturation vapor pressure of pure compound in Torr

MW = molecular weight

S_w = solubility in water in ppm.

Figure II-8 illustrates the limits of Henry's Law for an acetone-water mixture. Henry's Law is obeyed by acetone in region B (mole fraction of acetone $\leq$0.1) and by water in region A (mole fraction of acetone $\geq$0.95). Notice that the generally accepted limit of validity of Henry's Law (mole fraction $\leq$0.02) corresponds to concentrations of 34,000 mg/l to 227,000 mg/l for compounds with molecular weights between 30 to 200. Thus Henry's Law is likely to be applicable in nearly all cases of concern in the natural environment. For pollutants which happen to be largely soluble, however, care must be taken to calculate Henry's law by some method other than Equation II-32.

TABLE II-17

HENRY'S LAW CONSTANT FOR SELECTED HYDROCARBONS

Olefins and Acetylenes	K_H Henry's Law Constant (atm-m³/mole)	k_v (cm/hr)[a]
Ethene (g)	0.214	20.
Propene (g)	0.232	20.
1-Butene (g)	0.268	20.
1-Pentene (l)	0.398	20.
1-Hexene (l)	0.412	20.
2-Heptene (l)	0.418	20.
1-Octene (l)	0.905	20.
Propyne (g)	0.0110	19.8
1-Butyne (g)	0.0194	20.

Cycloalkanes Branched-Chain Alkanes	K_H	k_v
Cyclopentane (l)	0.187	20.
Cyclohexane (l)	0.196	20.
Methylcyclopentane (l)	0.362	20.
Methylcyclohexane (l)	0.428	20.
Propylcyclopentane (l)	0.893	20.
Isobutane (g)	1.24	20.
Isopentane (l)	1.364	20.
2-Methylpentane (l)	1.73	20.
2-Methylhexane (l)	3.42	20.
2,2-Dimethylpentane (l)	3.15	20.
3-Methylheptane (l)	3.71	20.
2,2,4-Trimethylpentane (l)	3.04	20.
4-Methyloctane (l)	9.936	20.

Polychlorinated Biphenyls	K_H	k_v
Aroclor 1242	5.7×10^{-4}	15.6
Aroclor 1248	3.5×10^{-3}	18.9
Aroclor 1254	2.8×10^{-3}	18.9
Aroclor 1260	7.1×10^{-3}	19.6

Aromatics	K_H Henry's Law Constant (atm-m³/mole)	k_v (cm/hr)[a]
Benzene (l)	5.49×10^{-3}	19.4
Toluene (l)	6.66×10^{-3}	19.5
Ethyl benzene (l)	8.73×10^{-3}	19.6
o-Xylene (l)	5.27×10^{-3}	19.4
Isopropylbenzene (l)	1.45×10^{-2}	19.8
Naphthalene (s)	4.25×10^{-4}	14.5
Biphenyl (s)	6.36×10^{-4}	16.0
Acenaphthene (s)	2.28×10^{-4}	11.7
Fluorene (s)	2.35×10^{-4}	11.9
Anthracene (s)	1.65×10^{-3}	18.2
Phenanthrene (s)	1.48×10^{-4}	9.6

n-Alkane	K_H	k_v
Methane (g)[a]	0.665	20.
Ethane (g)	0.499	20.
Propane (g)	0.707	20.
n-Butane (g)	0.947	20.
n-Pentane (l)	1.26	20.
n-Hexane (l)	1.85	20.
n-Heptane (l)	2.07	20.
n-Octane (l)	3.22	20.
n-Nonane (l)	3.29	20.
Decane (l)	4.93	20.
Dodecane (l)	7.12	20.
Tetradecane (l)	1.14	20.

Pesticides	K_H	k_v
DDT	3.9×10^{-5}	3.9
Lindane	4.9×10^{-7}	0.06
Dieldrin	2.0×10^{-7}	0.02
Aldrin	1.4×10^{-5}	0.60
Endrin	4.6×10^{-7}	0.06
Heptachlor	1.5×10^{-3}	18.
Chlordane	5×10^{-5}	4.8
Toxaphene	0.1	19.8

a These are estimated values based on k_l = 20 cm/hr and k_g = 3000 cm/hr.

● Consider acetone-water mixture
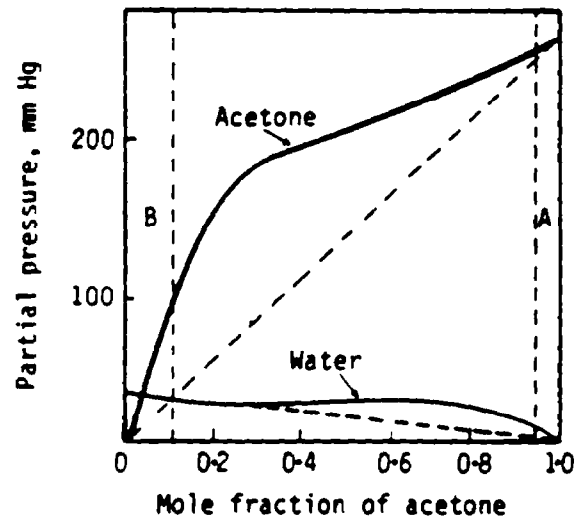
● Henry's Law is obeyed:

    by acetone when mole fraction of acetone ≤0.1 (Region B)
    by water when mole fraction of acetone ≥0.95 (Region A)

● General range of validity: mole fraction ≤0.02

MW	Concentration when mole fraction = 0.02
30	34000 mg/l
75	85000 mg/l
100	113000 mg/l
200	227000 mg/l

FIGURE II-8   RANGE OF VALIDITY OF HENRY'S LAW

Tables II-5 through II-9 presented vapor pressure and solubility data for the organic priority pollutants, which can be used to predict Henry's Law constant. Although Equation II-32 is not valid for highly soluble chemicals, generally the toxicants of interest here are only slightly soluble, so that the expression is adequate.. The dimensionless form of Henry's Law constant is expressible as:

$$K_H^{'} = \frac{16.04 \; P_s \times MW}{S_w \times T}$$
(II-33)

All variables have been previously defined.

———————————————— EXAMPLE II-4 ————————————————

Henry's Law Constant for Chloroform

Calculate Henry's Law constant in the two forms expressed by Equations II-32 and II-33. Chloroform (also called trichloromethane or $CHCl_3$) has the following properties:

Vapor pressure	= 150 Torr (from Table II-5)	
Solubility	= 8200 ppm at 20°C (from Table II-5)	
Molecular weight	=	12 (carbon)
		1 (hydrogen)
		3 x 35.5 (chlorine)
		Sum = 119

From Equation II-32:

$$K_H = \frac{150 \times 119}{760 \times 8200} = 2.86 \times 10^{-3} \quad atm \cdot m^3/mole$$

From Equation II-33, at 20°C (293°K):

$$K_H^{'} = \frac{16.04 \times 150 \times 119}{8200 \times 293} = 0.12$$

Henry's constant, expressed as $K_H^{'}$, had been found experimentally to be 0.12, the same as predicted here.

———————————————— END OF EXAMPLE II-4 ————————————————

2.4.2.3 Two Film Theory of Volatilization

When a chemical volatilizes from water, the process can be visualized as a mass transfer occurring over several distinct steps. Figure II-9 presents a schematic
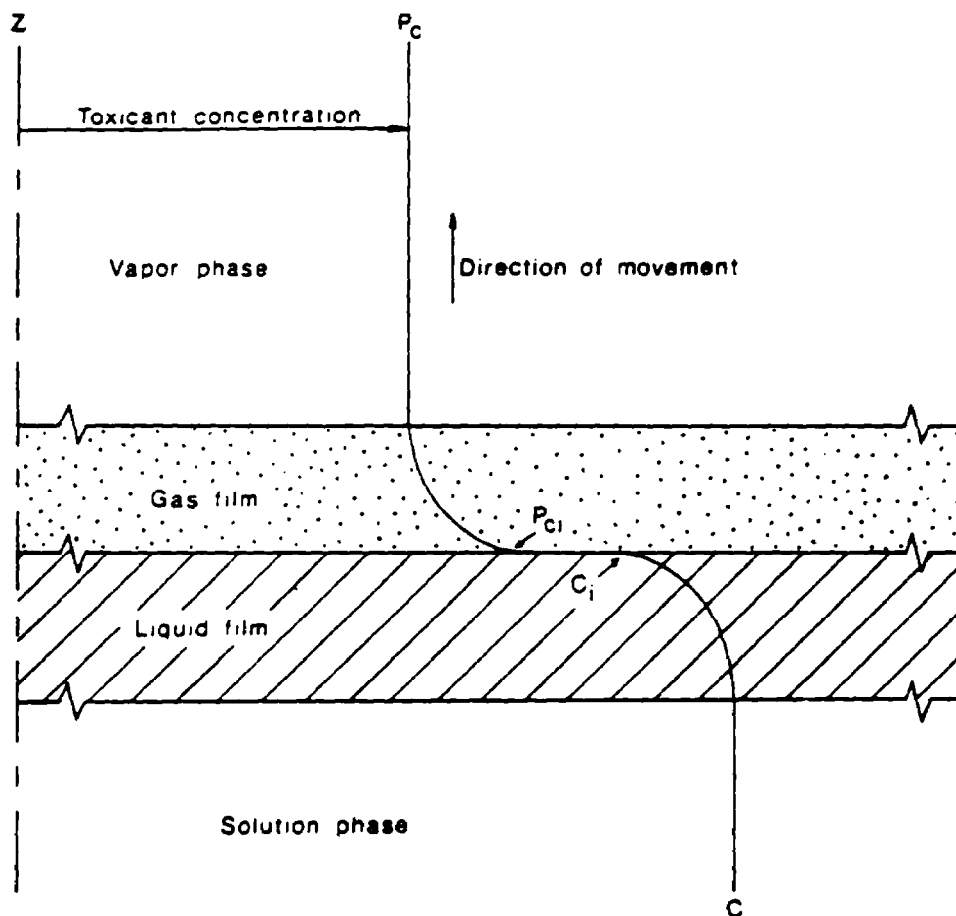
FIGURE II-9   SCHEMATIC REPRESENTATION OF VOLATILIZATION
FROM SOLUTION PHASE TO LIQUID PHASE

representation of the process. The concentration of the chemical is C in the bulk liquid solution. As the chemical moves upward in the bulk solution it moves through a thin "liquid film" where a concentration gradient develops because the transfer rate is limited by diffusion. The dissolved chemical then volatilizes and passes through a thin "gas film", where again transfer may be limited, before reaching the bulk vapor phase.

At the interface between the gas and liquid films the concentrations in the liquid (C_i) and in the gas $(P_{ci}$, expressed as partial pressure) are assumed to be in equilibrium and to obey Henry's Law:

$$P_{ci} = K_H C_i \qquad\qquad (II-34)$$

In the absence of net accumulation at the interface the mass flux from one phase must equal the mass flux from the other, or:

$$F_z = \frac{-k_{gi}}{R_u T} (P_c - P_{ci}) = k_{li} (C - C_i) \qquad \text{(II-35)}$$

where

F_z = flux of chemical in z direction

k_{gi} = mass transfer coefficient in the gas phase across "gas film"

k_{li} = mass transfer coefficient in the liquid phase across "liquid film"

P_c, P_{ci}, C, C_iD are defined in Figure II-9.

Since it is not convenient to measure the partial pressure and concentration at the interface, it is worthwhile to develop expressions for bulk transfer coefficients, given by:

$$F_z = \frac{-k_{vg}}{R_u T} (P_c - P_c') = k_{vl} (C - S_p) \qquad \text{(II-36)}$$

where

k_{vg} = overall volatilization rate defined for the gaseous phase

k_{vl} = overall volatilization rate defined for the liquid phase

S_p = saturation concentration of chemical in equilibrium with P_c

P_c' = partial pressure in equilibrium with C.

Combining Henry's Law equilibrium expressions with Equations ..-35 and II-36 the overall volatilization rates become:

$$\frac{1}{k_{vg}} = \frac{1}{R_u T} \cdot \frac{K_H}{k_{li}} + \frac{1}{k_{gi}} \qquad \text{(II-37)}$$

and

$$\frac{1}{k_{vl}} = \frac{1}{k_{li}} + \frac{R_u T}{K_H k_{gi}} \qquad \text{(II-38)}$$

Of the two expressions, normally Equation II-38 is more useful for the purposes of this document because the pollutants being analyzed are in the aqueous phase. To simplify terminology Equation II-38 will be rewritten as:

$$\frac{1}{k_v} = \frac{1}{k_1} + \frac{R_u T}{K_H k_g} \qquad \text{(II-39a)}$$

or

$$\frac{1}{k_v} = \frac{1}{k_1} + \frac{1}{K_H' k_g} \qquad \text{(II-39b)}$$

where the second subscripts to each variable have been dropped. The volatilization rate, k_v, is the same as shown earlier in Equation II-25 and depends on k_g, K_H', and k_l.

There are two special cases of Equation II-39, depending on the value of Henry's Law constant. They are:

$$
k_v = \begin{cases} k_l, & \text{for large } K_H' \text{ (liquid-phase limited)} \qquad\text{(II-40a)} \\[2em] K_H' k_g, & \text{for small } K_H' \text{ (gas-phase limited)} \qquad\text{(II-40b)} \end{cases}
$$

To make Equation II-40 usable, "large" and "small" values of K_H' have to be defined. For cases when the liquid phase is limiting the transfer rate, a large fraction, R, of the total resistance exists in the liquid phase, or:

$$
\frac{1}{k_l} = R\left(\frac{1}{k_v}\right) = R\left(\frac{1}{k_l} + \frac{1}{K_H' k_g}\right) \qquad\text{(II-41)}
$$

Similarly when the gas phase is limiting:

$$
\frac{1}{K_H' k_g} = R\left(\frac{1}{k_v}\right) = R\left(\frac{1}{k_l} + \frac{1}{K_H' k_g}\right) \qquad\text{(II-42)}
$$

Equations II-41 and II-42 can be rearranged to express Henry's Law constant explicitly:

$$
K_H' = \begin{cases} \dfrac{k_l}{k_g}\ \dfrac{R}{1-R}, & \text{for liquid-phase limited} \qquad\text{(II-43a)} \\[2em] \dfrac{k_l}{k_g}\ \dfrac{1-R}{R}, & \text{for gas-phase limited} \qquad\text{(II-43b)} \end{cases}
$$

At this point values for R, k_l, and k_g must be specified. "Typical" values of k_g and k_l for surface waters are in the range of 20 cm/hr and 3,000 cm/hr, respectively. For R values of 0.83, 0.90, and 0.95, the phase limiting values of Henry's Law constants, converted to units of atm m^3/mole using Equation II-31, are as follows:

	Henry's Constant (atm·m³/mole)	
R	Liquid-phase Limited	Gas-phase Limited
0.83	7.8×10^{-4}	3.3×10^{-5}
0.90	1.4×10^{-3}	1.8×10^{-5}
0.95	3×10^{-3}	8.4×10^{-6}

Hence, for Henry's Law constants larger than about 1.0×10^{-3} atm m^3/mole most of the resistance to volatilization lies in the liquid phase, and for Henry's Law constants less than about 1.0×10^{-5} atm m^3/mole, most of the resistance lies in the gas phase. When either of the two phases controls the volatilization rate, then the simplified Equation II-40 can be used in lieu of Equation II-39. The data in the tables presented earlier can be used to predict Henry's Law constant and then to decide whether the gas or liquid phase limits volatilization.

Based on the two-film model there are two methods which can be used to estimate volatilization rates. One approach is considerably more simple than the other. The simpler approach is based on the following reasoning. Using "typical" values of k_1 and k_g, k_v can be estimated based solely on K_H as the independent variable, where K_H is allowed to vary over its potential range of values. As Table II-18 shows, K_H can vary by at least seven orders of magnitude. Based on this variability of Henry's Law constant, Table II-19 presents the associated volatilization rates. As Henry's Law constant increases, the volatilization rate approaches 20 cm/hr, the liquid phase limiting rate. As Henry's Law constant decreases, so does the volatilization rate, with the lower limit being zero.

The second method of predicting k_v is based on finding k_g and k_1 individually, rather than assuming typical values. The gas-phase transfer rate can be found based on the evaporation rate of water as outlined in Mills (1981). Mills showed that:

$$k_g' = 700 \ V \qquad\qquad (II-44)$$

where

k_g' = gas transfer rate for water vapor, cm/hr

V = wind speed, m/sec.

This expression was derived from an empirical relationship shown in Linsley et al., (1979) for the evaporation of water. Liss (1973) conducted measurements in an experimental basin and found that:

$$k_g' = 1000 \ V \qquad\qquad (II-45)$$

where the units are the same in Equation II-44. Considering that the approaches used to develop Equations II-44 and II-45 are different, their agreement is good. Still other relationships exist between k_g' and V (e.g. Rathbun and Tai, 1983).

The values of k_g and k_g' are related by penetration theory (Bird et al. 1960) as follows:

$$k_g = \left(\frac{D_a}{D_{wv}}\right)^{\frac{1}{2}} k_g' \qquad\qquad (II-46)$$

TABLE II-18

HENRY'S LAW CONSTANTS FOR SELECTED COMPOUNDS

Compound	Henry's Law Constant (atm·m³/mole)
Vinyl Chloride	3.7
Carbon Tetrachloride	2×10^{-2}
Toluene	6.7×10^{-3}
Aroclor 1254	2.8×10^{-3}
Flourene	2.4×10^{-4}
DDT	3.9×10^{-5}
Dieldrin	2.0×10^{-7}

TABLE II-19

TYPICAL VALUES OF POLLUTANT VOLATILIZATION RATES
IN SURFACE WATERS

K_H(atm·m³/mole)	K_H'(dimensionless)	k_v(cm/hr)*	k_v(1/day)**	
10^0	41.6	20.	4.8	Liquid-film limited
10^{-1}	4.2	20.	4.8	
10^{-2}	4.2×10^{-1}	19.7	4.7	
10^{-3}	4.2×10^{-2}	17.3	4.2	
10^{-4}	4.2×10^{-3}	7.7	1.8	
10^{-5}	4.2×10^{-4}	1.2	0.3	
10^{-6}	4.2×10^{-5}	0.1	0.02	Gas-film
10^{-7}	4.2×10^{-6}	0.01	0.002	limited

*Using k_g = 3000 cm/hr
k_l = 20 cm/hr.
**For water depth = 1 m.

where

D_a = diffusion coefficient of pollutant in air

D_{wv} = diffusion coefficient of water vapor in air.

Diffusion coefficient data can be found in such references as Perry and Chilton (1973), or estimated using the Wilke-Chang method, also in Perry and Chilton. If an analytical method is used to estimate diffusion coefficients, note that it is easier to predict the ratio of two diffusion-coefficients than to predict each coefficient individually because some of the required information cancels out of the ratio, and consequently is not needed at all.

In many cases it is acceptable to approximate the ratio of diffusion coefficients as follows:

$$\frac{D_a}{D_{wv}} = \left(\frac{18}{MW}\right)^{\frac{1}{2}} \qquad (II-47)$$

where

MW = molecular weight of pollutant.

Table II-20 illustrates the difference between calculating the diffusion coefficient ratio by using tabulated data from Perry and Chilton and by using Equation II-47. The percent differences between the ratios range from 1 to 27 percent and average 15 percent. This agreement is acceptable for screening purposes. Combining Equations II-46, II-44, and II-47, the final expression for k_g (in units of cm/hr) is:

TABLE II-20

COMPARISON OF TABULATED AND PREDICTED VALUES OF DIFFUSION
COEFFICIENTS FOR SELECTED POLLUTANTS

Pollutant	Molecular Weight	Diffusion Coefficient Perry & Chilton (cm^2/sec)	Predicted (cm^2/sec)	Perry & Chilton $\left(\frac{D_a}{D_{wv}}\right)^{\frac{1}{2}}$	Predicted $\left(\frac{D_a}{D_{wv}}\right)^{\frac{1}{2}}$	Percent Difference
Chlorobenzene	113	0.075	0.088	.58	.63	9
Toluene	92	0.076	0.097	.59	.66	12
Chloroform	119	0.091	0.086	.64	.63	1
Naphthalene	128	0.051	0.083	.48	.61	27
Anthracene	178	0.042	0.070	.44	.56	27
Benzene	78	0.077	0.106	.59	.69	17

$$k_g = 700 \left(\frac{18}{MW} \right)^{\frac{1}{4}} v \qquad \qquad \text{(II-48)}$$

This expression is valid for rivers, lakes, and estuaries.

The liquid phase transfer coefficient k_l can be predicted based on the reaeration rate, k_a, for the system. The relationship proposed by Smith et al. (1981) is:

$$k_l = \left(\frac{D_w}{D_{O_2}} \right)^n k_a' \quad , \quad 0.5 \leq n \leq 1 \qquad \qquad \text{(II-49)}$$

where

D_w = diffusion coefficient of pollutant in water

D_{O_2} = diffusion coefficient of dissolved oxygen in water

k_a' = surface transfer rate of dissolved oxygen, expressed in the same units as k_l.

In other chapters of this report, the reaeration rate is presented as k_a, defined as:

$$k_a = k_a'/Z \qquad \qquad \text{(II-50)}$$

where

Z = mixed depth of water body.

For rivers the mixed depth is the total depth, while for estuaries the mixed depth is the total depth only if the estuary is well mixed. Otherwise, it is the depth to the pycnocline. Similarly for lakes, the mixed depth can be less than the total depth, and can be chosen to be the depth of the epilimnion.

The exponent n varies as a function of the theoretical approach used to develop Equation II-49. If film theory is used, i.e., the film is considered to be a laminar sublayer, then n = 1. If penetration or surface renewal theory is used, n = 0.5. Using experimental approaches, researchers have found n to vary from 0.5 to 1.0. Since the movement of water in natural water bodies is generally turbulent, the parameter n can be chosen to be 0.5.

Perry and Chilton (1973) provide data and methods to predict the diffusion coefficient of a pollutant in water. The Othner-Thakor relationship, described in Smith et al. (1981) can also be used. As an approximate approach, by using the square root of the molecular weights the following expression results:

$$k_l = \left(\frac{32}{MW} \right)^{\frac{1}{4}} k_a' \qquad \qquad \text{(II-51)}$$

A recent study (Rathbun and Tai, 1981) used a tracer technique to predict the volatilization rates of four priority pollutants from 12 different rivers. That

study provides an opportunity to compare, even if only to a limited degree, some of the methods presented here against field results. Table II-21 briefly summarizes the results of Rathbun and Tai (1981). As shown by the values of Henry's Law constant for the four pollutants, each pollutant is liquid phase limited, since all Henry's Law constants exceed 1.0×10^{-3} atm m^3/mole. The study results were unable to predict differences in volatilization rates for the four pollutants, and found that the best predictive expression was:

$$k_v = 0.655\ k_a'$$

Based on Equation II-51 the screening methods predict:

$$k_v = 0.7\ k_a'\ \text{to}\ 0.8\ k_a'$$

where the range reflects the variability in molecular weight among the four pollutants.

If the default value of 20 cm/hr, suggested earlier in this section were used as a rough estimate of the volatilization rate for liquid phase limited pollutants, this value would fall within the observed range of 1.5 to 24 cm/hr. It appears that the screening methods presented here generate acceptable estimates of volatilization rates.

Table II-22 summarizes the two methods presented in the manual for calculating the volatilization rate constant k_v. The first approach is more simplified and is based on typical values of k_g and k_1. In the second approach, k_g and k_1 are calculated rather than assumed.

2.4.2.4 Volatilization Half-Life

Numerous researchers have in the past calculated the volatilization half-life of toxicants under controlled laboratory conditions. The result of some of this work was shown earlier in Tables II-5 through II-9. Typically, researchers have used the following expression to calculate the half-life:

$$t_{\frac{1}{2}} = \frac{0.693\ Z}{k_v} \qquad \text{(II-52)}$$

where

$t_{1/2}$ = half-life (time required for the concentration of the contaminant to decrease by half).

It is important to understand that the volatilization half-life of a toxicant varies according to the environmental conditions. Under controlled laboratory

TABLE II-21

VOLATILIZATION RATES OF SEVERAL PRIORITY POLLUTANTS IN 12 RIVERS[a]

Pollutant	Henry's Constant (atm·m³/mole)	Molecular Weight
Benzene	5.5×10^{-3}	119
Chloroform	2.9×10^{-3}	78
Methylene Chloride	2.7×10^{-3}	85
Toluene	6.7×10^{-3}	92

<u>Study results showed</u>: $k_v = 0.655 \; k_a'$

<u>Range of values for 12 rivers</u>: 1.5 to 24 cm/hr

<u>Screening method predicts</u>: $k_v = 0.7 \; k_a'$ to $0.8 \; k_a'$

[a]Rathbun, R.E. and D.Y. Tai. 1981. Techniques for Determining the Volatilization Coefficients of Priority Pollutants in Streams. Water Research, Volume 15, pp. 243-250.

conditions, where the depth of water is extremely small, $t_{1/2}$ can be extremely small. If the water depth increases by 100 fold, for example, so does $t_{1/2}$.

The volatilization half-life is affected by suspended solids in the system. When suspended solids are present, Equation II-52 should be modified to:

$$t_{l_2} = \frac{0.693 \; Z}{k_v} \; (1 + SK_p) \qquad (II-53)$$

where

    S = suspended solids concentration

    K_p = partition coefficient.

The partition coefficient is the ratio of the sorbed pollutant concentration to the dissolved phase concentration. A method to predict K_p was discussed earlier in Section 2.3.2. Since the toxicant which sorbs to the sediments is not directly available for volatilization, the total flux of volatilizing particles decreases. The following example illustrates how sorption can influence the half-life.

TABLE II-22

PROCEDURE FOR PREDICTING VOLATILIZATION RATE

I: **Simplified Approach**

1. **Input:** Henry's Law Constant (Table II-17)

2. **Procedure:** Use Table II-19

3. **Result:** k_v (cm/hr) = ____

   To convert to units of per day:

   $$k_v \text{ (per day)} = k_v \text{ (cm/hr)} \times \frac{24}{100Z} = \underline{\qquad}$$

   where

   Z = depth of mixed surface layer, meters

II: **Two-Film Theory Approach**

$$\frac{1}{k_v} = \frac{1}{k_l} + \frac{1}{K_H k_g} \qquad (1)$$

1. **Input:** Henry's Law Constant (K_H, atm · m^3/mole) = ____
   Wind speed (V, m/sec) = ____
   Molecular weight of compound (MW) = ____
   Reaeration rate (k_a', cm/hr, or k_a, per day) = ____
   Water temperature (T, °C) = ____
   Water depth (Z, meters) = ____

2. **Procedure**

   a. **Find:** K_H' (unitless) = $\dfrac{K_H \text{ (atm · } m^3\text{/mole)}}{8.2 \times 10^{-5} \text{ (T + 273)}}$ = ____ $\qquad$ (2)

   b. **Find:** k_g (cm/hr) = $700 \left(\dfrac{18}{MW}\right)^{\frac{1}{2}} V$ = $\boxed{}$ $\qquad$ (3a)

   OR

   k_g (per day) = $700 \left(\dfrac{18}{MW}\right)^{\frac{1}{2}} V \times \dfrac{24}{100Z}$ = $\bigcirc$ $\qquad$ (3b)

   c. **Find:** k_l (cm/hr) = $\left(\dfrac{32}{MW}\right)^{\frac{1}{2}} k_a'$ = $\boxed{}$ $\qquad$ (4a)
   OR

   k_l (per day) = $\left(\dfrac{32}{MW}\right)^{\frac{1}{2}} k_a$ = $\bigcirc$ $\qquad$ (4b)

   d. Find k_v (cm/hr):

   $$\frac{1}{k_v} = \frac{1}{k_l} + \frac{1}{K_H' k_g} \implies k_v = \underline{\qquad}, \text{ answer}$$

   OR

   Find k_v (per day):

   $$\frac{1}{k_v} = \frac{1}{k_l} + \frac{1}{K_H' k_g} \implies k_v = \underline{\qquad}, \text{ answer}$$

—————————————— EXAMPLE II-5 ——————————————

The following data for hexachlorobenzene were obtained from Table II-8:

Solubility = 20 $\mu g/l$

Vapor pressure = 10^{-5} Torr at 20°C

$K_{ow} \approx 10^6$.

Under the conditions reported in the work of Mackay and Leinonen (1975):

L = 1 m

k_v = 8 cm/hr = 8×10^{-2} m/hr.

Hence:

$$t_{\frac{1}{2}} = \frac{0.693 \times 1}{8 \times 10^{-2}} = 8.7 \text{ hours}$$

Note that the half-life is small even though the vapor pressure is only 10^{-5} Torr. The results indicate that the vapor pressure is, by itself, not necessarily a good indicator of the importance of volatilization.

Now, consider the following conditions which might be encountered in a river:

k_a (reaeration rate) = 0.5/day

Suspended sediment concentration = 550 ppm

K_p = 5×10^4

Depth = 1 m.

The expression of volatilization half-life modified to account for the presence of the suspended solids is:

$$t_{\frac{1}{2}} = \frac{0.693\ Z}{k_v} (1 + S\ K_p)$$

From Equation II-51, the liquid-phase transfer rate for hexachlorobenzene is:

$$k_1 = \left(\frac{32}{285}\right)^{\frac{1}{4}} \times 0.5 \times 1 = 0.29 \text{ m/day} = 0.01 \text{ m/hr} = 1 \text{ cm/hr}$$

Henry's Law constant can be estimated based on Equation II-32. Using the data presented earlier:

$$K_H = \frac{10^{-5} \times 285}{760 \times .02} = 1.9 \times 10^{-6} \text{ atm·m}^3/\text{mole}$$

or

K'_H = 7.8×10^{-5}, dimensionless

Using a default value of 3,000 cm/hr for k_g, the volatilization rate is:

$$\frac{1}{k_v} = \frac{1}{1} + \frac{1}{3000 \times 7.8 \times 10^{-3}} = 1.04 \text{ cm/hr}$$

so

$$k_v \cong 1 \text{ cm/hr}$$

The half-life becomes:

$$t_\frac{1}{2} = \frac{0.693 \times 1}{1 \times 10^{-2}} \left(1 + \frac{550}{10^6} \times 5 \times 10^4\right) \cong 1800 \text{ hr} = 75 \text{ days}$$

A comparison of half-lives shows that:

$\quad$ t = 8.7 hours under laboratory conditions

$\quad$ t = 75 days under instream conditions.

This example illustrates that half-lives are not always extrapolatable from one type of system to another due to the combined difference in sorption effects and volatilization rates.

————————————— END OF EXAMPLE II-5 —————————————

2.4.2.5 Flux of Volatilizing Pollutants

The preceding sections have provided techniques for predicting volatilization rates of pollutants. Obviously, if the volatilization rate of one pollutant exceeds that of a second pollutant, then the first pollutant is more volatile than the second. However, this criterion alone does not determine whether volatilization is important in a specific situation. The volatilization flux is the rate at which mass is transferred to the gaseous phase from the liquid phase and is given by the following expression:

$$\text{Flux} = k_v C - \frac{P}{K_H} \qquad (II\text{-}54)$$

$$= k_v C, \text{ when } P = 0 \qquad (II\text{-}55)$$

where

$\quad$ C = concentration of pollutant in water as solute

$\quad$ P = partial pressure of pollutant in atmosphere.

Hence both the volatilization rate and the dissolved phase concentration have to be considered jointly to predict the flux being volatilized. Table II-23 illustrates

TABLE II-23

RELATIVE VOLATILIZATION MASS FLUXES OF SEVERAL CHEMICALS IN SATURATED SOLUTIONS

Chemical	Henry's Law Constant ($atm \cdot m^3/mole$)	Volatilization Rate Constant (cm/hr)	Solubility (ppm)	K_{ow}	Flux Ratio[a]
Carbon Tetrachloride	2.3×10^{-2}	20.	785	400	1
DDT	3.9×10^{-5}	3.9	.002-.085	10^4-10^6	$5 \times 10^4-2 \times 10^6$
Dieldrin	2.0×10^{-4}	0.02	0.2	-	4×10^6
Phenanthrene	1.5×10^{-3}	9.6	1.0	29,000	2×10^3

[a]This is the ratio of volatilization flux of a saturated solution of carbon tetrachloride to the volatilization of the specified chemical.

these principals for several chemicals. The volatilization rates for these pollutants range from a high of 20 cm/hr for carbon tetrachloride to a low of 0.02 cm/hr for dieldrin. Anthracene has a volatilization rate constant of 18 cm/hr, 90 percent as high as the volatile carbon tetrachloride. However, the solubility of anthracene in water is much lower (0.06 ppm versus 785 ppm). Hence if each of these two chemicals were to volatilize from saturated solutions, the flux of carbon tetrachloride would be 15,000 times as great. The same type of comparison can be made for DDT and carbon tetrachloride. The volatilization rate constant for DDT is relatively high (about 20 percent that of carbon tetrachloride), but the solubility is so low that the ratio of volatilization flux would be about 100,000:1.

These comparisons have not considered the relative differences in sorption characteristics of the pollutants. Since only the solute volatilizes, the volatilization flux of a pollutant which is mostly sorbed to suspended material is lower than in the absence of suspended material, all other factors remaining the same. Tables II-5 through II-9 show the octanol-water partition coefficient, which provides a measure of relative importance of sorption for the four pollutants. Because both DDT and anthracene have higher octanol-water partition coefficients than does carbon tetrachloride, the ratio of volatilization of mass fluxes is likely to be even greater than calculated above for natural systems containing suspended material.

2.5 TRANSFORMATION PROCESSES

2.5.1 Biodegradation

2.5.1.1 Introduction

Microorganisms are ubiquitous in the aquatic environment. Microbes are also very active chemically due to their ability to supply energy for reactions through normal metabolic processes and to catalyze reactions through enzymatic activity. Chemical reactions which proceed very slowly or not at all in the absence of biota occur at rates of up to eleven orders of magnitude faster in the presence of biological enzymes. Some of the reactions catalyzed by microorganisms transform or degrade organic pollutants. Frequently, microbial degradation, or biodegradation, is the most important, if not the only process which can decompose an organic pollutant in the aquatic environment.

Although microbial communities catalyze countless reactions, many of them fall into a few classes of important reactions. Oxidative reactions make up one very important class of biochemical reactions. The hydroxylation of aromatic compounds, such as benzene, is an example of an oxidative reaction which generates polar compounds from non-polar ones:

Benzene   Enzyme   Catechol
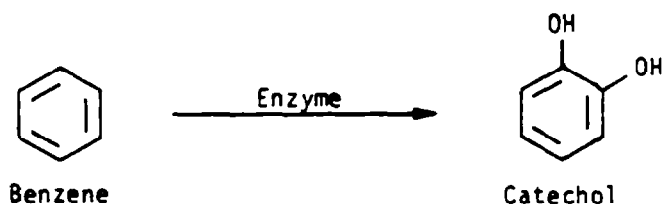
An extremely important oxidative reaction unique to microbial organisms is aromatic ring fission:

Catechol
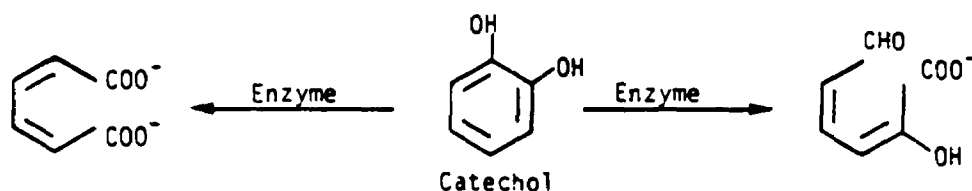
Microbes also catalyze reductive reactions. A notorious example is the dehydrochlorination of DDT to produce DDE:

DDT   Enzyme   DDE
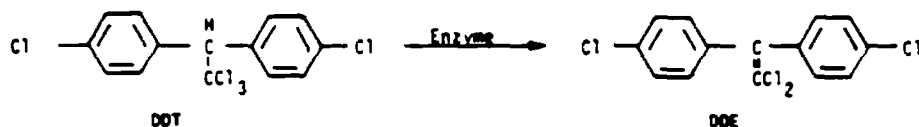
2.5.1.2.1 Metabolism of Growth Substances

Heterotrophic bacteria degrade certain organic compounds to provide the energy and carbon required for their growth. Many toxic substances function as growth substrates for bacteria in a manner similar to naturally occurring organic compounds. These growth substrates are identifiable by their ability to serve as the sole carbon source for a bacterial culture. The metabolic transformation of these growth substrates generally results in relatively complete degradation or mineralization, thus detoxifying toxic growth substrates. The detoxifying effect and relatively rapid rates of growth metabolism imply that potential growth substrates pose a lesser threat to the environment than compounds which cannot be used in this way (Tiedje, 1980).

Before the utilization of a compound can begin, the microbial community must adapt itself to the chemical. Investigations of biodegradation of a compound to which the biota have not been recently exposed, both in the field (Spain et al. 1980) and in the laboratory (Shamat and Maier, 1980) have shown the existence of a lag time (lag phase) of 2 to 50 days before the microbial community acclimates. Since the degradation of a growth substrate is relatively rapid once a microbial population has adapted to it, Tiedje (1980) has suggested that the primary concern in assessing biodegradation of such substances should be the conditions and time period required for adaptation or acclimation.

The lag time depends on several biological and environmental constraints. The primary constraint is the development of a sufficiently large bacterial population which is capable of utilizing the pollutant as a growth substrate. Frequently, specific organisms with specific enzymes are required to metabolize a pollutant. The processes of species selection and enzyme induction by which a microbial community adapts itself to a pollutant require time. The adaptation time is influenced both by prior exposure of the community to a pollutant and the initial numbers of suitable species. Spain et al. (1980) have demonstrated that prior exposure to a compound reduces or eliminates the adaptation period. Thus, lag times in pristine environments should be much longer than in locations which have been chronically exposed to a compound. In addition, Ward and Brock (1976) have shown that lag time preceding the onset of petroleum degradation depends on the initial size of the bacterial population. Water with larger microbial communities should require relatively shorter times to develop a viable population of degraders. High microbial biomass levels are associated with higher BOD_5 concentrations.

The presence of more easily degraded carbon sources may delay the adaptation of a microbial community to the metabolism of a pollutant. Ward and Brock (1976) found that microorganisms in lake water metabolized added glucose completely before degrading hydrocarbons. This diauxic pattern may result in longer lag times.

A final factor which influences lag time is the concentration of the pollutant

In the water. There may be concentration thresholds below which adaptation does not take place. (For example, no adaptation for metabolism of 4-nitrophenal occurred at concentrations below about 40 μg/l (Spain et al, 1981). Too high a pollutant concentration, on the other hand, may be toxic to the microbes (Tabak et al., 1981). The user should be aware of these possibilities when extremely low or high concentrations are involved.

Once the microbial community has adapted to the organic pollutant, it is of interest to know the rate at which biodegradation occurs. Kinetic expressions for compounds used as a growth substrate can be relatively complicated since both the substrate and bacterial concentrations change with time. The Monod equation has been used to describe the degradation rate of a compound which serves as a sole carbon source:

$$- \frac{dC}{dt} = \frac{1}{Y} \cdot \frac{dB}{dt} = \frac{\mu_{max}}{Y} \cdot \frac{B \cdot C}{K_s + C} \qquad (II-56)$$

where

C	=	pollutant concentration
B	=	bacterial concentration
Y	=	biomass produced per unit C consumed
μ_{max}	=	maximum specific growth rate
K_s	=	half-saturation constant.

Frequently, the Monod equation is reduced to a second-order biodegradation expression by assuming C $\ll K_s$, in which case:

$$- \frac{dC}{dt} = k_{B2} \cdot B \cdot C \qquad (II-57)$$

where

k_{B2} = second-order biodegradation rate constant

$= \frac{\mu_{max}}{Y \cdot K_s}$

Although Monod kinetics accurately describe some laboratory results, they are inapplicable in the environment due to the presence of other carbon sources. As a simple alternative, first order kinetics are frequently applied:

$$- \frac{dC}{dt} = k_B \cdot C \qquad (II-58)$$

where

k_B = first-order biodegradation rate constant.

Enzymes can catalyze otherwise slow hydrolytic reactions as well:

$$(CH_3O)_2 - \overset{\overset{S}{\|}}{P} - S - \underset{\underset{CHCOOC_2H_5}{|}}{CHCOOC_2H_5} \xrightarrow{\text{Enzyme}} (CH_3O)_2 - \overset{\overset{S}{\|}}{P} - S - \underset{\underset{CH_2COOH}{|}}{CHCOOC_2H_5} + C_2H_5OH$$

Malathion   **Malathion ß-monoacid**
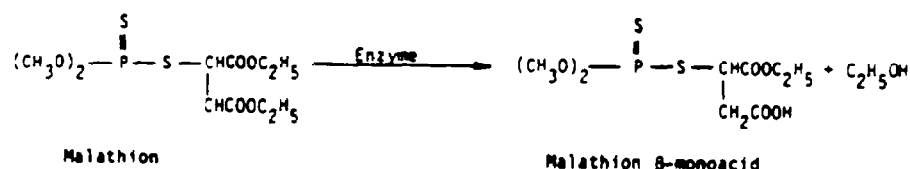
The term "biodegradation" encompasses these and other biologically mediated processes which chemically alter a pollutant. Although each reaction causes the disappearance or primary degradation of a compound, different reactions affect the toxicity of a compound in markedly different ways (Alexander, 1980).

"Mineralization" refers to the complete degradation of an organic compound to inorganic products:

$$\text{Toxic Organic Compound} \longrightarrow CO_2 + \text{Inorganic Products} \quad (\text{e.g., } NO_3^-, PO_4^{3-}, SO_4^{2-})$$
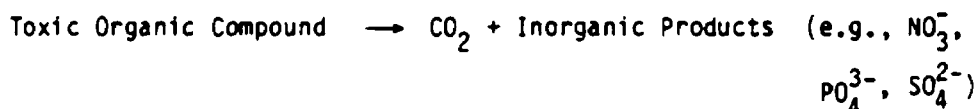
In many reactions, however, organic products remain.

"Detoxification" reactions produce innocuous metabolities from a toxic substance:

$$\text{Toxic Organic Compound} \longrightarrow \text{Innocuous Compounds}$$
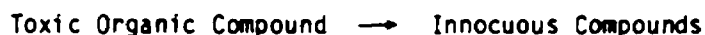
In "activation" reactions, microbes convert an innocuous compound into a toxic compound:

$$\text{Innocuous Compound} \longrightarrow \text{Toxic Compound}$$

The "defusing" of potentially hazardous compounds occurs when biota produce an innocuous compound before the parent compound's harmful form is generated.

$$\text{Potentially Toxic Compound} \longrightarrow \text{Innocuous Compound}$$

Finally, a toxic compound may be transformed chemically but still retain its toxicity. Figure II-10 illustrates some of these types of reactions as they occur among the phenoxy herbicides.

Because of the wide variety of toxicological effects metabolic transformations may have, evaluating the impact of a compound on the environment requires a knowledge of the potential products which form. However, for the purposes of estimating the concentration of a pollutant in a natural water body, the user may simply consider biodegradation to be a decay process. Methods of estimating the rates of biodegradation constitute the subject matter of the remainder of this section.

FIGURE II-10 MICROBIAL TRANSFORMATIONS OF PHENOXY HERBICIDES

2.5.1.2 Rates of Biodegradation in the Environment

The rate at which a compound biodegrades in the aquatic environment depends on its role in microbial metabolism. Some organic pollutants serve as food sources which provide energy and carbon for growth and cell maintenance when metaboi.zed by a microorganism. In other cases, microorganisms transform the pollutant, but are unable to derive energy for growth from the reaction. These two metabolic patterns, growth metabolism and cometabolism, exhibit distinct characteristics and rates of degradation. Because of the important differences between these two types of biodegradation, they are treated separately in the following discussion.

This first-order expression is analagous to the equation commonly used for the decay of BOD (see Chapter 4). Larson (1981) has shown that first-order kinetics which include a lag phase (lag time) represent the degradation of growth substrates reasonably well at initial bacterial concentration of 10^6 cells/ml or less, a condition which is usually met in the environment.

2.5.1.2.2 Cometabolism

Microorganisms also degrade compounds which they cannot use as a nutrient or growth substrate through cometabolism. Cometabolism is thought to occur when enzymes of low specificity alter a compound to form products which the other enzymes in the organism cannot utilize. The metabolites formed in the process are structurally similar to their parent molecules and frequently retain their toxicity. In some cases, the product of cometabolism can be used as nutrients by other organisms, but often these intermediate products accumulate (Alexander, 1980).

The kinetics of microbial cometabolism differ significantly from that of growth metabolism. Often no lag occurs before cometabolism begins. The degradation rates, though, are generally slower than the fully adapted rates of growth metabolism (Tiedje, 1980). Since cometabolism does not provide the microbes with any energy, it has no effect on the population size. The rate of cometabolism, however, is directly proportional to the size of the microbial population. Paris et al. (1981) showed that a second-order rate law described microbially catalyzed hydrolytic reactions:

$$-\frac{dC}{dt} = k_{B2} \cdot B \cdot C \qquad (II-59)$$

Since the bacterial population, B, is independent of the rate of cometabolism, it is possible to reduce Equation II-59 to a first-order law by making the following substitution:

$$k_B = k_{B2} \cdot B \qquad (II-60)$$

In order to use literature values of the second-order biodegradation rate constant in Equation II-60, it is necessary to make an estimate of the size of the bacterial population. Since different techniques of bacterial enumeration can yield results which vary over several orders of magnitude, it is important to use estimates of B based on the same method used to calculate k_{B2}. Table II-24 lists bacterial densities which are typical of lakes and rivers. Obviously, large uncertainties in environmental rates of cometabolism exist due to the wide range of possible bacterial densities. Generally, the user should make conservative assumptions unless other data, e.g., a high BOD, indicate larger bacterial densities.

TABLE II-24

SIZE OF TYPICAL BACTERIAL POPULATIONS IN NATURAL WATERS

Water Body Type	Bacterial Numbers (cells/ml)	Ref.
Oligotrophic Lake	50- 300	a
Mesotrophic Lake	450- 1,400	a
Eutrophic Lake	2000-12,000	a
Eutrophic Reservoir	1000-58,000	a
Dystrophic Lake	400- 2,300	a
Lake Surficial Sediments	$8 \times 10^9 - 5 \times 10^{10}$ cells/g dry wt	a
40 Surface Waters	$500-1 \times 10^6$	b
Stream Sediments	10^7-10^8 cells/g	c
Rur River (winter)	3×10^4	d

[a]Wetzel (1975). Enumeration techniques unclear

[b]Paris et al. (1981). Bacterial enumeration using plate counts.

[c]Herbes & Schwall (1978). Bacterial enumeration using plate counts.

[d]Larson et al. (1981). Bacterial enumeration using plate counts.

2.5.1.2.3 Summary

Table II-25 summarizes some of the major differences between growth metabolism and cometabolism. Although the exceptions to the generalizations about each process are numerous and some compounds can undergo both processes, the distinction between the metabolic processes can serve a useful function in a screening method. The generalizations about each process suggest the following approaches when the user has some knowledge of a compound's metabolic pathway:

Cometabolism

a) Find a second-order rate constant and estimate biomass density. Apply Equations II-59, 60.

b) When a) is not possible, assume cometabolism is negligible, i.e., $k_B = 0$.

TABLE II-25

SUMMARY OF THE CHARACTERISTICS OF THE TWO GENERAL TYPES OF BIODEGRADATION: METABOLISM AND COMETABOLISM (After Tiedje, 1980)

Topics	Metabolism for Growth	Cometabolism[*]
Distinguishing characteristics	Organism will grow on substance as sole C source. Generally ultimate degradation.	Organism will not grow on substance as sole C source. Accumulation of intermediate products likely.
Degradation rates	High rates.	Generally slow rates.
Behavior at low pollutant concentrations	Possible anamalous behavior due to threshold for enzyme induction.	No anomalous behavior, rates are first order in pollutant concentration.
Acclimation	Major effect: lag may be quite variable or lengthy due to low initial density of degraders, and perhaps starvation state of organisms in natural sample.	Often no effect; rarely causes induction, may increase tolerance to toxic chemical.
Relation of degradation kinetics to total biomass, e.g. decay rate = $k_{B2} \cdot B \cdot C$	Likely not valid, use first-order kinetics.	May be valid since activity of interest is often proportional to general biomass.
Extrapolation	General: expect eventual degradation in nature. Quantitative: difficult to be precise because of growth kinetics and acclimation effects, but may not be important problem because of generally fast rates.	Measure kinetic parameters accurately: because of the generally slower rates, extrapolations will be made over longer times, and thus measured parameters need to be accurate. Also environmental influence factors. e.g. temperature. pH, play a more important role.
Effect of added carbon	Diauxic pattern--more easily metabolized substrates are used first.	Generally effect is proportional to microbial population unless specific carbon source happens to induce or inhibit activity of interest.

[*]Alteration of a substrate, for purposes other than growth, e.g. for detoxification.

Growth Metabolism

a) Find a first- or second-order rate constant.

b) Estimate a range of lag times. For chronically exposed water bodies, assume that no lag time (t_L) occurs. For water bodies not recently exposed (within 200 days), proceed as follows:

1. Estimate lag time using available information. If no information is available use a range of 2-20 days.

2. Assume adaptation occurs as follows:

Rivers   - At travel times $< t_L$, $k_B = 0$

                - At travel times $\geq t_L$, $k_B \neq 0$

Lakes   - For well mixed lakes, first determine C at time = t_L, C_{t_L} due to all processes except biodegradation. Then using C_{t_L} as C_0 solve for C_t with a modified time, t_m, $(t_m = t - t_L)$. (Use equations in Section 5.6.1)

                - For stratified lake use only the volume through which the inflow passes (e.g., the hypolimnion volume) in calculating the hydraulic residence time (τ_w). Then proceed as above.

Estuaries   - Consider all processes except biodegradation through that downstream segment for which τ_w, as measured from the injection point, becomes greater than t_L. Thereafter include biodegradation.

When no data on which metabolic pathway a compound follows are available, the user should apply any available kinetic information and allow for the possibility of a lag phase prior to the onset of degradation.

2.5.1.3 Chemical Properties Influencing Biodegradation

The chemical properties of a compound determine whether microbes can potentially utilize it as a growth substrate or not. Compounds which serve as bacterial growth substrates usually decay more rapidly than those which microbes cometabolize. Thus, significant differences in the aquatic fate of pollutants can arise depending on which degradation process takes place.

Unfortunately, it is not possible at this time to predict whether a toxic compound is a potential source of energy and carbon solely on the basis of its chemical structure. Rather, the biodegradability of a compound is usually investigated in laboratory tests (Gilbert and Lee, 1980). Compounds which are growth substrates should be able to serve as sole carbon sources for a microbial community. Compounds which cometabolize should degrade only in the presence of another carbon

source. A systematic study of the metabolic pathways of the priority pollutants is desperately needed.

Table II-26 contains the results of a preliminary degradation test on the organic priority pollutants (Tabak et al., 1981). Because the experimental conditions were so favorable for biodegradation, the tests serve as a good indicator of a compound's potential biodegradability. Since the pollutants were not the sole carbon sources, no conclusions can be reached about their metabolic pathways. Some information on the rates of adaptation and decay, through, can be extracted from the results.

The adaptation summary results may be used as follows:

- Rapid Adaptation (D) - Use a range of adaptation times from zero days upward depending upon conditions described above

- Gradual Adaptation (A) - Use a range of adaptation times from 7 days to more than 20 depending upon the conditions described above.

The rate summary results represent estimates of the biodegradation rate constants assuming the compounds decay according to first-order kinetics. General values presented at the bottom of the table are gross estimates and should only be used if no better data is available. The rate constants should represent an upper limit for biodegradation rates by adapted populations observed in the environment.

Table II-27 contains literature values of biodegradation rate constants. Where possible, the likely metabolic pattern has been indicated. Some of these constants were measured under environmentally relevant conditions. In general, rate constants should be compared with those in Table II-27 before use.

2.5.1.4 Environmental Influences on Biodegradation Rates

Environmental conditions strongly influence the metabolic activity of a microbial population. The environment affects the types of metabolic reactions microbes are able to carry out, the availability of nutrients for these reactions, and the rates at which these reactions occur. The environmental variables which are responsible for these effects are discussed in the following sections.

2.5.1.4.1 Temperature

In general, a molecule must have an energy greater than a threshold or activation level in order for it to react chemically. Since increasing the temperature increases the number of molecules which have this minimum energy, both biotic and abiotic reactions generallv proceed more rapidly at higher temperatures. However, because enzymes catalyze most biochemical reactions and microbial populations can adapt to changes in ambient temperatures, the temperature dependence of microbially mediated reactions is complicated.

TABLE II-26

POTENTIAL BIODEGRADABILITY OF ORGANIC POLLUTANTS
IN AN AEROBIC ENVIRONMENT
(After Tabak et al., 1981)

Test Compound	Adaptation Summary	Rate Summary	Test Compound	Adaptation Summary	Rate Summary
Pesticides					
Aldrin	N	0	Endrin	N	0
Dieldrin	N	0	Heptachlor	N	0
Chlordane	N	0	Heptachlor epoxide	N	0
DDT p,p'	N	0	Hexachlorocyclohexane a-BHC-alpha	N	0
DDE p,p'	N	0	Hexachlorocyclohexane B-BHC-beta	N	0
DDD p,p'	N	0	Hexachlorocyclohexane e-BHC-delta	N	0
Endosulfan-alpha	N	0	Hexachlorocyclohexane ʌ-BHC-gamma (lindane)	N	0
Endosulfan-beta	N	0	Acrolein	D	2
Endosulfan sulfate	N	0			
PCB's and Related Compounds					
PCB-1016	N	0	PCB-1248	N	0
PCB-1221	D	2	PCB-1254	N	0
PCB-1232	D	2	PCB-1260	N	0
PCB-1242	N	0	2-Chloronaphthalene	B	2
Halogenated Aliphatic Hydrocarbons					
Chloroethanes			Chloroethylenes		
1,1-Dichloroethane	A	1	1,1-Dichloroethylene	A	2
1,2-Dichloroethane	B	1	1,2-Dichloroethylene-cis	B	1
1,1,1-Trichloroethane	B	1	1,2-Dichloroethylene-trans	B	1
1,1,2-Trichloroethane	C	1	Trichloroethylene	A	1
1,1,2,2-Tetrachloroethane	N	0	Tetrachloroethylene	A	1
Hexachloroethane	D	2	Chloropropanes		
Halomethanes			1,2-Dichloropropane	A	1
Methylene chloride	D	2	Chloropropylenes		
Bromochloromethane	D	2	1,3-Dichloropropylene	A	1
Carbon tetrachloride	D	2	Chlorobutadienes		
Chloroform	A	2	Hexachloro-1,3-butadiene	D	2
Dichlorobromomethane	A	1	Chloropentadienes		
Bromoform	A	1	Hexachlorocyclopentadiene	D	2
Chlorodibromomethane	N	0			
Trichlorofluoromethane	N	0			
Halogenated Ethers					
Bis-(2-chloroethyl) ether	B	2	4-Bromodiphenyl ether	N	0
2-Chloroethyl vinyl ether	D	2	Bis-(2-chloroethoxy) methane	N	0
4-Chlorodiphenyl ether	N	0	Bis-(2-chloroisopropyl) ether	D	2

TABLE II-26 (Continued)

Test Compound	Adaptation Summary	Rate Summary	Test Compound	Adaptation Summary	Rate Summary
Monocyclic Aromatics					
Benzene	D	2	Hexachlorobenzene	N	0
Chlorobenzene	D	2	Nitrobenzene	D	2
1,2-Dichlorobenzene	T	1	Ethylbenzene	D	2
1,3-Dichlorobenzene	T	1	Toluene	D	2
1,4-Dichlorobenzene	T	1	2,4-Dinitrotoluene	T	1
1,2,4-Trichlorobenzene	T	1	2,6-Dinitrotoluene	T	1
Phenolic Compounds					
Phenol	D	2	p-Chloro-m-cresol	D	2
2-Chloro phenol	D	2	2-Nitro phenol	D	2
2,4-Dichloro phenol	D	2	4-Nitro phenol	D	2
2,4,6-Trichloro phenol	D	2	2,4-Dinitro phenol	D	2
Pentachloro phenol	A	1	4,6-Dinitro-o-cresol	N	0
2,4 Dimethylphenol	D	2			
Phthalate Esters					
Dimethyl phthalate	D	2	Bis-(2-ethyl hexyl) phthalate	A	1
Diethyl phthalate	D	2	Di-n-octyl phthalate	A	1
Di-n-butyl phthalate	D	2	Butyl benzyl phthalate	D	2
Polycyclic Aromatic Hydrocarbons					
Napthalene	D	2	Fluorene	A	1
Acenapthene	D	2	Fluoranthene	A*	2
Acenaphthylene	D	2	1,2-Benzanthracene	N	0
Anthracene	A	1	Pyrene	D*	2
Phenanthrene	D	2	Chrysene	A*	1
Nitroso Amines and Miscellaneous Compounds					
Nitrosamines N-Nitroso-di-N-propylamine	N	0	Substituted benzenes Isophorone	D	2
N-Nitrosodiphenylamine	D	2	1,2-Diphenylhydrazine	T	1
			Acrylonitrile	D	2

Results of Tabak et al (1981) using Bunch and Chambers screening test. Results reflect potential biodegradability under favorable conditions. The test measures disappearance rather than mineralization of a compound. A domestic sewage innoculum was used. Test duration = 28 days.

Key to Test Summary
N   Not significantly degraded under conditions of test method.
D   Significant degradation with rapid adaption; < 7 days.
D* Same as D except slower adaptation at higher pollutant concentration.
A   Significant degradation with gradual adaptation; 7-21 days.
A* Same as A except no degradation evident at higher pollutant concentration.
B   Slow degradation.
C   Very slow degradation with long adaption period required; > 28 days.
T   Significant degradation with gradual adaptation followed by deadaption (toxicity).

Key to Rate Summary
Very crude estimates of first-order biodegradation rate constants may be made from the information given in Tabak et al.

0   No significant degradation rate
1   $.05 \text{ day}^{-1} < k_B < .5 \text{ day}^{-1}$; use $.05 \text{ day}^{-1}$
2   $k_B > .5 \text{ day}^{-1}$, use $.5 \text{ day}^{-1}$

TABLE II-27

BIODEGRADATION RATE CONSTANTS UNDER AEROBIC CONDITIONS

Compound	k_{B2} Second-Order Rate Constant (ml cell^{-1} day^{-1})	k_B First-Order Rate Constant (1/day)	$t_{1/2}$ Half-Life (days)	T_0 Reference Temperature (°C)	Compound Used as a Growth Substrate?	Experimental Conditions	Ref
Pesticides							
2,4-D Butoxyethyl ester	1.2×10^{-5}[3]	1.3×10^{-2}[1	53	20	?	Natural surface water samples	a
Malathion	1.1×10^{-6}[3]	1.1×10^{-1}[1	6.3×10^2	20	Yes	Natural surface water samples	a
Chlorpropham	6.2×10^{-10}[3]	6.2×10^{-7}[1	1.1×10^6	20	?	Natural surface water samples	a
Furadan	2.4×10^{-8}	2.4×10^{-5}[1	3×10^4	?	?	?	b
Atrazine	2.4×10^{-8}	2.4×10^{-5}[4	3×10^4	?	?	?	b
Polychlorinated Biphenyls							
Aroclor 1221	-	.8[2	.9	?	?	Acclimated activated sludge	c
Aroclor 1016	-	.2[2	3.5	?	?	Acclimated activated sludge	c
Aroclor 1242	-	.15[2	4.5	?	?	Acclimated activated sludge	c
Aroclor 1254	-	.1[2	7.	?	?	Acclimated activated sludge	c
Halogenated Ethers							
4-Chlorophenyl phenyl ether	-	.011-.016[2	43-63	?	?	River water; Log = 5-13 days	c
	-	3.8[4	.2	?	?	Activated sludge	c
Monocyclic Aromatics							
Nitrobenzene	-	.7[2	1.	20	Yes	Adapted activated sludge. COD decay	d
2-Chlorotoluene	6.5×10^{-8}[3]	6.5×10^{-4}	1.1×10^3	?	?	Natural surface water sample	e
Phenolic Compounds							
Phenol	-	4.[2	.2	20	Yes	Adapted activated sludge. COD decay	d
	-	6.[2	.1	?	?	Polluted river water	c
2-Chlorophenol	-	1.[2	.7	20	Yes	Adapted activated sludge	d
	-	.3	2.3	?	?	Soil suspension	c
2,4-Dichlorophenol	-	.5[2	1.4	20	Yes	Adapted activated sludge. COD decay	d
	-	.1[4	6	25	?	Natural lake waters	c
Pentachlorophenol	-	.1[2	7	25	Yes	Unadapted; Nutrient Broth	f
	-	1.[2	.7	25	Yes	Adapted; Nutrient Broth	f
2,4-Dimethylphenol	-	1.[2	.7	20	Yes	Adapted activated sludge	d
2,4-Dinitrophenol	-	.2[2	3.5	20	Yes	Adapted activated sludge	d
2,4,6-Trinitrophenol	-	0		20	No	Activated sludge	d
Phthalate Esters							
Dimethyl	1.2×10^{-4}	.12[1	5.6	?	?	?	g
Di-ethyl	7.7×10^{-8}	7.7×10^{-5}[1	9.0×10^3	?	?	?	g
Di-n-butyl	7.0×10^{-7}	7.0×10^{-4}[1	1.0×10^3	?	?	?	g
Di-n-octyl	7.4×10^{-9}	7.4×10^{-6}[1	9.3×10^4	?	?	?	g
Di-(2-ethylhexyl)	1.0×10^{-10}	1.0×10^{-7}	6.9×10^6	?	?	?	g
	-	2.5×10^{-2}[4	28	?	?	River Water	c
Butyl Benzyl	-	>.35[4	<2	?	?	River Water	c

-90-

TABLE II-27 (Continued)

Compound	k_{b2} Second-Order Rate Constant (ml/cell/day)	k_b First-Order Rate Constant (1/day)	$t_{\frac{1}{2}}$ half-life (days)	T_0 Reference Temperature (°C)	Compound Used as a Growth Substrate?	Experimental Conditions	Ref
Polycyclic Aromatic Hydrocarbons							
Naphthalene	-	.14	5.0	12	Yes	Contaminated stream sediments	h
	-	< 4.x10^{-4}	1.7x10^3	12	?	Pristine stream sediments	h
Anthracene	-	.0025	2.8x10^2	12	Yes	Contaminated stream sediments	h
	-	2.5x10^{-4}	2.8x10^3	12	?	Pristine stream sediments	h
	-	1.5	.5	?	?	Contaminated stream	c
Benz[a]anthracene	-	1.x10^{-4}	6.9x10^3	12	yes	Contaminated stream sediments	h
	-	4.x10^{-6}	1.7x10^5	12	?	Pristine stream sediments	h
Benz[a]pyrene	-	< 3x10^{-5}	large	12	?	Contaminated stream sediments	h
	-	< 3x10^{-5}	large	12	?	Pristine stream sediments	h
Phenanthrene	3.8x10^{-6}	3.8x10^{-3}(1)	1.8x10^2	?	?	?	e

Notes:

1) First-order rate constant computed using Equation II-60 and $B = 10^9$ cells/ml.

2) First-order constant calculated from percent disappearance and elapsed time.

3) Bacterial enumeration using plate count technique.

4) First-order rate constant computed from reported half-life

References:

a) Paris et al. (1981)

b) Schnoor (1981)

c) Callahan et al. (1979)

d) Pitter (1976)

e) Paris et al. (1980)

f) Kirsch and Etzel (1973)

g) Wolfe et al. (1980)

h) Herbes & Schwall (1978)

It is common practice to represent the temperature dependence of biodegradation using the following empirical formula:

$$k_B(T) = k_B(T_0) \cdot \theta_B^{(T-T_0)} \qquad (II\text{-}61)$$

where

$k_B(T)$ = specific biodegradation rate constant at temperature = T

$k_B(T_0)$ = specific biodegradation rate constant at temperature = T_0

T = ambient temperature, $^{\circ}C$

T_0 = reference temperature, $^{\circ}C$

θ_B = temperature coefficient for biodegradation.

The results of Larson et al. (1981) and Ward and Brock (1976) show that the rates of nitrilotriacetate and hydrocarbon biodegradation increased approximately two-fold over a ten degree temperature range (θ_B = 1.072). Either this value or the standard value of 1.047 for BOD decay is adequate for screening purposes.

2.5.1.4.2 Nutrient Limitation

Microbes require nutrient such as nitrogen and phosphorus in order to metabolize an organic substrates. Several researchers have suggested that inorganic nutrient limitation is a significant factor influencing biodegradation rates in the aquatic environment (Ward and Brock, 1976; Roubel and Atlas, 1978; Herbes and Schwall, 1978). Ward and Brock (1976) found a high correlation between hydrocarbon degradation rates and phosphorous concentrations in natural waters. The data fit a saturation relationship of the Michaelis-Menten type:

$$k_B(C_p) = k_B(C_p^*) \cdot \frac{.0277 \cdot C_p}{1 + .0277 \cdot C_p} \qquad (II\text{-}62)$$

where

$k_B(C_p)$ = specific biodegradation rate constant at dissolved inorganic phosphorus concentration, C_p

C_p = dissolved inorganic phosphorus concentration, $\mu g/l$

$k_B(C_p^*)$ = non-nutrient limited biodegradation rate constant.

This relationship should serve as a good indicator of possible phosphorus limitation of biodegradation in the environment. Generally surface waters downstream of domestic sewage treatment plants are not limited in either nitrogen or phosphorus. Equation II-62 should be applied only when other nutrients such as carbon and nitrogen are not limiting.

2.5.1.4.3 Sorption of Substrates

Many organic pollutants adsorb strongly on sediments, (See Section 2.3.2. The difference in the physical and chemical environments between sorbed and dissolved pollutants is likely to influence their availability to microbial organisms. Baughman et al. (1980) showed that the dissolved fraction of the compounds studied was available to biota for degradation while the sorbed fraction was not. In such cases, the rate of disappearance of the pollutant is:

$$\frac{dC_T}{dt} = k_B \cdot C_W = \alpha_W \cdot k_B \cdot C_T \qquad (II-63)$$

where

C_W = the pollutant concentration in the aqueous phase

α_W = the decimal fraction of the total analytical pollutant concentration which is in the aqueous phase (α_W = 1 - fraction sorbed).

It is well known, however, that bacteria grow very readily on surfaces and that increasing available surface area in the form of clays and sediments can increase rates of microbial metabolism. If specific information regarding the effects of sorption on the rates of biodegradation are not available for a compound, it is best to assume that sorption does not change this rate.

2.5.1.4.4 Solubility

Wodzinski and Bertalini (1972) have shown that in the dissolved state, naphthalene and biphenyl were degradable while in the pure crystalline state they were not. Thus, sparingly soluble compounds could degrade slowly for this reason alone. The extent to which this phenomenon applies to other biodegradation reactions has not been established. The user may assume that only dissolved chemicals are degraded.

2.5.1.4.5 pH

The hydrogen ion concentration also influences rates of biodegradation. Each bacterial species has a pH range for which it is best suited. Thus, at different pH values, different species may exist, or a given species may metabolize the pollutant at a different rate. Hambrick et al. (1980) found that the mineralization rate of naphthalene in oxidizing sediments varied in the proportions 1:6:5 at pH 5, 6.5, and 8. The same study found that the mineralization rates of octadecane varied in the proportions 4:5:7 at the same three pH's. Until more general rules for predicting pH effects are available, the user should assume biodegradation rates are independent of pH in the pH range 5-9 and decrease outside this range.

2.5.1.4.6 Anoxic Conditions

As the concentration of dissolved oxygen in natural water is depleted, metabolic pathways shift. When the dissolved oxygen concentration drops to about 1 mg/l, the rate of biodegradation becomes dependent on oxygen concentration in addition to

substrate concentration and the rate of degradation starts to decrease. At a dissolved oxygen concentration of about 0.5 to 1.0 mg/l nitrate begins to substitute for molecular oxygen as an oxidant.

When oxygen is depleted, anaerobic metabolism prevails with its generally lower energy yields and growth rates. Most organic substances are biodegraded more slowly under anaerobic conditions. Rate constants derived for oxygenated systems are no longer appropriate; their use may overpredict the amount of degradation.

Exceptions do exist to the rule of slower degradation under anoxic conditions. Reactions such as dehydrochlorinations and reductive dechlorinations lead to much higher degradation rates for many chlorinated hydrocarbons. Example compounds include lindane, heptachlor, pentachlorophenol, and some one and two carbon chlorinated alkanes.

─────────── EXAMPLE II-6 ───────────

Biodegradability of Naphthalene

Evaluate the biodegradability of naphthalene discharged into the Lepidoptera River by a point source just upstream from Northville's sewage treatment plant. Assume the following water quality parameters at the upstream discharge:

Temperature	= 10°C
Suspended sediment	= 10 mg/l
Inorganic phosphorus	= 5 µg/l
Dissolved oxygen	= 5 mg/l.

First, check the potential biodegradability of naphthalene in Table II-26. The table indicates that naphthalene degrades rapidly, k_B = .5 day^{-1}, and that bacteria adapt quickly to it.

Next, examine Table II-27 for further information on naphthalene's biodegradability. Naphthalene is a potential growth substrate. In addition, the data in this table concur with the rapid degradation rates suggested by Table II-26. In sediment, which had been previously exposed to naphthalene, a biodegradation rate constant of 0.14 day^{-1} was measured. As one would expect for a growth substrate, degradation rates are much lower, e.g., k_B < 4 x 10^{-4}day^{-1}, in sites not previously exposed to naphthalene.

Since naphthalene is a growth substrate, estimating the adaptation time in the Lepidoptera River is a primary issue. Because the point source continuously discharges naphthalene into the Lepidoptera River, it is safe to assume that the bacterial populations have adapted.

In a complete analysis, the user would check whether the oxygen is depleted

from the river. If so, degradation could be neglected until dissolved oxygen levels exceed 1.0 mg/l again.

Sorption by suspended sediment could potentially reduce the rate at which naphthalene biodegrades. Table II-9 gives a K_{ow} for naphthalene of 2,300. Using Equations II-16 and II-18 and assuming a suspended sediment organic carbon content of 2 percent, the partition coefficient is:

$$K_p = (.02) (.63) (2,300)$$
$$= 29$$

At the suspended sediment levels in the Lepidoptera River 10 mg/l, Table II-16 shows that sorption will not significantly reduce water column concentrations of naphthalene. Although phosphorus levels are low, assume carbon is the growth-limiting substrate.

Finally, the degradation rate is adjusted to the river water temperature using Equation II-61:

$$k_B = 0.14 \cdot 1.072^{(10-12)}$$
$$= 0.12 \ day^{-1}$$

———————————— END OF EXAMPLE II-6 ————————————————

2.5.2 Photolysis

2.5.2.1 Introduction

The sun provides the aquatic environment with a large supply of energy. Substances which absorb sunlight transform much of its radiant energy into thermal energy. But, molecules which absorb sunlight in the ultraviolet and visible portion of the spectrum may gain sufficient energy to initiate a chemical reaction. Plants use very specific photochemical reactions to provide energy for the synthesis of sugar from carbon dioxide. In other photochemical reactions, the absorption of light leads to the decomposition of a molecule. The latter type of reaction, known as photolysis, strongly influences the fate of certain pollutants in the aquatic environment.

Photolysis is truly a pollutant decay process since it irreversibly alters the reacting molecule. However, the products of the photochemical decomposition of a toxic compound may still be toxic. For example, irradiated 2,4-D esters form 2,4-D acid, a priority pollutant, in aerated waters (Zepp et al., 1975). Upon irradiation, DDT reacts to form DDE, which persists in the environment longer than DDT (Tinsley, 1979). Thus, even though the methods in this section assume that pollutants irreversibly decay through photolysis, the planner should remember that the decomposition of a pollutant does not imply the detoxification of the environment.

The rate at which a pollutant photolyzes depends on numerous chemical and environmental factors. The light absorption properties and reactivity of a compound,

the light transmission characteristics of natural waters, and the intensity of solar radiation are some of the most important factors influencing environmental photolysis. These factors will be covered by the following discussion. Understanding these factors facilitates the computation of rate constants and the identification of pollutants likely to photolyze - the final two topics of this section.

2.5.2.2 Factors Influencing Photolysis in the Aquatic Environment

2.5.2.2.1 Photochemical Reactions

All chemical reactions which occur at finite rates require the reacting molecule to gain sufficient energy to become "activated" or form a reactive intermediate. In dark or thermal reactions, the thermal energy of the environment supplies the activation energy. In photochemical reactions, the absorption of light provides the activation energy.

The "activated" molecules in photochemical reactions differ in important respects from those of thermal reactions. Thermally activated molecules usually remain in the normal or "ground" electronic energy state, whereas photochemically activated molecules exist in higher, "excited" electronic states. Because of the excess energy and the alteration of the chemical bonds of photoactivated molecules, the range of potential reaction products is much greater than that for thermally activated molecules.

The mechanism by which photoactivated molecules form and react is divided into three steps: 1) the absorption of light to produce an electronically excited molecule, 2) the "primary photochemical processes" which transform or de-excite the excited molecule, and 3) the secondary or "dark" thermal reactions which the intermediates produced in step 2 undergo (Turro, 1978).

The mechanism of photochemical reactions provides a convenient structure for a discussion of the factors which influence photolysis in the aquatic environment. Environmental factors affecting the absorption of light, step 1, will be considered first. Then, the factors influencing the fate of molecules which become excited by the absorption of light, steps 2 and 3, are discussed.

2.5.2.2.2 Light Absorption

"Only that light which is absorbed by a system can produce chemical changes (Grotthaus-Draper Law)."

(Glasstone, 1946)

As this "first law of photochemistry" implies, it is necessary to know the rate at which reacting molecules absorb light in order to determine the rate of a photo-

chemical reaction in the environment. The following factors which influence light
absorption in the aquatic environment are discussed here: 1) molecular absorption of
light, 2) solar radiation, and 3) light attenuation in natural waters.

2.5.2.2.2.1 Molecular Absorption of Light

Both light and molecules have quantized energies. Light interacts with matter
as quanta with energies inversely proportional to their wavelengths. A molecule has
quantized internal energy states associated with the configuration of its electrons
and the rotation and vibration of its chemical bonds. Since a molecule can absorb
light only as a whole photon, light absorption is possible only if the energy of the
photon corresponds to the energy change of an allowed transition between the molecule's
internal energy states. Consequently, the probability of a photon being absorbed
varies strongly with wavelength of the light in a way that is unique to every chemi-
cal species.

To initiate a chemical reaction, the absorbed light must be sufficiently
energetic to cause a change in the absorbing molecule's electronic structure.
Generally, radiation with wavelengths in the ultraviolet-visible range, or shorter,
has sufficient energy to initiate photochemical reactions while radiation with
wavelengths in the infrared range, or longer, does not. Thus, the ultraviolet-visible
light absorption properties of a chemical are of primary interest in photochemistry.

Photochemical reactions in the aquatic environment depend on the rate at which
molecules in aqueous solution absorb light. According to Beer's Law, the rate of
light absorption by a single compound (I_a) in a cross-section of solution with
infinitesimal thickness (Δz) is proportional to the concentration of the light
absorbing specie (C), i.e.,

$$I_a(z) = I(z) \cdot 2.3 \cdot \varepsilon \cdot C \cdot \Delta z \qquad (II\text{-}64)$$

where

$\qquad$ I(z) $\quad$ = $\quad$ intensity of the light at a depth z in the solution

$\qquad$ ε $\qquad$ = $\quad$ base 10 molar extinction coefficient.

ε reflects the probability of the light being absorbed by the dissolved molecules and
therefore varies with the wavelength of the incident light as shown in Figure II-11.
Absorption spectra, such as shown here, contain information necessary to compute the
rate at which pollutants absorb radiation available in the environment.

2.5.2.2.2.2 Solar Radiation

The only radiant energy available for absorption by pollutants in the aquatic
environment comes from the sun. The sun emits radiation of nearly constant intensity
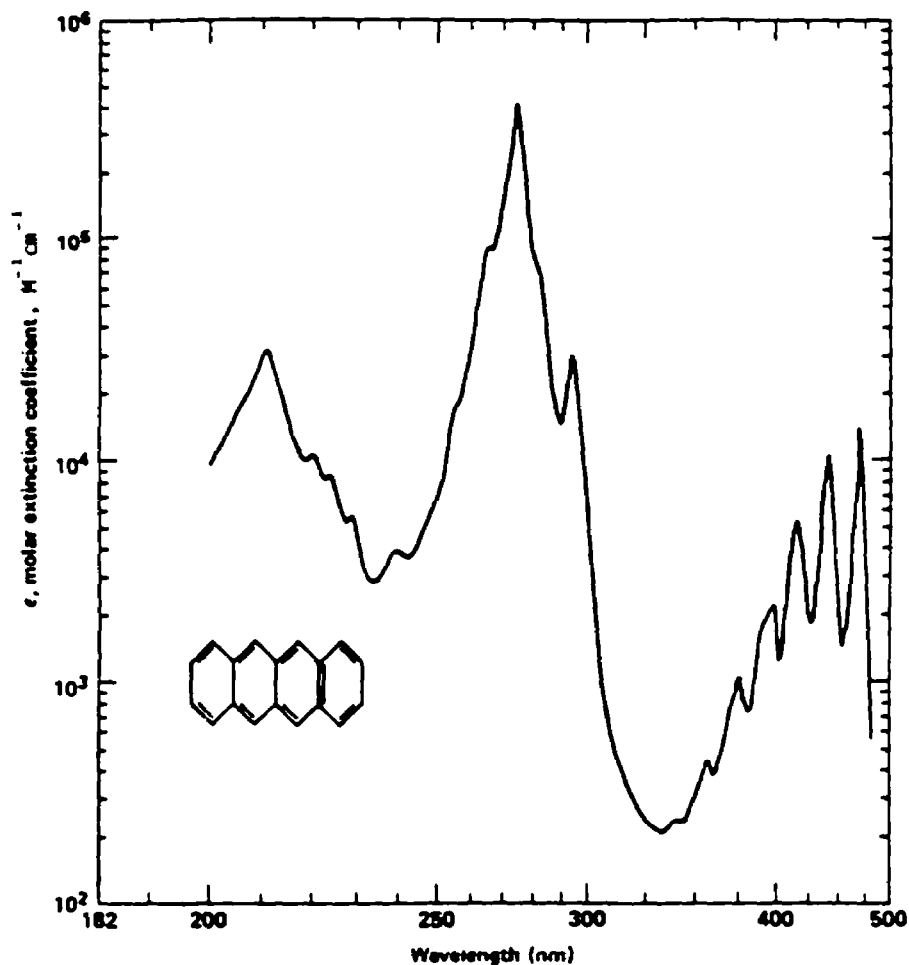
Source: U.V. Atlas of Organic Compounds.

FIGURE II-11   ULTRAVIOLET ABSORPTION SPECTRUM OF NAPHTHACENE

and spectral distribution. But, gases and particles in the earth's atmosphere alter the incoming solar radiation through scattering and absorption. Scattering of the direct solar beam creates the diffuse or sky radiation visible at the earth's surface. Absorption of both diffuse and direct radiation reduces the intensity of solar radiation reaching the earth. Since the strength of absorption and scattering depends strongly on the wavelength of the light involved, the interaction of sunlight with the atmosphere alters the spectral distribution of solar radiation as well, as Figure II-12 shows.

The composition of the earth's atmosphere and the geometrical relationship of the sun and earth change over time causing the solar radiation incident upon the earth's surface to vary as well. A comparison of the total solar irradiance under clear skies at various times, seasons, and latitudes (Table II-28) to the extra-
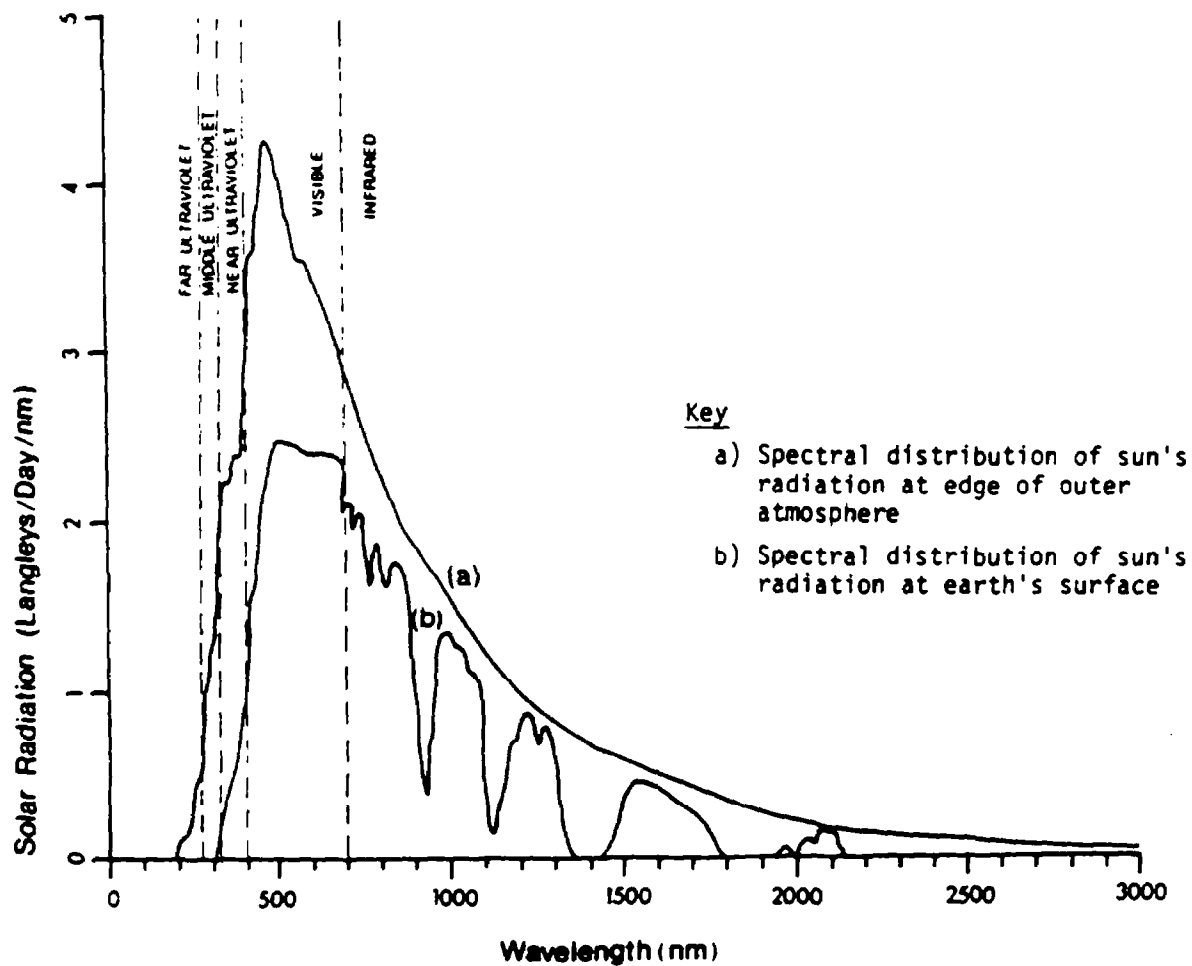
Sources: (a) Weast and Astle (1980); (b) Moon (1940).

FIGURE II-12   SPECTRAL DISTRIBUTION OF SOLAR ENERGY
(A) OUTSIDE THE EARTH'S ATMOSPHERE, AND
(B) AT THE EARTH'S SURFACE

atmospheric solar flux of 2800 langleys/day demonstrates the effects of changes in earth-sun geometry. The composition of the atmosphere differs greatly from place to place and, of the factors influencing the total solar flux, is the most difficult to accurately quantify. Historical records of the solar radiation, such as shown in Figure II-13, are the best way to estimate the mean solar energy flux at a given locale. However, care should be taken to account for the influence of riparian vegetation on incoming radiation. Section 4.4.3 discusses how to approximate the effects of shading.

Information concerning the variability of the spectral distribution of solar energy incident upon the earth's surface is not as readily available. It is known

TABLE II-28

CALCULATED SOLAR RADIANT ENERGY FLUX TO A HORIZONTAL SURFACE UNDER A CLEAR SKY
(langleys/day)

Latitude	Time Of Day	Spring	Summer	Fall	Winter	Annual Mean
30°N	Mean[1]	680	750	530	440	600
	Mid-Day[2]	2100	2200	1700	1400	1900
40°N	Mean	650	740	440	320	540
	Mid-Day	1900	2100	1400	1000	1600
50°N	Mean	590	710	330	190	460
	Mid-Day	1700	1900	1000	650	1300

1 Mean values represent calculated seasonal means under a clear sky. These should represent upper limits for solar radiant energy at sea level. Reference: Weast and Astle (1980).

2 Mid-Day values represent mid-day flux extended over a 24-hour period. These assume an atmospheric turbidity of 0, precipitable water content of 2 cm, and an atmospheric ozone content of .34 cm NTP. Reference: Robinson (1966).

that the fraction of the solar energy in the ultraviolet region decreases with increased attenuation of light by the atmosphere. The fraction of the energy which is visible remains relatively constant. For the purpose of this document, it is sufficiently accurate to assume that the reduction in UV-visible radiation is proportional to the reduction in the total flux.

2.5.2.2.2.3 Light Attenuation in Natural Waters

Just as the earth's atmosphere reduces the intensity of solar radiation reaching the earth's surface, natural waters reduce the intensity of radiation available for absorption by aquatic pollutants. The first process which reduces the availability of light in the water column is reflection. In most cases, the surface of the water reflects less than 10 percent of solar radiation (Zepp and Cline, 1977). Reflection also alters the solar spectrum slightly. A calculated spectral distribution of solar radiation, expressed in photons, immediately below the surface of a water body is presented in Table II-29.
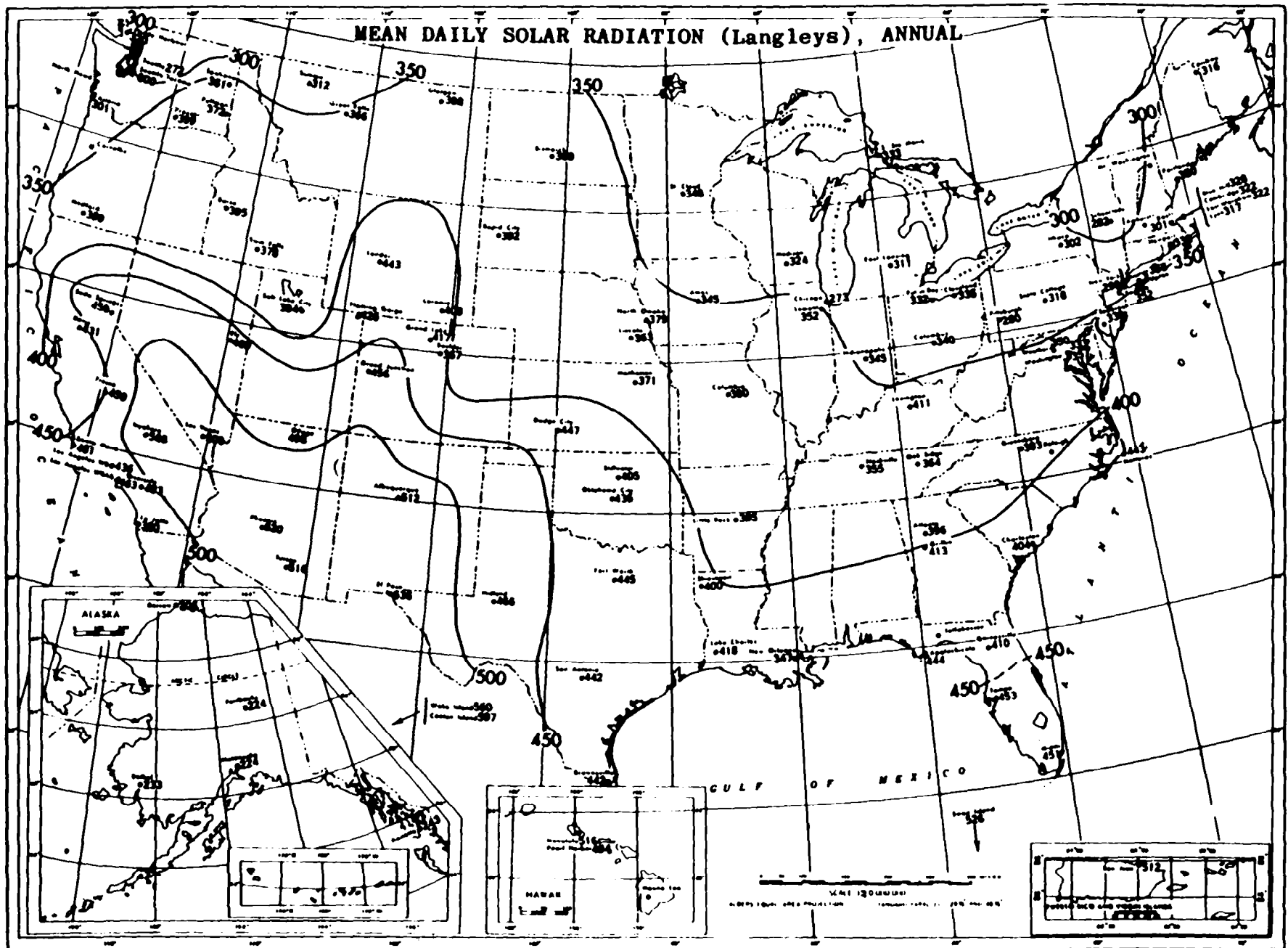
FIGURE 11-13   SOLAR RADIATION IN THE UNITED STATES

TABLE II-29

CALCULATED SOLAR IRRADIANCE IN A WATER BODY JUST BENEATH
THE SURFACE, ANNUAL MEAN AT 40°N

Wavelength[b] (nm)	Photon Spectral Irradiance[a] $W(\lambda)$[c] (10^{14} photons cm^{-2} $sec^{-1}nm^{-1}$)	$W'(\lambda)$[d] (10^{14} photons cm^2 sec^{-1})
300	.00303	.0303
310	.0388	.388
320	.113	1.13
330	.181	1.81
340	.211	2.11
350	.226	2.26
360	.241	2.41
370	.268	2.68
380	.294	2.94
390	.366	3.66
400	.526	5.26
410	.692	6.92
420	.712	7.12
430	.688	6.88
440	.814	8.14
450	.917	9.17
460	.927	9.27
470	.959	9.59
480	.983	9.83
490	.930	9.30
500	.949	9.49
510	.962	9.62
520	1.00	10.0
550	1.04	52.0
600	1.07	53.5
650	1.08	54.0
700	1.07	53.6
750	1.03	51.5
800	.988	49.4

[a]Estimated reference solar flux, I_o = 540 langleys/day. D_o = 1.0

[b]Centric wavelength of waveband X nm in width,
for $300 < \lambda \leq 520$, X=10 nm. For $\lambda \geq 550$, X=50 nm

[c]Mean irradiance over wavelength interval of width X.

[d]Integrated irradiance over wavelength interval of width X.
$W'(\lambda)=W(\lambda) \cdot \Delta\lambda=W(\lambda) \cdot X$.

Reference: Burns et al. (1981).

As solar radiation penetrates deeper into natural waters, it is absorbed and scattered by particulates, dissolved substances, and water itself. Measurements of light attenuation in natural waters have been based on the decrease of solar irradiance, which includes both collimated and scattered light. Lambert's Law expresses the decrease in the irradiance, $I(z)$, i.e., the total flux incident upon an element of surface divided by its area, with depth z, as follows:

$$-\frac{dI(z)}{dz} = K \cdot I(z) \qquad (II-65)$$

where

K = diffuse light attenuation coefficient.

The diffuse attenuation coefficient can be expressed as a sum of terms accounting for absorption, a, and backward scattering of light, s_b (Smith and Tyler, 1976):

$$K = Da + s_b \qquad (II-66)$$

where

D = radiance distribution function.

Usually, s_b is small compared to the absorption term. The absorption term constitutes part of the beam attenuation coefficient, α, which can be measured in a spectrophotometer:

$$\alpha = a + s_b + s_f \qquad (II-67)$$

where

s_f = the forward scattering coefficient of the solution.

The inclusion of the distribution function, D, in Equation (II-66) accounts for the difference in mean light pathlength of collimated and diffuse light. Perfectly diffuse light has a mean path through an element of water which is twice as long as that of a beam of light. The distribution function, generally increases asymptotically with depth due to the increasing fraction of the total light which is scattered. In water bodies where scattering can be ignored, D has a value of 1.2. Miller and Zepp (1979) reported that the mean value of D for six sediment laden waters was 1.6.

The diffuse light attenuation coefficient of natural waters differs greatly due to variations in the types and amounts of particles and dissolved substances in the water. Miller and Zepp (1979), Zepp and Schlotzhauer (1981), and Smith and Baker (1978) have investigated the contributions of suspended sediments, dissolved organic carbon, and chlorophyll pigments to the light attenuation coefficient. By using Equation (II-66) to integrate the results of these investigations, and assuming

backscattering to be negligible, Burns et al. (1981) derived the following expression to estimate the diffuse light attenuation coefficient:

$$K = D \cdot \left[a_w + (a_a \cdot chl\ \underline{a}) + (a_{DOC} \cdot DOC) + (a_{ss} \cdot SS) \right]$$ (II-68)

where

a_w	=	absorptivity of water
a_a	=	absorptivity of chlorophyll-$\underline{a}$ pigment
chl $\underline{a}$	=	concentration of chlorophyll-$\underline{a}$ pigment
a_{DOC}	=	absorptivity of dissolved organic carbon
DOC	=	concentration of dissolved organic carbon
a_{ss}	=	absorptivity of suspended sediments
SS	=	concentration of suspended sediments.

Each absorptivity term varies with the wavelength of light, as shown in Table II-30.

Diffuse light attenuation coefficients can also be estimated using turbidity indicators such as Secchi disc depth. Empirical studies have shown that the diffuse light attenuation coefficient is inversely proportional to the Secchi disc depth, Z_{sd}:

$$K = \frac{R}{Z_{sd}}$$ (II-69)

The proportionality constant, R, has a value between 1.44 and 1.7 for visible light, i.e. 400-800 nm. In the middle ultraviolet portion of the spectrum, i.e. near 312 nm, R has a value of 9.15 (Zepp, 1980).

2.5.2.2.3 Fate of Excited Molecules

"Each molecule taking part in a chemical reaction which is a direct result of the absorption of light takes up one quantum of radiation (Stark-Einstein Law)." (Glasstone, 1946)

According to this "second law of photochemistry", the extent to which a photochemical reaction progresses depends on the number of quanta of light absorbed. Each absorbed photon produces an electronically excited molecule which can undergo numerous processes, including reaction. Factors which influence the fraction of excited molecules which undergo reaction, called the quantum yield, comes first in the following discussion of the fate of excited molecules. Then, the two major classes of environmental photolysis reactions, direct and sensitized, are discussed.

2.5.2.2.3.1 The Quantum Yield

Although all photochemical reactions are initiated by the absorption of a photon, not every absorbed photon induces a chemical reaction. Besides chemical

TABLE II-30

CONTRIBUTIONS TO LIGHT ATTENUATION COEFFICIENT

Waveband Center (nm)	a_w^a (m^{-1})	a_a^b [(mg/l)$^{-1}$ m^{-1}]	a_{DOC}^c [(mg/l)$^{-1}$ m^{-1}]	a_{ss}^d [(mg/l)$^{-1}$ m^{-1}]
300	.141	69.*	6.25	.35
310	.105	67.*	5.41	.35
320	.0844	63.*	4.68	.35
330	.0678	61.*	4.05	.35
340	.0561	58.*	3.50	.35
350	.0463	55.	3.03	.35
360	.0379	55.	2.62	.35
370	.0300	51.	2.26	.35
380	.0220	46.	1.96	.35
390	.0191	42.	1.69	.35
400	.0171	41.	1.47	.35
410	.0162	39.	1.27	.35
420	.0153	38.	1.10	.35
430	.0144	35.	0.949	.35
440	.0145	32.	0.821	.35
450	.0145	31.	0.710	.35
460	.0156	28.	0.614	.35
470	.0156	26.	0.531	.35
480	.0176	24.	0.460	.35
490	.0196	22.	0.398	.35
500	.0257	20.	0.344	.35
510	.0357	18.	0.297	.35
520	.0477	16.	0.257	.35
550	.0638	10.	0.167	.35
600	.244	6.	0.081	.35
650	.349	8.	-	.35
700	.650	3.	-	.35
750	2.47	2.	-	.35
800	2.07	0.	-	.35

[a]Source: Smith and Baker (1981)
[b]Source: Smith and Baker (1978)   Calculated using $a_a = K_2/D$, $D = 1.2$
[c]Source: Zepp and Schlotzhauer (1981)
[d]Source: Miller and Zepp (1979). Calculated using $a_{ss} = K_s/D$.

*Denotes extrapolated values.

reactions, possible processes which excited molecules may undergo include the reemission of light through fluorescence and phosphorescence, the internal conversion of the photons' energy into heat, and the excitation of other molecules, as shown in Figure II-14. The fraction of absorbed photons which cause the desired reaction(s) is termed the quantum yield, ϕ

$$\phi \equiv \frac{\text{moles of a given species formed or destroyed}}{\text{moles of photons absorbed by the system}} \qquad (II-70)$$

The quantum yields for photochemical reactions in the solution phase exhibit two properties which greatly simplify their use:

• The quantum yield is less than or equal to one
• The quantum yield is independent of the wavelength of the absorbed photons.

Although exceptions to these rules exist, they are rare for photochemical reactions in the aquatic environment.

Environmental conditions influence photolysis quantum yields. Molecular oxygen acts as a quenching agent (see Figure II-14) in some photochemical reactions, reducing the quantum yields (Wolfe et al., 1978). In other cases, it has no effect or may even be a reactant. In any case, rate constant and quantum yield measurements should be performed in water with oxygen concentrations representative of environmental conditions.

Suspended sediments also influence rates of photolysis. Not only do suspended sediments increase light attenuation, but they change the reactivity of compounds sorbed on them (Miller and Zepp, 1979). Sorption may either increase or decrease a compound's reactivity depending on the reaction it undergoes. This effect, however, is of secondary importance in comparison to the increase in light attenuation by the suspended sediments (Burns et al., 1981). Thus, the effects of sorption will be neglected.

Chemical speciation also affects rates of photolysis. Different forms of an organic acid or base may have different quantum yields, as well as absorptivities, causing the apparent photolysis rate of the compound to vary with pH. The possibility of this should be kept in mind when the pK_a of a photolyzing compound is 7 ± 2. Except where stated otherwise, data contained herein may be assumed independent of pH over the range of values observed in natural waters.

Photochemically initiated reactions may show a temperature effect depending upon the actual mechanisms involved. General methods for predicting this effect have yet to be developed. Users of this screening manual should assume thermal effects on photolysis to be negligible.

Quantum yields vary over several orders of magnitude depending on the nature of the molecule which absorbs light and the reactions it undergoes. The two major

A_o + heat

Internal
conversion

A_o + hν'

Flourescence

A_o + heat

Internal
conversion

A_o + hν''

Phosphorescence

A_o

hν

Absorption

A*

Intersystem crossing

A*

Chemical reaction

Quenching

·Q_o

A_o + Q*

Quenching

·Q_o

A_o + Q*

Chemical reaction

A_o — ground state of reactant molecule
A* — excited state

Q_o — ground state of quenching molecule
Q* — excited state
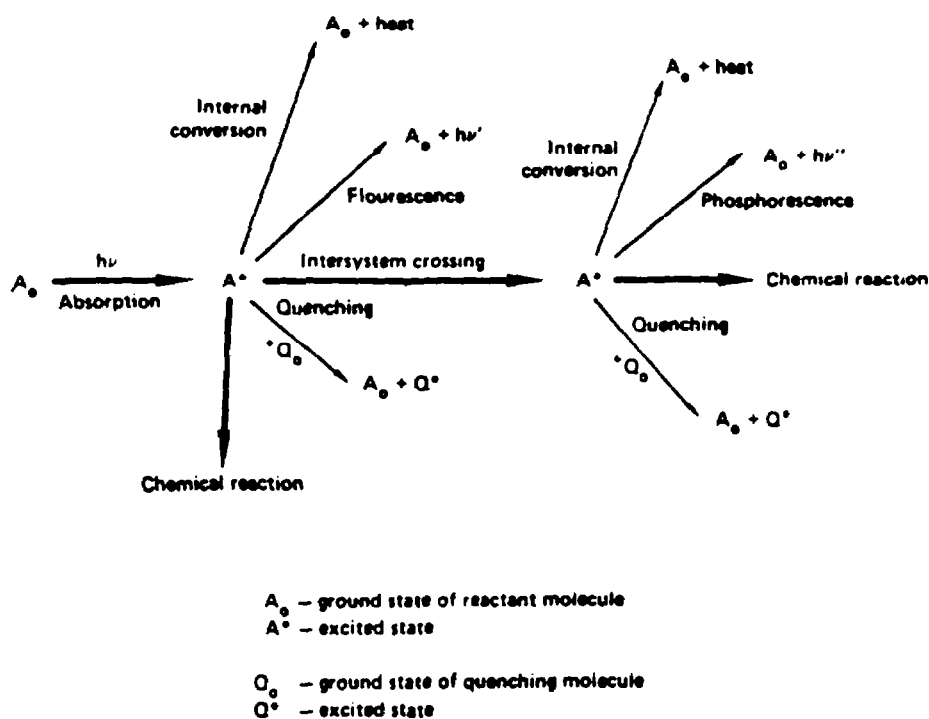
FIGURE II-14   PHOTOCHEMICAL PATHWAYS OF AN EXCITED
MOLECULE. EXCITED MOLECULES DO NOT
ALWAYS CHEMICALLY REACT.

classes of photochemical reactions of interest in the aquatic environment are direct
and sensitized photolysis. A closer examination of each reaction type follows.

2.5.2.2.3.2 Direct Photolysis

Direct photolysis occurs when the reacting molecule itself directly absorbs
light. The excited molecule can undergo various types of reactions, including
fragmentation, reduction, oxidation, hydrolysis, acid-base reaction, addition,
substitution, isomerization, polymerization, etc. Figure II-15 shows examples of the
reactions undergone by three toxic substances which directly photolyze.

The quantum yield for the direct photolysis, ϕ_d, of a compound is a constant
defined as follows:

$$\phi_d = \frac{-dC}{dt} \Big/ I_{ad} \qquad (II-71)$$

where

C   = concentration of the compound

I_{ad} = rate at which the compound absorbs light.

Table II-31 lists several disappearance quantum yields for direct photolysis of
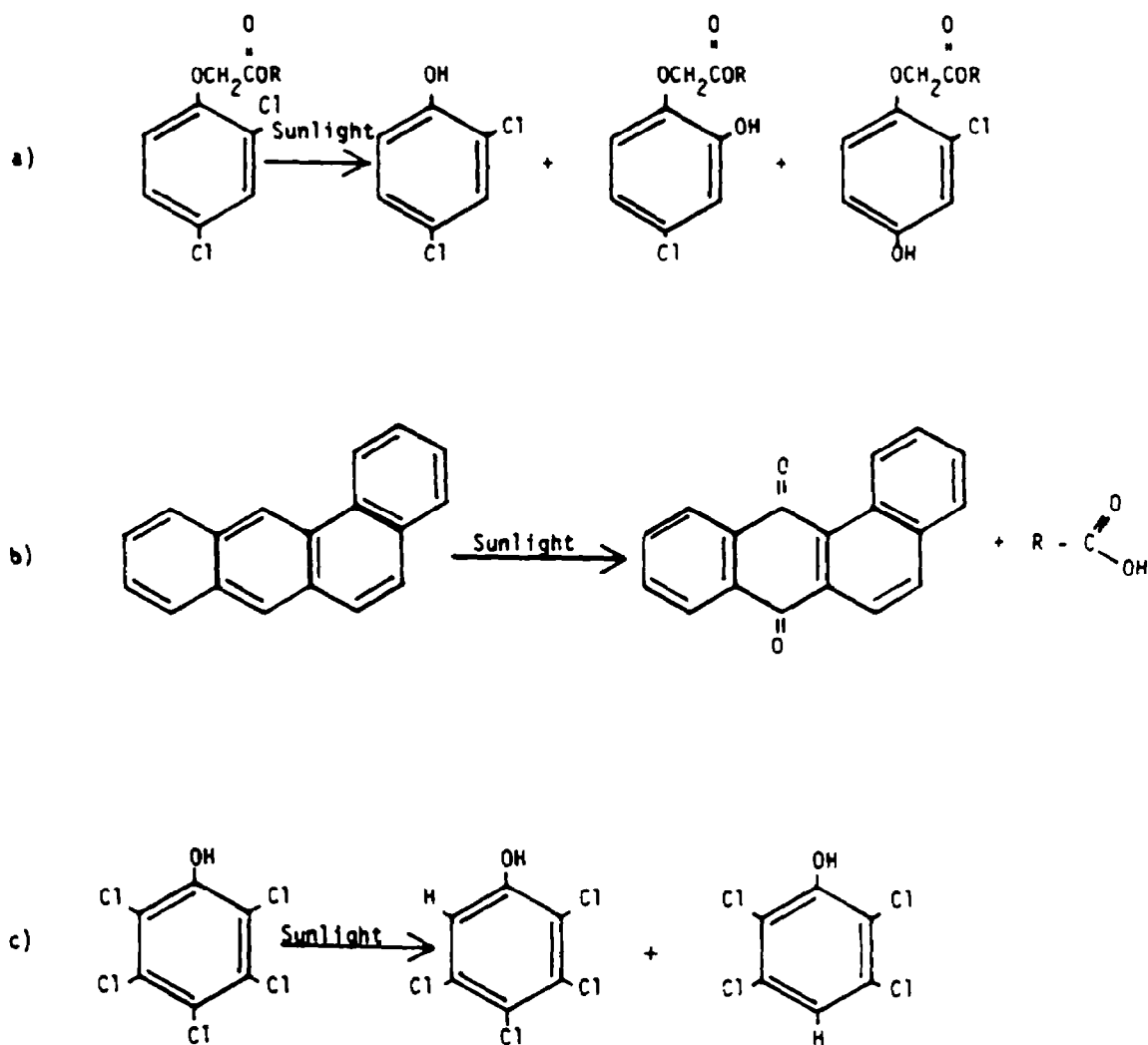
FIGURE II-15   DIRECT PHOTOCHEMICAL REACTIONS OF (A) 2,4-D ESTER,
                (B) BENZ(A)ANTHRACENE, AND (C) PENTACHLOROPHENOL.

aquatic pollutants.

By comparing molecular absorption spectra with the spectral distribution
of sunlight, it is possible to determine whether or not a compound may directly
photolyze. Benzene, as shown in Figure II-16a, does not directly photolyze because
it does not absorb light above 275 nm. Naphthacene, shown in Figure II-16b, does
directly photolyze because of its strong absorptivity in the sunlight region of the
spectrum. Humic acids, Figure II-16c, by virtue of their absorption of sunlight may
initiate indirect, or sensitized, photochemical reactions.

TABLE II-31

DISAPPEARANCE QUANTUM YIELDS, ϕ_d FOR DIRECT PHOTOLYSIS

Compound		ϕ_d	Reference
Polycyclic Aromatic Hydrocarbons			
Naphthalene		.015	a
1-Methylnaphthalene		.018	a
2-Methylnaphthalene		.0053	a
Phenanthrene		.010	a
Anthracene		.0030	a
9-Methylanthracene		.0075	a
9,10-Dimethylanthracene		.0040	a
Pyrene		.0021	a
Fluoranthrene	(313 nm)	.00012	a
	(366 nm)	.000002	a
Chrysene		.0028	a
Naphthacene		.013	a
Benz(a)anthracene		.0033	a
Benz(a)pyrene		.00089	a
2,4-D Esters			
Butoxyethyl ester		.056	b
Methyl ester		.031	b
Carbaryl		.0055	c
N-Nitrosoatrazine		.30	d
Trifluralin		.0020	d
DMDE		.30	d

[a] Zepp and Schlotzhauer (1979)   [c] Wolfe et al. (1978)

[b] Zepp et al. (1975)   [d] Zepp and Cline (1977)
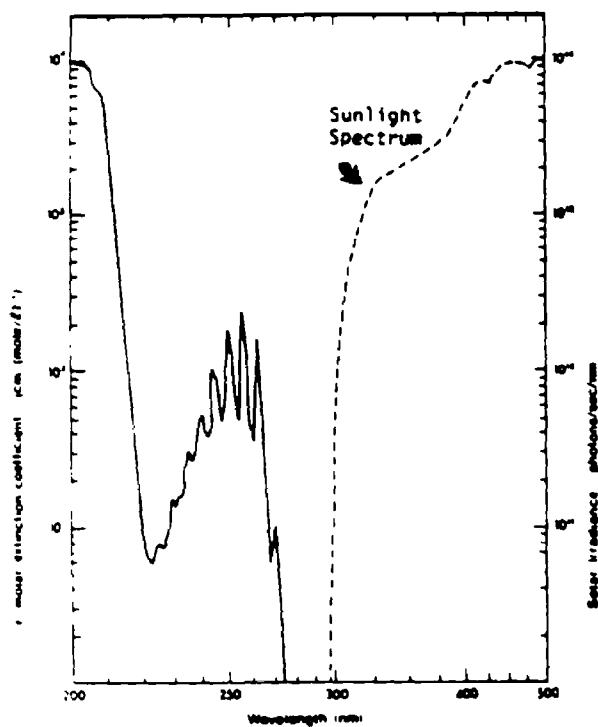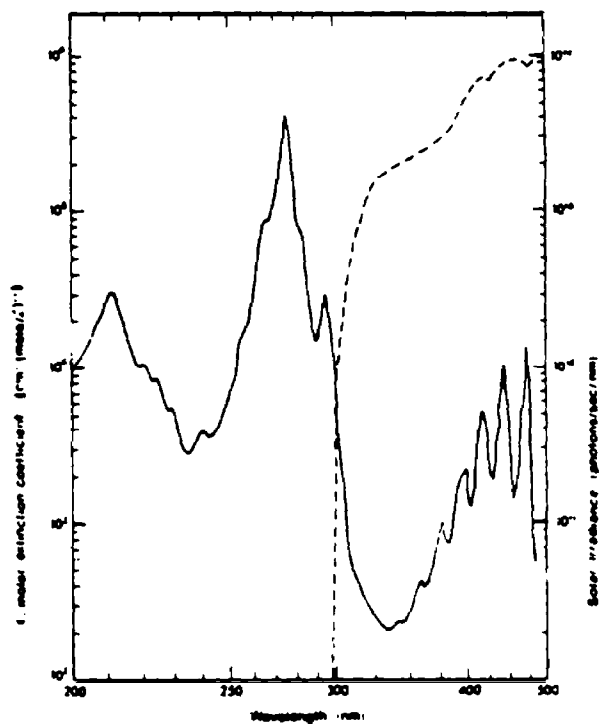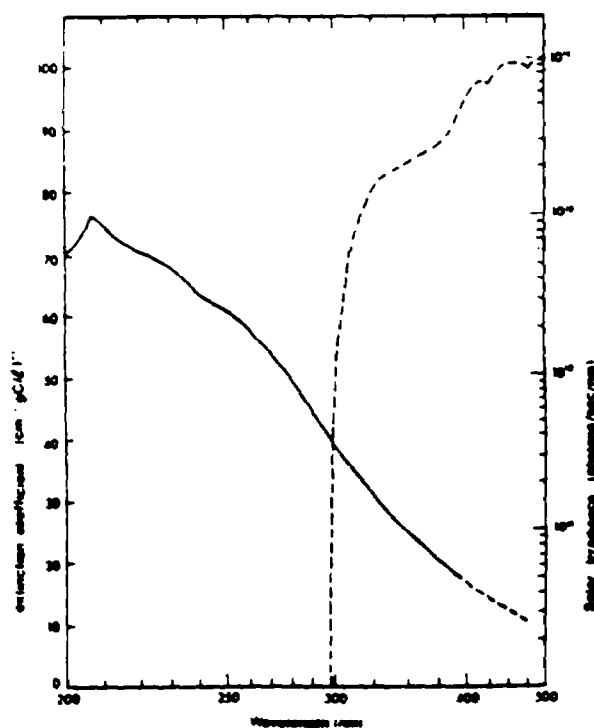
FIGURE II-16

COMPARISON OF SOLAR IRRADIANCE
WITH THE ABSORPTION SPECTRA OF
(A) A COMPOUND WHICH DOES NOT
DIRECTLY PHOTOLYZE, (B) A
COMPOUND WHICH DOES DIRECTLY
PHOTOLYZE, AND (C) A SUBSTANCE
WHICH INITIATES INDIRECT
PHOTOCHEMICAL REACTIONS

References: Sunlight spectrum, Burns et al. (1981); Benzene and naphthacene
spectra, U.V. Atlas of Organic Compounds; Humic acid spectrum,
Schnitzer (1971).

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2.5.2.2.3.3 Sensitized Photolysis

Sunlight can cause the degradation of aquatic pollutants by means other than direct photolysis. A light-absorbing molecule can transfer its excess energy to an acceptor molecule causing the acceptor to react as if it had absorbed the radiant energy directly. This reaction mechanism, known as photosensitization, contributes to the degradation of aquatic pollutants when suitable light absorbing substances, or photosensitizers, are present. 2,5-Dimethylfuran is an example of a compound which degrades by sensitized photolysis. It does not react when exposed to sunlight in distilled water but degrades rapidly in waters containing natural humic acids (Zepp et al. 1981a).

Numerous substances, including humic acids, titanium dioxide, and synthetic organic compounds, can sensitize photochemical reactions. But, most potential sensitizers occur at such low environmental concentrations that they have negligible effects on photolysis rates. Humic acids, the naturally occurring by-products of plant matter decay, frequently attain concentrations of 1-10 mg as carbon per liter in natural systems. Humic acids strongly absorb sunlight with wavelengths shorter than 500 nm, as the absorption coefficients for dissolved organic carbon, a_{DOC}, in Table II-27, indicate.

The quantum yield for photosensitized reactions, ϕ_s, is defined in a manner similar to the quantum yield for direct photolysis:

$$\phi_s = \frac{-dC}{dt} \bigg/ I_{as} \qquad (II-72)$$

where

$\quad$ C $\quad$ = concentration of the pollutant

$\quad$ I_{as} = rate of light absorption by the sensitizing molecule.

The quantum yield for sensitized photolysis, however, is not constant but depends on the pollutant concentration, such that:

$$\phi_s = Q_s \cdot C \qquad (II-73)$$

where

$\quad$ Q_s = a constant.

This is due to the fact that the probability of the sensitized molecule donating its energy to a pollutant molecule is proportional to the concentration of the pollutant molecule. Published values of Q are very rare. Zepp et al. (1981b) report a Q of 19 $(mol/l)^{-1}$ for the photosensitized oxidation of 2,5-dimethylfuran.

2.5.2.2.4 Preliminary Screening of Direct Photolysis

As the preceding discussion indicates, a number of environmental parameters influence photolysis. The following sections show that the procedure for calculating the photolysis rate can be quite involved. Therefore, a preliminary screening which attempts to determine whether photolysis rates are likely to be significant or insignificant (without actually calculating the rate itself) is useful.

If $\epsilon = 0$ (i.e. if the molecule does not absorb solar radiation) for $290 < \lambda < 700$ nm, then direct photolysis does not occur. References which show ϵ versus λ relationships include Luman et al.(1982), Sadtler (undated), and Schnitzer (1971). Numerous other references contain λ^* values (i.e. the wavelength of maximum absorption.) If λ^* $< \sim 270$ nm or $\lambda^* > \sim 730$ nm, then direct photolysis is probably unimportant. References which contain λ^* values (in addition to Table II-32 of this document) include Lyman et al. (1982), Friedel and Orchin (1951), Hershenson (1966) and Kamlet (1960). The Kamlet reference is a series of 20 volumes from 1960 to present and contains λ^* values for many thousands of organics.

It should be recognized that small ϕ_d or small ϵ_{max} are not good indicators of the importance of photolysis. For example, consider the tabulations below:

$$\phi_d \text{ (benzo[a]pyrene)} = 0.00089 \text{ at } \lambda = 313 \text{ nm}$$

but

$$\epsilon_{max} = 13,000; \ \lambda = 347 \text{ nm}$$
$$\epsilon_{max} = 24,000; \ \lambda = 364 \text{ nm}$$
$$\epsilon_{max} = 29,000; \ \lambda = 384 \text{ nm}$$

and

$$k_{do} \text{ (near surface photolysis rate)} = 17./\text{day}$$

The quantum yield for benzo[a]pyrene is small (0.00089) considering that quantum yields can be as high as 1.0. However, the near surface photolysis rate (i.e. the photolysis rate in a very thin layer of clear water) is 17./day, a very large rate. This result is caused by the high extinction coefficients for benzo[a]pyrene, and it is evident that photolysis can be important for this compound.

Now consider the case of small ϵ_{max}

For naphthalene :

$$\epsilon_{max} = 250 \text{ at } \lambda = 311 \text{ nm}$$

but

$$\phi_d = 0.015$$

and

$$k_{do} = 0.2/\text{day}$$

For the small ϵ_{max} (250), the near surface photolysis rate is 0.2/day. While this is not an extremely large rate, it may also not be negligible either, depending on the particular environmental condition.

Certain categories or groups of chemicals are likely to be poor absorbers of sunlight. A number of these groups are shown below:

Group	Examples
alcohols	R-OH: ethyl alcohol
ethers	R-O-R': diphenyl ether
amines	R-NH$_2$(primary): methylamine
nitriles (cyanides)	R-CN: hydrogen cyanide

For these groups, photolysis is likely to be unimportant. Other groups, however, do tend to absorb sunlight. Figure II-17 shows a number of these groups.

A final preliminary screening is to compare an estimated upper limit photolysis rate (e.g., using ϕ_d = 1) against other first-order rates which have already been calculated. If these rates are high enough, the photolysis rate, even under optimal light-absorbing conditions, may be relatively small and therefore negligible. For example, an upper limit photolysis rate which is calculated to be 20 percent as large as a hydrolysis rate is relatively insignificant.

2.5.2.3 Computing Environmental Photolysis Rates
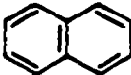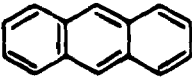
The overall rate at which a pollutant photolyzes in the aquatic environment is the sum of the rates of direct and sensitized photochemical reactions. At the low pollutant concentrations observed in the environment, the rates of both direct and sensitized photolysis are proportional to the concentration of the pollutant. Thus, photolysis follows a first-order rate law:

$$\frac{dC}{dt} = -k_p \cdot C \qquad\qquad (II-74)$$

where

k_p = overall photolysis rate constant, day^{-1}

= $k_d + k_s$

k_d = direct photolysis rate constant, day^{-1}

k_s = sensitized photolysis rate constant, day^{-1}.

Due to the complexity of the units for the parameters in the photolysis section, it is essential that the user employ the specified units in each equation. All resulting first-order photolysis rate constants have units of day^{-1}.

Group	λ_{max} (nm)	Molar Absorptivity, ϵ (L/mol-cm)
$>$C=O (aldehyde, ketone)	295	10
$>$C=S	460	weak
-N=N-	347	15
-NO$_2$	278	10
(naphthalene)	311 270	250 5000
(anthracene)	380	8000
O=⟨ ⟩=O	440 300	20 1000
$>$C=C-C=O	330	20

SOURCE: CALVERT AND PITTS

FIGURE II-17   CHROMOPHROIC GROUPS WHICH ABSORB SUNLIGHT

The determination of rate constants for direct and sensitized photolysis
is the subject of the remainder of this section. Section 2.5.2.3.1 includes a
derivation of the equations for k_d and k_s. Sections 2.5.2.3.2 and 2.5.2.3.3
describe how to calculate these constants on the basis of near surface rate constants
or molecular absorption spectra.

2.5.2.3.1 Derivation of Rate Constant Equations

2.5.2.3.1.1 Direct Photolysis

Figure II-18 shows the major processes which influence direct photolysis of
pollutants in natural waters and indicates data requirements. This figure can be
translated into mathematics as follows:

Light absorption within a small wavelength band $\Delta\lambda$:

$$\epsilon_\lambda W_\lambda \Delta\lambda$$

Light absorption in a water body of depth Z:

$$\frac{1-e^{-KZ}}{KZ} \epsilon_\lambda W_\lambda \Delta_\lambda$$

PROCESS   DATA

```
┌─────────────────────────────────────┐          ┌─────────────────────┐
│ LIGHT ABSORPTION BY POLLUTANTS:      │          │   EXTINCTION        │
│ MUST BE IN ULTRAVIOLET-VISIBLE       │◄─────────│   COEFFICIENT, ε    │
│ SPECTRUM FOR PHOTOLYSIS TO OCCUR     │          │                     │
└─────────────────────────────────────┘          └─────────────────────┘
                  │
                  ▼
┌─────────────────────────────────────┐          ┌─────────────────────┐
│ LIGHT ATTENUATION IN NATURAL         │          │   DIFFUSE           │
│ WATERS: LIGHT REMAINING              │◄─────────│   ATTENUATION       │
│ AVAILABLE FOR PHOTOLYSIS             │          │   COEFFICIENT, K    │
│ DECREASES WITH DEPTH                 │          │                     │
└─────────────────────────────────────┘          └─────────────────────┘
                  │
                  ▼
┌─────────────────────────────────────┐          ┌─────────────────────┐
│ LIGHT UTILIZED FOR PHOTOLYSIS:       │          │   REACTION          │
│ ONLY A FRACTION OF THE AVAILABLE     │◄─────────│   QUANTUM YIELD,    │
│ LIGHT IS USED FOR PHOTOCHEMICAL      │          │      Φd             │
│ REACTIONS                            │          │                     │
└─────────────────────────────────────┘          └─────────────────────┘
                  │
                  ▼
┌─────────────────────────────────────┐
│ PREDICTION OF DIRECT                 │
│ PHOTOLYSIS RATE: $K_d$               │
│                                      │
└─────────────────────────────────────┘
```

FIGURE II-18   MAJOR PROCESSES WHICH INFLUENCE PHOTOLYSIS
                OF POLLUTANTS IN NATURAL WATERS

Photolysis rate for wavelength band $\Delta\lambda$:

$$\Phi_\lambda \epsilon_\lambda W_\lambda \; \frac{1-e^{-KZ}}{KZ} \; \Delta\lambda$$

The equation for direct photolysis becomes:

$$k_d = 2.3 \; j \; \dot{z}_d \; D \int_{\lambda_0}^{\lambda_1} \epsilon \; W \; \frac{1-e^{-K \cdot Z}}{K \cdot Z} \; d\lambda \tag{II-75}$$

where

Z	=	mixed depth of water body, m
λ_1	=	700 nm
λ_0	=	300 nm
j	=	conversion factor = 1.43×10^{-16} mole·cm^3·sec·l^{-1}·day^{-1}
ϵ	=	base 10 molar extinction coefficient of pollutant, 1 $mol^{-1}cm^{-1}$
C	=	concentration of pollutant, mol/l
D	=	radiance distribution function
W	=	photon irradiance near the surface, photons $cm^{-2}sec^{-1}nm^{-1}$
K	=	diffuse light attenuation coefficient of the water, m^{-1}

Equation II-75 can be written in summation notation as:

$$k_d = 2.3 \; j \; \phi \; D \sum_{\lambda=290}^{700} \epsilon_\lambda W_\lambda \; \frac{1-e^{-KZ}}{KZ} \; \Delta\lambda \tag{II-76}$$

Equation (II-75) incorporates the assumption that C, K, and D are independent of depth.

2.5.2.3.1.2 Sensitized Photolysis

The rate at which a compound decays through sensitized photolysis is proportional to the rate at which sensitizing molecules absorb light. The rate at which sensitizers absorb light in the aquatic environment is:

$$I_{as} = \frac{1}{Z} \int_0^Z \int_{\lambda_0}^{\lambda_1} j \cdot a_s (\lambda) \cdot C_s (z) \cdot D(z) \cdot W(\lambda) \cdot e^{-K(\lambda)z} \; d\lambda dz \tag{II-77}$$

where

I_{as}	=	rate of light absorption by sensitizers, einstein $l^{-1}day^{-1}$
a_s	=	base e absorption coefficient of the sensitizer, e.g., 1 mg-DOC$^{-1}cm^{-1}$
C_s	=	concentration of sensitizer, e.g., mg-DOC/l.

The rate constant for sensitized photolysis of a compound, k_s, is then:

$$k_s = j \cdot C_s \cdot D \cdot Q_s \cdot \int_{\lambda_o}^{\lambda_1} a_s \cdot W \cdot \frac{1 - e^{-K \cdot Z}}{K \cdot Z} \cdot d\lambda \qquad (II-78a)$$

Equation II-78a includes the assumptions that C_s, K, and D are independent of depth and that Q_s is independent of wavelength.

In terms of summation notation, this equation becomes:

$$k_s = j \cdot Q_s \cdot D \cdot C_s \cdot \sum_i a_s \cdot W' \cdot \frac{1 - e^{-K \cdot Z}}{K \cdot Z} \qquad (II-78b)$$

2.5.2.3.2 Use of Near Surface Rate Constants

Experimental data for direct photolysis are generally reported as near surface rate constants, as in Table II-32. Near the surface of a water body ($K \cdot z \leq 0.2$), the mean irradiance is approximately equal to the surface irradiance. This fact permits Equation II-75 to be simplified to the following expression which defines the near surface rate constant, k_{do}:

$$k_{do} = 2.3 \cdot \phi_d \cdot D_o \cdot j \cdot \int_{\lambda_o}^{\lambda_1} \varepsilon \cdot W \cdot d\lambda \qquad (II-79)$$

where

k_{do} = near-surface direct photolysis rate constant, day^{-1}

D_o = radiance distribution near the surface (approximate value = 1.2).

According to Equation (II-79), the near surface rate constant is independent of the properties of the water it is measured in, except for the small variation in D_o. Thus, when the difference in solar irradiance between the experimental and environmental conditions is accounted for, the user can apply a near surface rate constant to other bodies of water using the following expression:

$$\frac{k_d}{k_{do}} = \frac{2.3 \, j \, \phi \, D \, \sum_{\lambda=290}^{700} \varepsilon_\lambda \, W_\lambda \frac{1 - e^{-KZ}}{KZ} \, \Delta\lambda}{2.3 \, j \, \phi \, D_o \, \sum_{\lambda=290}^{700} \varepsilon_\lambda \, W_{\lambda o} \Delta\lambda} \qquad (II-80a)$$

TABLE II-32

NEAR-SURFACE DIRECT PHOTOLYSIS RATE CONSTANTS

Compound[1]	k_{dp} [1] (day^{-1})	I_o [2] (langleys day)	[3] (nm)	Ref
Polycyclic Aromatic Hydrocarbons	9			
Naphthalene	.23	2100	310	a
1-Methylnaphthalene	.76	2100	312	a
2-Methylnaphthalene	.31	2100	320	a
Phenanthrene	2.0	2100	323	a
Anthracene	22.0	2100	360	a
9-Methylanthracene	130.0	2100	380	a
9,10-Dimethylanthracene	48.0	2100	400	a
Pyrene	24.0	2100	330	a
Fluoranthrene	.79	2100	-	a
Chrysene	3.8	2100	320	a
Naphthacene	490.0	2100	440	a
Benzo(a)pyrene	31.0	2100	380	a
Benzo(a)anthracene	28.0	2100	340	a
Carbamate Pesticides				
Carbaryl	.32	2100	313	b
Propham	<.003	740	-	c
Chlorpropham	<.006	740	-	c
Phthalate Esters				
dimethyl ester	5×10^{-3}	600	-	d
diethyl ester	5×10^{-3}	600	-	d
di-n-butyl ester	5×10^{-3}	600	-	d
di-n-octyl ester	5×10^{-3}	600	-	d
di-,2-ethylhexyl, ester	5×10^{-3}	600	-	d
2,4-D Esters				
butoxyethyl ester	050	420	-	e
methyl ester	.030	420	-	e
Hexachlorocyclopentadiene	94.	540	-	f
Pentachlorophenol (anion)	46	600	318[*]	f
3,3'-dichlorobenzidine	670.	2000	280-330[*]	f
N-nitrosoatrazine	300.	1800	-	g
Trifluralin	30.	1800	-	g
DMDE(1,1-bis(p-methylphenyl 1)-2,2-dichloroethylene)	17.	2200	-	g

Notes.

1 Parenthetic comments after name of compound indicate when the form of the compound undergoing photolysis is something other than the neutral form

2 Estimated Solar Flux - usually high estimates to give conservative photolysis rates.

3 Wavelength of maximum sunlight absorption

* Indicates the maximum of the absorption spectrum is used

References:

a) Zepp and Schlotznauer (1979)

b) Zepp, (1978)

c) Wolfe et al (1978)

d) Wolfe et al (1980)

e) Zepp et al. (1979)

f) Callahan et al 1979

g) Zepp and Cline (1977)

$$\bullet \quad \frac{D \displaystyle\sum_{\lambda=290}^{700} \epsilon_\lambda \lambda_\lambda \, I \, \dfrac{1-e^{-KZ}}{KZ} \, \Delta\lambda}{D_o \displaystyle\sum_{\lambda=290}^{700} \epsilon_\lambda \lambda_\lambda \, I_o \Delta\lambda} \qquad\qquad\qquad (II\text{-}80b)$$

$$\approx \quad \frac{DI}{D_o I_o} \quad \frac{1-e^{-K(\lambda^*)Z}}{K(\lambda^*)Z} \qquad\qquad\qquad (II\text{-}80c)$$

so:

$$k_d = k_{do} \cdot \frac{I}{I_o} \cdot \frac{D}{D_o} \cdot \frac{1-e^{-K(\lambda^*)Z}}{K(\lambda^*)Z} \qquad\qquad (II\text{-}80d)$$

where

I = total solar radiation (langleys/day)

I_o = total solar radiation under conditions at which k_{do} was measured (langleys/day)

λ^* = wavelength of maximum light absorption, i.e. wavelength where the product $\epsilon(\lambda) \cdot W(\lambda)$ is greatest.

This approximate expression is valid if the following assumptions are sufficiently accurate: 1) the solar irradiance at a wavelength is a constant fraction of the total solar irradiance (Park et al., 1980) and 2) the light attenuation coefficient, K, is constant over the range of wavelength that the compound absorbs solar radiation at high rates (Burns et al., 1981).

Although it is possible to derive a similar expression for sensitized photolysis, variation in the absorptivity and reactivity of natural humic substances make extrapolations based on the concentration of dissolved organic carbon subject to large errors. An approach taken by Zepp (1980) was to correlate the sensitized photolysis rate constant with the absorbance of a solution at 366nm. Such an empirical relationship was found for 2,5-dimethylfuran:

$$\log k_{so} = .67 \log a_{366} - 1.15 \qquad\qquad (II\text{-}81)$$

where

a_{366} = absorbance of solution at 366nm

k_{so} near surface rate constant, $day^{-1}cm^{-1}$ (I_o= 1 langley/day).

At present, data on sensitized photolysis are difficult to obtain. The planner should be aware of its potential significance even if it is not possible to estimate rates at this time.

2.5.2.3.3 Evaluation of Direct Photolysis Rate

The simplest and preferred method of calculating the direct photolysis rate is

shown in a step-wise fashion in Table II-33. Note that the effects of water depth and light attenuation can be estimated based on water-body characteristics from Table II-34. Thus the method essentially consists of multiplying several numbers together to find k_d.

If k_{do}, which is required to use the method outlined in Table II-33, is not directly obtainable, it can be calculated from Table II-35 and then used in conjunction with the near-surface approach described above. One advantage of using the near-surface approach (in addition to its simplicity) is that the photolysis rate in different classes of natural waters can be readily evaluated using Table II-33, once k_{do} has been calculated a single time.

In some cases, the near-surface approach may not be applicable. Equations II-80a through II-80c show some of the simplifications required to develop a near-surface approach. Photolysis rates for chemicals which have multiple ϵ_{max} values within the wavelength range 290 nm $< \lambda < 700$ nm should not be calculated using the near-surface approach. Rather, the direct approach outlined in Table II-37 should be used in conjunction with the procedure shown in Table II-36.

Very little emphasis is given here on rates of indirect photolysis because little data are available on indirect photolysis rates. Table II-38 summarizes the pertinent work of Zepp (1977). Zepp found that the near-surface half-life for indirect photolysis for several chemicals in Okefenokee Swamp waters was very short: from 0.02 hr to 7 hrs. The near-surface rate constant translates to between 2.4/day to 830./day. However, on a depth-averaged basis, four of the five photolysis rates are below 0.06/day. Only for pentacene is the depth-averaged photolysis rate high (5.8/day). Thus, the same factor (humic material) that is responsible for the high near-surface rate constants, is also responsible for the small depth-averaged values because much of the sunlight is rapidly absorbed near the water surface. For this reason, and because of the lack of data, indirect photolysis is ignored in these assessment procedures.

TABLE II-33

SUMMARY OF NEAR SURFACE APPROACH

1. Predictive Equation:

$$k_d = k_{do} \frac{DI}{D_o I_o} \frac{1-e^{-K(\lambda^*)Z}}{K(\lambda^*)Z}$$

2. Find:

   $k_{do} = $ _____

   - See Table II-32, or
   - See Table 8-12, p. 8-38, Lyman et al., where half-lives are given:

   $$k_{do} = \frac{0.693}{t_{\frac{1}{2}}}$$

   $D = $ _____ (1.2-1.6)
   $D_o = $ _____ (1.2)
   $I = $ _____ (500-700 langleys/day)
   $I_o = $ _____ (500-2100 langleys/day; see Table II-29)
   $\lambda^* = $ _____

   - Table II-32
   - Table 8-5, p. 8-14, of Lyman et al.
   - Friedel and Orchin, 1951.
   - Hershenson, 1966.
   - Kamlet (ed.), 1960.

3. Knowing λ^* and Depth of Water body, Z, Find

$$\frac{1-e^{-K(\lambda^*)Z}}{K(\lambda^*)Z}$$

   Table II-34 shows some typical values of this expression.

4. Find k_d using equation shown in step 1.
5. Suppose k_{do} is not known from experimental studies. It can be calculated from the procedure shown in Table II-35.

TABLE II-34

$$\text{RANGE OF } \frac{1-e^{-K(\lambda^*)Z}}{K(\lambda^*)Z}$$

λ^* (nm)	Water Type [a]	Depth of Water (m)				
		1	2	3	5	10
300	A	0.9	0.8	0.8	0.6	0.4
	B	0.5	0.4	0.2	0.14	0.07
	C	0.1	0.06	0.04	0.03	0.01
	D	0.03	0.01	0.009	0.005	0.003
340	A	0.9	0.9	0.9	0.8	0.7
	B	0.7	0.5	0.4	0.2	0.1
	C	0.2	0.08	0.06	0.03	0.02
	D	0.04	0.02	0.01	0.007	0.004
380	A	1.0	1.0	1.0	0.9	0.9
	B	0.8	0.6	0.5	0.3	0.2
	C	0.2	0.1	0.07	0.04	0.02
	D	0.05	0.02	0.02	0.009	0.005
420	A	1.0	1.0	1.0	1.0	0.9
	B	0.8	0.6	0.5	0.4	0.2
	C	0.3	0.1	0.09	0.05	0.03
	D	0.06	0.03	0.02	0.01	0.006
460	A	1.0	1.0	1.0	1.0	0.9
	B	0.8	0.7	0.6	0.4	0.2
	C	0.3	0.2	0.1	0.06	0.03
	D	0.07	0.3	0.02	0.01	0.007
500	A	1.0	1.0	1.0	0.9	0.9
	B	0.8	0.7	0.6	0.4	0.2
	C	0.3	0.2	0.1	0.07	0.03
	D	0.07	0.4	0.02	0.01	0.007

[a] Water Type	chla (mg/l)	DOC (mg/l)	SS (mg/l)
A	0.0	0.0	0.0
B	0.001 (Lake Tahoe)	0.1	0.5
C	0.01 (eutrophic)	0.5	5.0
D	0.1 (highly eutrophic)	2.0	20.0

TABLE II-35

DIRECT PREDICTION OF NEAR SURFACE RATE

- Predictive Equation:

$$k_{do} = 2.3 \ j\phi_d D_0 \sum_{\lambda=290}^{700} \epsilon_\lambda W_\lambda \Delta\lambda$$

- Data Required:

    1. ϕ_d (quantum yield for direct photolysis:

        - Table II-31, or
        - Table 8-11, p. 8-37, in Lyman et al.

    2. D_0 (~1.2)

    3. ϵ_λ versus λ relationship

        - Table 8-7, p. 8-20, in Lyman et al.

        - Sadtler, undated.

        - Schnitzer, 1971.

    4. W versus λ (typical values for central U.S.A. are given in Table II-36 for I = 540 langleys/day)

- Approach

    Use procedure shown in Table II-36

    a) Enter ϵ_λ versus λ values in column 5 and appropriate rows.
    b) Find each $\epsilon W \Delta\lambda$ in column 6.
    c) Find $\Sigma \epsilon W \Delta\lambda$ at bottom of column 6.
    d) Use Equation 3 on right-hand side of table to find k_{do}.

TABLE 11-36

PROCEDURE FOR CALCULATING DIRECT PHOTOLYSIS RATE CONSTANT
FOR A REFERENCE LIGHT INTENSITY OF 540 LANGLEYS/DAY

TABLE II-37

DIRECT PREDICTION OF DEPTH-AVERAGED PHOTOLYSIS RATE

● Predictive Equation:

$$k_d = 2.3 \, j\phi_d D \sum_{\lambda=290}^{\lambda=700} \varepsilon_\lambda W_\lambda \frac{1-e^{-KZ}}{KZ} \Delta\lambda$$

● Data Required:

1. ϕ_d

2. D

3. ε_λ versus λ

4. W_λ versus λ

5. Water body characteristics: depth, chla, DOC, SS

● Approach: Use Table II-36

a) Enter λ versus ε in column 5 and appropriate rows, and calculate $\varepsilon W \Delta\lambda$ in column 6.

b) Enter D (column 7), chla (column 9), DOC (Column 10), and SS (column 11) in appropriate rows.

c) Calculate K (column 12) for appropriate rows.

d) Knowing water depth Z, calculate appropriate values for column 13.

e) Transfer column 6 entries to column 14.

f) Multiply column 13 entries by column 14 entries and record in column 15.

g) Sum column 15 entries and use Equation 1 on RHS of sheet to find k_d.

TABLE II-38

ESTIMATED HALF-LIVES FOR INDIRECT PHOTOLYSIS OF
ORGANICS IN OKEFENOKEE SWAMP WATER[a]

Organic	Half-Life (hr)[b]	Near-Surface Rate Constant (1/day)[b]	Depth-Averaged Rate Constant (1/day)[c]
Naphthacene	7	2.4	0.01
Pentacene	0.02	830.	5.8
Histidine	2	8.3	0.06
Tryptophan	2	8.3	0.06
Methionine	3	5.5	0.04

[a] Zepp, R.G. et al., 1977. Singlet Oxygen in Natural Waters.
Nature, Vol. 267.

[b] Near-Surface (1 cm) rate constant

[c] Depth-averaged rate constant. Assume humic materials
12 mg/l, depth = 3m.

EXAMPLE II-7

Computation of Photolysis Rate Constants

Compute the mean annual photolysis rate constant for the pesticide carbaryl
in a hypothetical river near Fresno, California. Use both the evaluation of
integral and near surface rate constant methods described above. Assume the
following physical and chemical parameters apply to the river:

Mean depth = 2 m
Suspended sediments = 10 mg/l
Humic acid = 2 mg-DOC/l
Chlorophyll a = 0 mg/l

Zepp (1978) reported a quantum yield, ϕ_d, of .0060 and the follow-
ing absorptivities, ϵ, for carbaryl:

Wavelength (nm)	Absorptivity $(M^{-1}cm^{-1})$
300	918
310	356
320	101
330	11

A. Near Surface Rate Constant Method

Table II-32 contains the following information regarding carbaryl:

k_d = .32 day^{-1}

I_o = 2100 langleys/day

λ^* = 313 nm.

According to Figure II-13, the mean annual solar irradiance at Fresno, California is 450 langleys/day.

Assume that the radiance distribution function under reference, D_o, and environmental, D, conditions have values of 1.2 and 1.6 respectively.

To calculate the light attenuation coefficient at the wavelength of maximum light absorption, 313 nm, we use Equation II-68 and the data in Table II-30, at 310 nm:

K = 1.6 (.105 + 67 · 0 + 5.41 · 2 + .35 · 10)

= 23.1m^{-1}

When the water absorbs nearly all of the incident radiation, i.e., kZ $\geq$ 3, the following approximation is valid:

$$\frac{1 - e^{-KZ}}{KZ} \sim \frac{1}{KZ}$$

This approximation can be applied to Equation II-76 and Equation II-80d. It both simplifies the calculations and eliminates the dependence of the rate constant on the radiance distribution function, D, in cases where the light attenuation coefficient is calculated from D, as in this example. In such a case, the user's choice of a value of D does not affect the result.

Using this approximation in Equation (II-80d), the mean photolysis rate constant is computed to be:

k_d = .32 day^{-1} · $\frac{450}{2100}$ · $\frac{1.6}{1.2}$ · $\frac{1}{23.1 \cdot 2}$

= 2.0 x 10^{-3} day^{-1}

This example demonstrates the significant difference, 100 fold in this case, which may exist between near surface and mean photolysis rate constants. The strong attenuation of light by the river water was the primary cause of the reduction in rates.

B. Evaluation of Integrals

The absorption data for carbaryl indicate that we need to concern ourselves only with light of wavelength 300-330nm in order to determine a mean rate constant.

First, we assume that D has the same value as above, ~1.6. Then, we compute the light attenuation coefficients using Equation II-68 and the data in Table II-36.

$$ D \cdot \left[a_w + \left(a_{DOC} \cdot c_{DOC} \right) + \left(a_{SS} \cdot c_{SS} \right) \right] \cdot K $$

(nm)	D	a_w (m^{-1})	a_{DOC} $[(mg/l)^{-1}m^{-1}]$	c_{DOC} (mg/l)	a_{SS} $[(mg/l)^{-1}m^{-1}]$	c_{SS} (mg/l)	K (m^{-1})
300	1.6	.141	6.25	2	.35	10	25.8
310	1.6	.105	5.41	2	.35	10	23.1
320	1.6	.0844	4.68	2	.35	10	20.7
330	1.6	.0678	4.05	2	.35	10	18.7

Table II-36 lists the photon spectral irradiance, W', at a reference total solar flux, I_o, of 540 langleys/day. The local solar flux, as in part A, is 450 langleys/day.

Next, evaluate the sum indicated in Equation II-76.

Since $KZ > 3$ for all wavelengths of interest, use the approximation discussed in part A.

λ (nm)	ϵ $(M^{-1}cm^{-1})$	$W' \times 10^{-14}$ (photons/cm^2/s)	$(K \cdot Z)$	$\dfrac{\epsilon \cdot W'}{K Z}$
300	918	.0303	51.6	$.539 \times 10^{14}$
310	356	.388	46.2	2.99×10^{14}
320	101	1.13	41.4	2.76×10^{14}
330	11	1.81	37.4	$.532 \times 10^{14}$

$$ \sum_i = 6.82 \times 10^{14} $$

Given that the quantum yield is .006, the mean photolysis rate constant can be computed using Equation II-82 and the above information:

$$ k_d = 2.3 \cdot 1.43 \times 10^{-16} \cdot \frac{450}{540} \cdot .0060 \cdot 1.6 \cdot 6.82 \times 10^{14} $$

$$ = 1.8 \times 10^{-3} \text{ day}^{-1} $$

The small difference between the rate constants calculated in parts A and B is due to the difference in the reference solar intensities. The assumption made here that the spectral distribution of solar energy is independent of intensity

2.5.3 Hydrolysis

Some toxic compounds can be altered by direct reaction with water. The chemical reaction of a compound with water is called hydrolysis. Typically in hydrolysis reactions hydroxide replaces another chemical group.

An example hydrolysis reaction for a toxic organic compound is given below:

| Carbaryl | + | Water ——▶ α-Naphthanol | + | Methylamine | + | Carbon Dioxide |
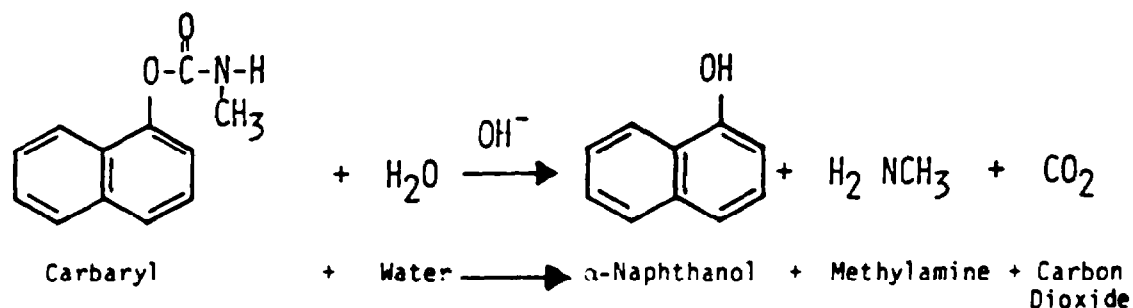
Generalized hydrolytic reactions of organic compounds are presented in Table II-39.

Hydrolysis reactions alter the reacting molecules but do not always produce less noxious products. For example the more toxic 2,4-D acid is produced from the hydrolysis of certain 2,4-D esters. Alternatively the hydrolysis of carbaryl (shown above) produces less toxic products, i.e. α-naphthanol and methylamine.

Hydrolysis products may be more or less volatile than the original compound. Hydrolysis products which ionize may have essentially zero volatility depending upon pH. Hydrolysis products are generally more readily biodegraded than the parent compounds, although there are some exceptions.

Hydrolysis reactions are commonly catalyzed by hydrogen or hydroxide ions. This produces the strong pH dependence often observed for hydrolysis reactions. Examples of this dependency are shown in Figure II-19, where the logarithms of reaction rate constants (k_H) are plotted versus pH. The hydrolysis rate of carbaryl can be seen to increase logarithmically with pH. The rate at pH = 8 is ten times that at pH = 7 and 100 times that at pH = 6. The hydrolysis rate of parathion is high at low pH

TABLE II-39

GENERALIZED HYDROLYTIC REACTIONS OF ORGANIC COMPOUNDS

Reactant	Reaction Conditions	Products
CARBOXYLIC ACID ESTERS $R-C(=O)-O-R'$	ACIDIC, NEUTRAL, BASIC	CARBOXYLIC ACID $R-C(=O)-OH$ + ALCOHOL $R'OH$
AMIDES $R-C(=O)-N(H)-R'$	ACIDIC, BASIC	CARBOXYLIC ACID $R-C(=O)-OH$ + AMINE $H-N(H)-R'$
CARBAMATES $R-N(H)-C(=O)-O-R'$	ACIDIC, BASIC	AMINE $R-N(H)(H)$ + ALCOHOL $R'OH$ + CARBON DIOXIDE CO_2
ORGANOPHOSPHATES (AND DERIVATES) $RO-P(=O)(OR)-OR$	BASIC (ACIDIC, NEUTRAL)	PHOSPHATE DIESTER $RO-P(=O)(OR)-OH$ + ALCOHOL ROH
HALOGENATED ALKANES $R'-C(R)(R'')-X$	NEUTRAL, BASIC	ALCOHOL $R'-C(R)(R'')-OH$ + HALIDE ION X^-

SOURCE: I.J. TINSLEY, CHEMICAL CONCEPTS IN POLLUTANT BEHAVIOR, J. WILEY, NEW YORK (1979).
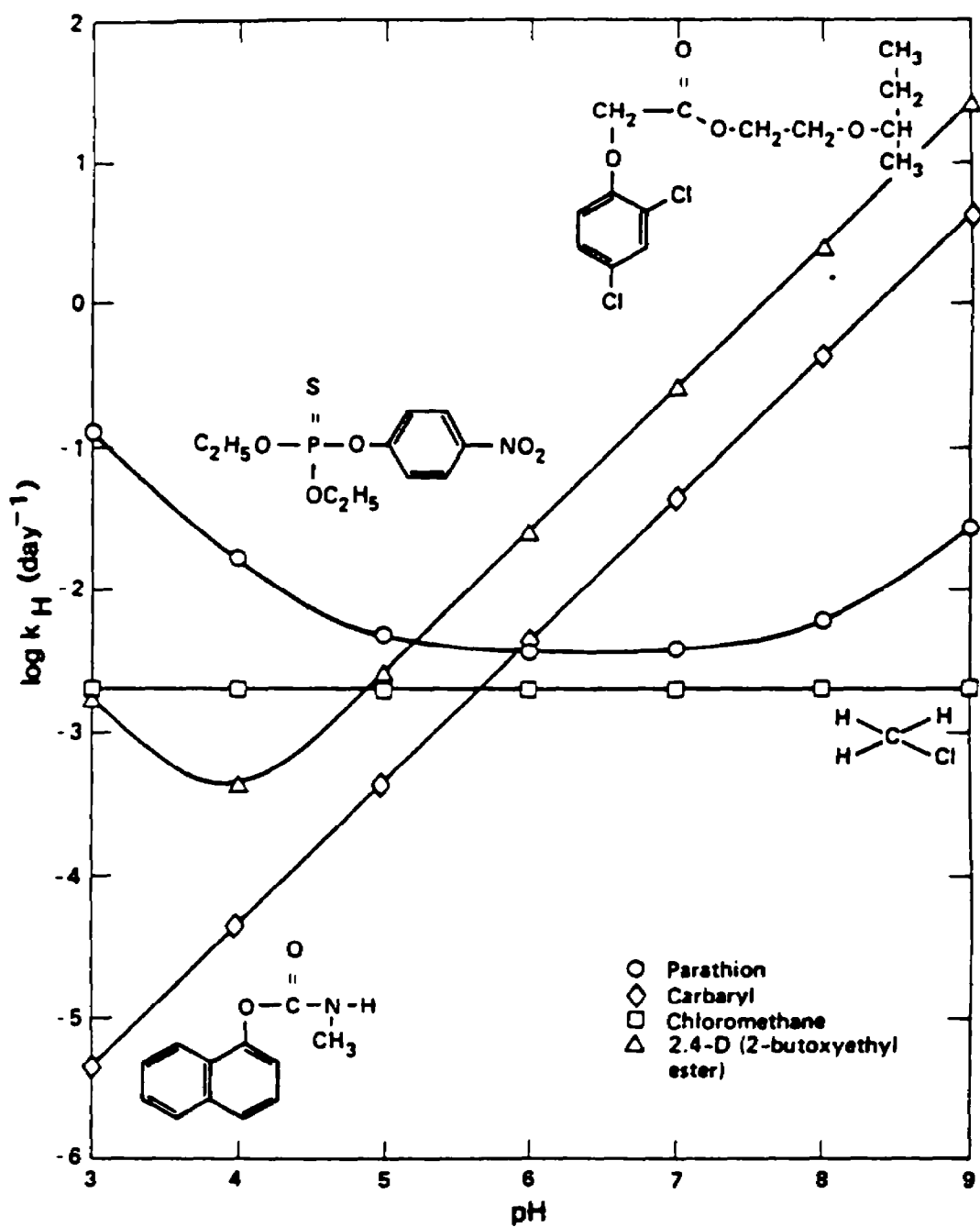
FIGURE II-19   pH DEPENDENCE OF HYDROLYSIS RATE CONSTANTS

values, reaches a minimum at pH = 6, and then increases with increasing pH. The hydrolysis rate of chloromethane shows minimal dependence on pH over the range presented.

Adsorption can also influence hydrolysis rates. Adsorption of an organic molecule protects it from acid or base catalyzed hydrolysis (Wolfe, 1981). The amount of adsorption can be predicted using the principles presented in Section 2.3.2.

Microbially mediated hydrolysis reactions are responsible for the breakdown of many complex molecules, including natural polymers such as cellulose. Microorganisms catalyze hydrolysis reactions in the process of using organic compounds as energy and/or carbon sources. In cometabolism microbes may hydrolyze toxic organic compounds to hasten their removal from cell protoplasm. Microbially mediated processes are covered under the general heading of biodegradation in Section 2.5.1. Here only abiotic hydrolysis is treated.

Abiotic hydrolysis reactions are represented by rate expressions which are first order in the concentration of the compound being hydrolyzed:

$$R = \frac{\partial C}{\partial t} = -k_H \, C_T \qquad \qquad (II-82)$$

where

R = the rate of hydrolysis, mole liter^{-1} sec^{-1} or μg liter^{-1} sec^{-1}

k_H = specific hydrolysis rate constant, sec^{-1}

C_T = the dissolved plus sorbed phase concentration of compound C mole liter^{-1} or μg liter^{-1}.

In the literature k_H is typically defined as:

$$k_H = k_n + k_a \, [H^+] + k_b \, [OH^-] \qquad \qquad (II-83)$$

In this document the specific hydrolysis rate constant, k_H, is defined to include the effects of adsorption:

$$k_H = \left[k_n + \alpha_w \left(k_a \, [H^+] + k_b \, [OH^-] \right) \right] \qquad \qquad (II-84)$$

where

k_n = the neutral hydrolysis rate constant, sec^{-1}

α_w = the decimal fraction of the total amount of compound C which is dissolved (Calculation procedures in Section 2.3.2)

k_a = the acid catalyzed hydrolysis rate constant, liter mole^{-1} sec^{-1}

$[H^+]$ = the molar concentration of hydrogen ion, mole liter^{-1}
$([H^+] \approx 10^{-pH})$

k_b = the base catalyzed hydrolysis rate constant, liter mole^{-1} sec^{-1}

$[OH^{-1}]$ = the concentration of hydroxide ion, mole liter^{-1}
$[OH^-] = 10^{(pH-pK_w)} = 10^{(pH-14)}$.

Equation II-84 is a convenient definition of k_H because specific rate constants which act on the dissolved and total concentrations do not have to be used separately.

Values for the three rate constants k_n, k_a, k_b for selected compounds are presented in Table II-40. Additional values can be found in the literature (e.g. Mabey and Mill, 1978). The three constants can also be determined by simple laboratory tests.

Water body pH values must be obtained for hydrolysis reactions which are pH dependent (i.e. those for which $k_a \neq 0$ and/or $k_b \neq 0$). It should be noted that in poorly buffered waters (alkalinity ≤ 50 mg/l as $CaCO_3$), pH values may change by 1-2 units daily due to natural processes alone. In these cases either additional data must be gathered to characterize the system's pH regime or conservatively low values of k_H must be used. Table II-41 summarizes the procedures.

— EXAMPLE II-8 —

A biodegradation rate constant, k_B for the fungicide Captan has been given as 0.5 per day. Compare this with the abiotic hydrolysis rate constant, k_H, at pH = 8.4, a temperature of 25°C, and with 90 percent of the compound adsorbed on suspended matter. Values for k_a, k_b, and k_n can be found in Table II-31.

$k_a = 0$
$k_b = 4.9 \times 10^7$ day^{-1}
$k_n = 1.6$ day^{-1}

$$k_H = \left[\alpha_w \left(k_a[H^+] + k_b[OH^-]\right)\right] + k_n$$

$$[OH^-] \approx 10^{pH-14} = 10^{8.4-14} = 10^{-5.6} = 2.51 \times 10^{-6}$$

thus

$$k_H = \left[(1.0-0.9)\cdot(4.9 \times 10^7 \times 2.5 \times 10^{-6})\right] + 1.6$$

$$= 12.3 + 1.6 = 13.9 \text{ day}^{-1}$$

TABLE II-40

HYDROLYSIS RATE PARAMETERS AND ESTIMATED ENVIRONMENTAL HYDROLYSIS RATES

Compound	Hydrolysis Rate Parameters			Environmental Hydrolysis Rates (pH=7)		Ref. Temp. (°C)	Ref.
	k_a ($1 \cdot m^{-1} day^{-1}$)	k_n (day^{-1})	k_b ($1 \cdot m^{-1} day^{-1}$)	k_H (day^{-1})	$t_{\frac{1}{2}}$ (days)		
Pesticides							
Endosulfon	-	-	3.3×10^5	3.5×10^{-2}	21	27	a
Heptachlor	?	?	?	.7	1.	30	a
Carbaryl	-	-	4.3×10^5	4.3×10^{-2}	16.	27	b
Propham	-	-	.66	6.6×10^{-8}	1.1×10^7	27	b
Chlorpropham	-	-	1.7	1.7×10^{-7}	4.0×10^6	27	b
2,4-D(2-Butoxyethyl ester)	1.7	-	2.6×10^6	.26	2.7	28	c
2,4-D(methyl ester)	-	-	1.5×10^6	.15	4.6	28	c
Parathion	1.3×10^2	3.6×10^{-3}	2.46×10^3	3.9×10^{-3}	1.8×10^2	?	d
Phosmet	?	?	?	2.3	.30	20	e
Dialifor	?	?	?	1.2	.58	20	e
Malathion	?	?	?	6.6×10^{-2}	11.	20	e
Captan	-	1.6	4.9×10^7	5.6	.13	27	f
Atrazine	3.4	6.6	-	6.6	.10	25	f
Methoxychlor	-	2.6×10^{-3}	31.	2.6×10^{-3}	2.7×10^2	25	f
Halogenated Hydrocarbons							
Chloromethane	-	2.1×10^{-3}	.53	2.1×10^{-3}	3.4×10^2	25	f
Bromomethane	-	3.5×10^{-2}	12.	3.5×10^{-2}	20.	25	f
Chloroethane	-	1.8×10^{-2}	-	1.8×10^{-2}	38.	25	f
Dichloromethane	-	2.8×10^{-6}	1.8×10^{-3}	2.8×10^{-6}	2.6×10^5	25	f
Trichloromethane	-	-	6.0	6.0×10^{-7}	1.3×10^6	25	f
Bromodichloromethane	-	-	1.4×10^3	1.4×10^{-5}	5.0×10^4	25	f
Dibromochloromethane	-	-	69.	6.9×10^{-6}	1.0×10^5	25	f
Tribromomethane	-	-	28.	2.8×10^{-6}	2.5×10^5	25	f
Hexachlorocyclopentadiene	-	4.8×10^{-2}	-	4.8×10^{-2}	14.	25	a
Halogenated Ethers							
Bis(chloromethyl) ether	-	1.6×10^3	-	1.6×10^3	4.5×10^{-4}	20	a
2-Chloroethyl vinyl ether	3.8×10^2	-	-	3.8×10^{-5}	1.8×10^4	25	a
Phthalate Esters							
Dimethyl ester	1.	-	6.0×10^3	6.0×10^{-4}	1.2×10^3	30	g
Diethyl ester	1.	-	1.9×10^3	1.9×10^{-4}	3.7×10^3	30	g
Di-n-butyl ester	1.	-	9.1×10^2	9.1×10^{-5}	7.6×10^3	30	g
Di-n-octyl ester	1.	-	1.4×10^3	1.4×10^{-4}	4.9×10^3	30	g
Di(2-ethylhexyl) ester	1.	-	9.6	9.6×10^{-7}	7.2×10^5	30	g
Monocyclic Aromatics							
Pentachlorophenol	1.1×10^4	5.8×10^{-3}	3.3	6.9×10^{-3}	1.0×10^2	?	d

Notes

"?" denotes rate parameter not given and not estimable from data in reference
"-" denotes zero or very small rate parameter

References:

a Callahan et al. (1979)
b Wolfe et al. (1978)
c Zepp et al. (1975)
d Pork et al. (1980)
e Tinsley (1979)
f Mabey and Mill (1978)
g Wolfe et al. (1980)

TABLE II-41

PROCEDURE FOR CALCULATING HYDROLYSIS RATE CONSTANT

1. **Hydrolysis Rate Constant**

$$k_H = \left[k_n + \alpha_w \left(k_a [H^+] + k_b [OH^-] \right) \right] \qquad (1)$$

2. **Procedure**

   a) Find the hydrolysis rate parameters. Use Table II-40.

   $$k_n = \underline{\hspace{2cm}} \frac{1}{day}, \; k_a = \underline{\hspace{2cm}} \frac{liters}{mole \; day}, \; k_b = \underline{\hspace{2cm}} \frac{liters}{mole \; day}$$

   b) Does the compound sorb? (Table II-11, Column 1)

   <u>If it does</u>, find, α_w, the fraction of the total amount of compound which is not sorbed

   $$\alpha_w = \frac{C_w}{C_T} = \frac{1}{1 + K_p S} \qquad \text{(See Section 2.3.2)}$$

   If it <u>does not</u> sorb set $\alpha_w = 1$

   c) If the hydrolysis is <u>acid catalyzed</u> (a k_a value exists) determine the hydrogen ion concentration, $[H^+]$.

   $$[H^+] = 10^{-pH} = 10^- \underline{\hspace{1cm}}$$

   d) If the hydrolysis is <u>base catalyzed</u> (a k_b value exists) determine the hydroxide ion concentration, $[OH^-]$.

   $$[OH^-] = 10^{(pH-pK_w)} = 10^{-(\underline{\hspace{0.5cm}} - \underline{\hspace{0.5cm}})} = 10^- \underline{\hspace{1cm}}$$

   Note: $pK_w = 14.2$ for freshwater at 20°C

   $\qquad\qquad = 13.4$ for seawater at 20°C

   $\qquad\qquad$ (More precise values for pK_w are given in Table II-13)

3. **Substitute** k_n, α_w, k_a, $[H^+]$, k_b, $[OH^-]$ into equation (1) above.

   $$K_H = \underline{\hspace{2cm}}$$

Comparing k_H to k_B:

$$\frac{k_H}{k_B} = \frac{13.9}{0.5} = 27.8$$

Comparison of k_H with k_B for the above situation shows that the abiotic hydrolysis rate is about 28 times faster than the biodegradation rate. Biodegradation could be neglected here with minimal effect on the results.

——————————————— END OF EXAMPLE II-8 ———————————————————

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CHAPTER 3

WASTE LOADING CALCULATIONS

3.1 INTRODUCTION

Receiving water bodies are subject to waste loads from point sources, nonpoint sources and atmospheric deposition. Point sources are identifiable discrete discharges from municipal, institutional and industrial waste water collection and treatment systems. Nonpoint sources (also known as diffuse or distributed sources) are associated with land drainage which enters a water body through dispersed and often poorly-defined pathways. Atmospheric waste loads are chemicals and particulate matter which settle from the atmosphere or are scavenged by precipitation. These distinctions are not absolute. For example, municipal waste water may be applied to the land and become nonpoint source pollution in runoff and percolation. Similarly, chemicals in precipitation may become a portion of a nonpoint source runoff load.

This chapter describes computational methods or "loading functions" for estimating waste loads to both surface waters and aquifers. These methods share several attributes:

- Required computations are relatively straightforward.
- Necessary data for the functions are generally available. Much of these data are provided in this chapter.
- Notwithstanding computational ease and data availability, use of the functions is not trivial. Considerable information regarding the physical characteristics of the study area must often be compiled.
- The accuracy of loading functions is not high. In general, the best results are obtained when input parameters are based on local pollutant data, such as chemical concentrations in sediment, runoff and wastewater.

The loading functions presented in this chapter are appropriate for water quality screening studies in which the approximate magnitudes of waste loads are needed. In situations requiring higher precision, waste loads must be based on monitoring programs and detailed process modeling.

The chapter places major emphasis on nonpoint sources. Point source loads can often be obtained from available water quality monitoring data. Atmospheric loads are also best determined by monitoring; reliable computational methods are not available to handle such major problems as acid rain. By contrast, monitoring of nonpoint sources is often infeasible and as a result, a number of procedures have been developed and tested for calculation of nonpoint source loads.

3.2 BACKGROUND POLLUTION LOADS

Background water quality "represents the chemical and biological composition of surface waters which would result from natural causes and factors" (Novotny and

Chesters, 1981). A comparable definition could be given for groundwater. The
concept of background water quality or pollution is somewhat artificial. Few, if
any, water bodies in the United States remain unaffected by human activity. For
example, synthetic organic compounds are routinely found in streams and lakes far
from any obvious source. In spite of this ambiguity, estimation of background
loads is a useful component of water quality planning. These loads represent
a baseline or minimum level of water pollution which cannot be eliminated by local or
area-wide water quality management.

Background pollution levels can be measured by water quality sampling of surface
waters in upstream portions of watersheds which are free of human activity and in
aquifers in undeveloped areas. In the absence of such local data, very crude esti-
mates can be determined from the information given in Figures III-1, 2, and 3. These
figures show mean surface water concentrations of selected water quality parameters
obtained from the U.S. Geological Survey's Hydrologic Benchmark Network (McElroy et
al., 1976). The concentrations are based on water quality samples from 57 monitoring
locations considered free of human disturbance. More accurate concentration data for
nutrients are available from the U.S. National Eutrophication Survey (Omernik, 1977).
Nitrogen and phosphorus concentrations in streamflow are grouped according to land
use and location in Figures III-4 and 5. Concentrations for the "90% Forest" category
can be assumed to represent background concentrations.

Annual mass background loads to surface waters are obtained by multiplying
concentrations by streamflow values. Average annual streamflow values for the United
States are shown in Figure III-6. Obviously, when local streamflow data are available
they are preferable to the regional values given in Figure III-6.

---------------------------- EXAMPLE III-1 -------------------------------

Background Loading Estimates

Determine the annual background loads of BOD and total phosphorus from
a 50 km^2 watershed in northern Illinois.

Solution:

From Figure III-1(b), background BOD concentration is 3.0 mg/l in northern
Illinois. Total phosphorus concentrations can be determined from the National
Eutrophication Survey data in Figure III-5. Northern Illinois is in the eastern
area shown in Figure III-5, and the total phosphorus concentration for the 90
percent Forest category is 0.011 mg/l. Average annual streamflow for the area is
10 in (Figure III-6) or 0.254 m.
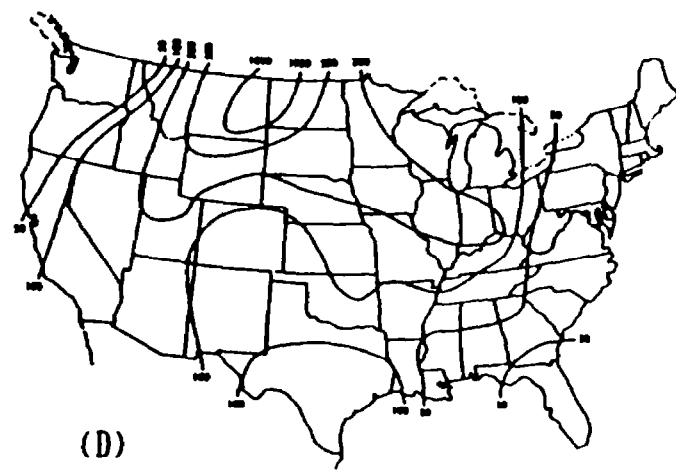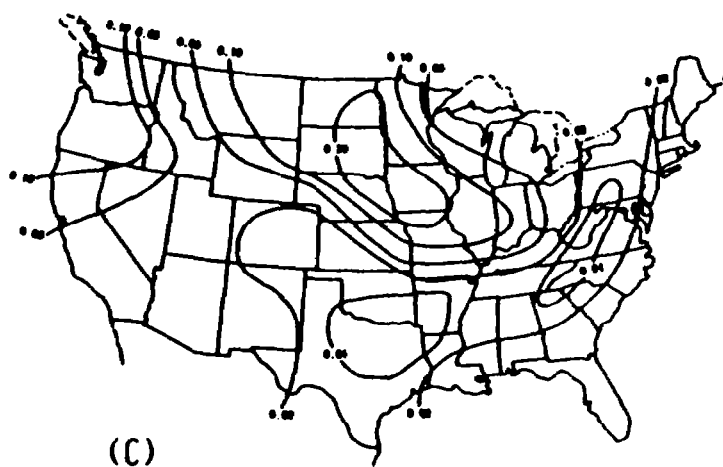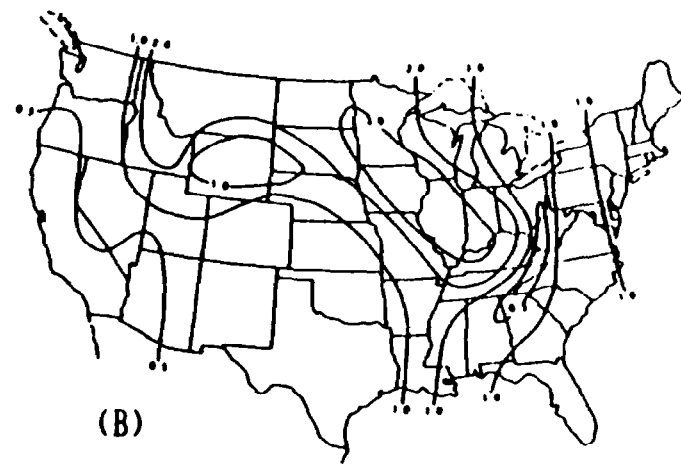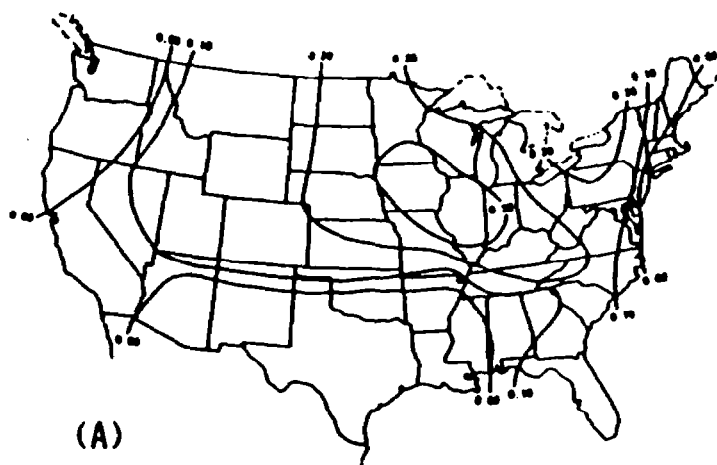
FIGURE III-1 BACKGROUND CONCENTRATION (MG/L) OF (A) NITRATE-NITROGEN, (B) BOD, (C) TOTAL PHOSPHORUS AND (D) DISSOLVED SOLIDS (MCELROY ET AL, 1976)
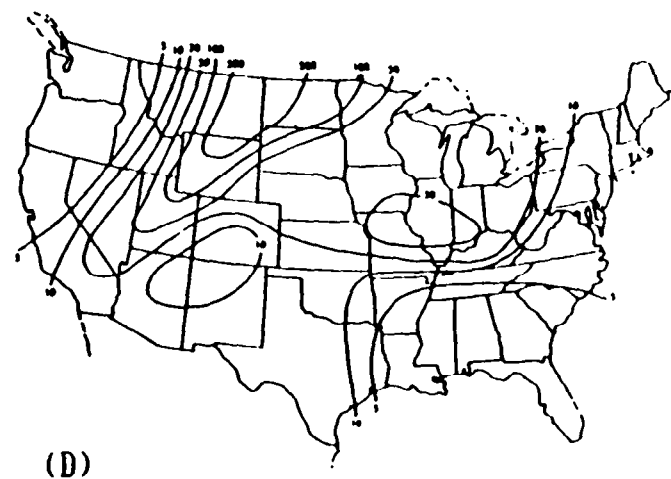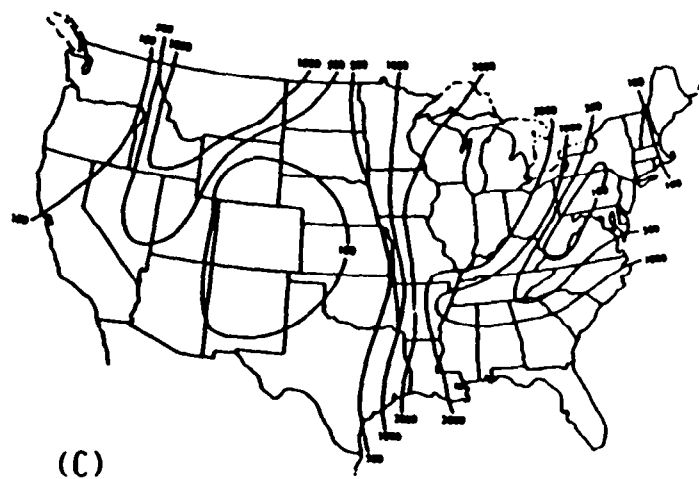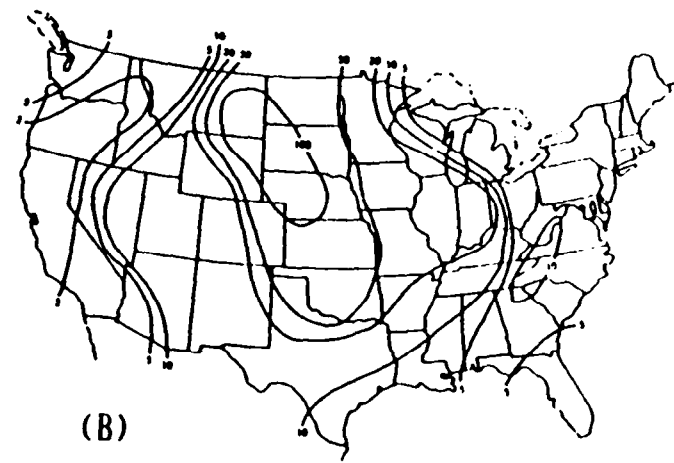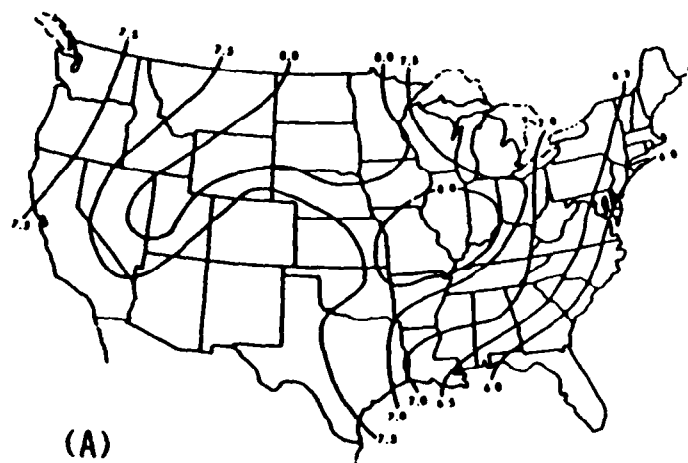
FIGURE III-2 BACKGROUND LEVELS OF (A) pH, (B) SUSPENDED SEDIMENT (MG/L)
(C) TOTAL COLIFORMS (MPN/100 ML) AND (D) SULFATE (MG/L) (MCELROY ET AL, 1976)
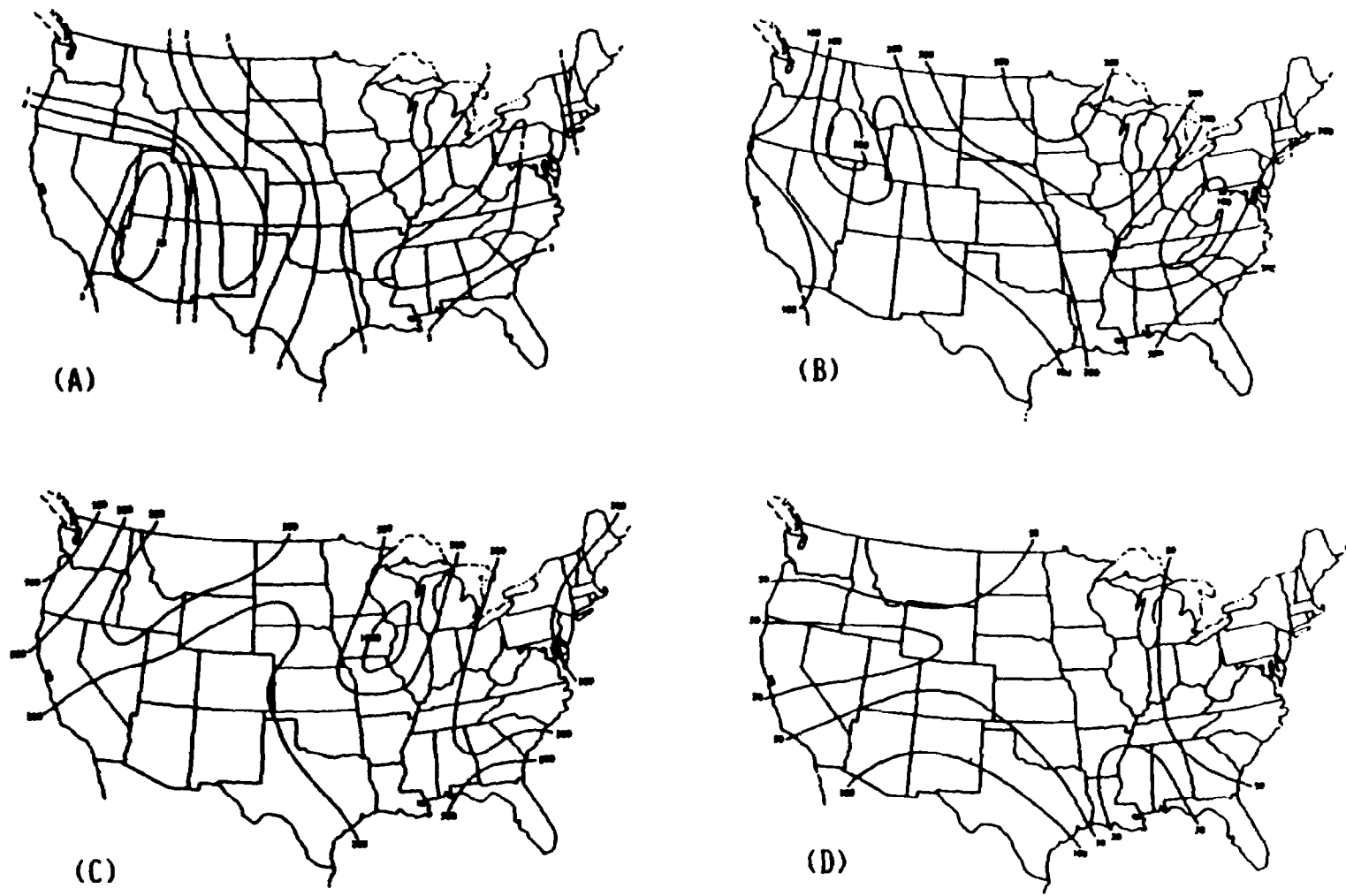
FIGURE III-3 BACKGROUND CONCENTRATIONS OF (A) CHLORIDE (MG/L), (B) IRON + MANAGNESE (UG/L),
(C) TOTAL HEAVY METALS (UG/L) AND (D) ARSENIC + COPPER + LEAD + ZINC (UG/L)
(MCELROY ET AL, 1976)
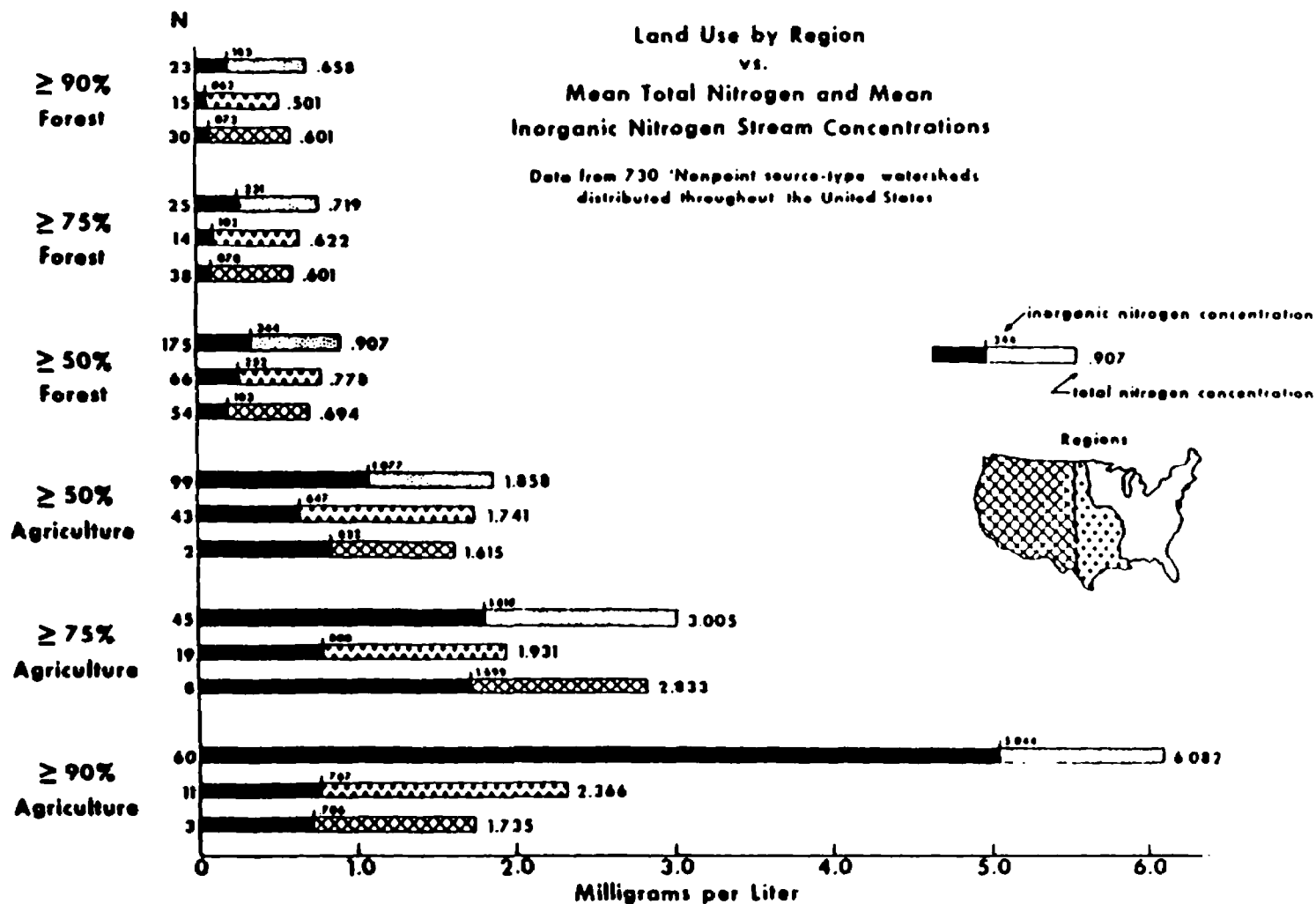
FIGURE III-4 RELATIONSHIPS BETWEEN STREAMFLOW NITROGEN CONCENTRATIONS AND LAND USE FROM THE NATIONAL EUTROPHICATION SURVEY (OMERNIK, 1977)
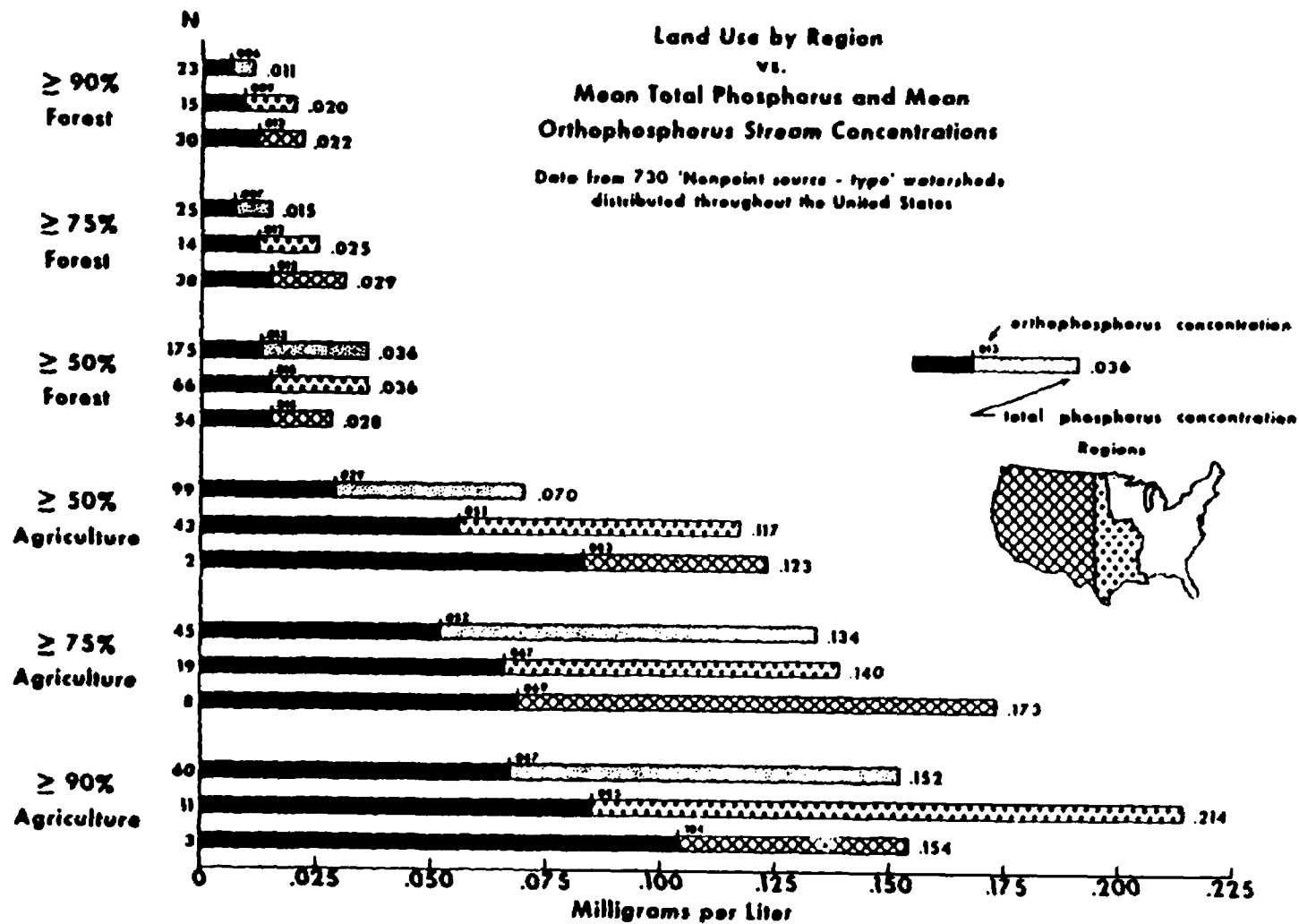
FIGURE III-5 RELATIONSHIPS BETWEEN STREAMFLOW PHOSPHORUS CONCENTRATIONS AND LAND USE FROM THE NATIONAL EUTROPHICATION SURVEY (UMERNIK, 1977)
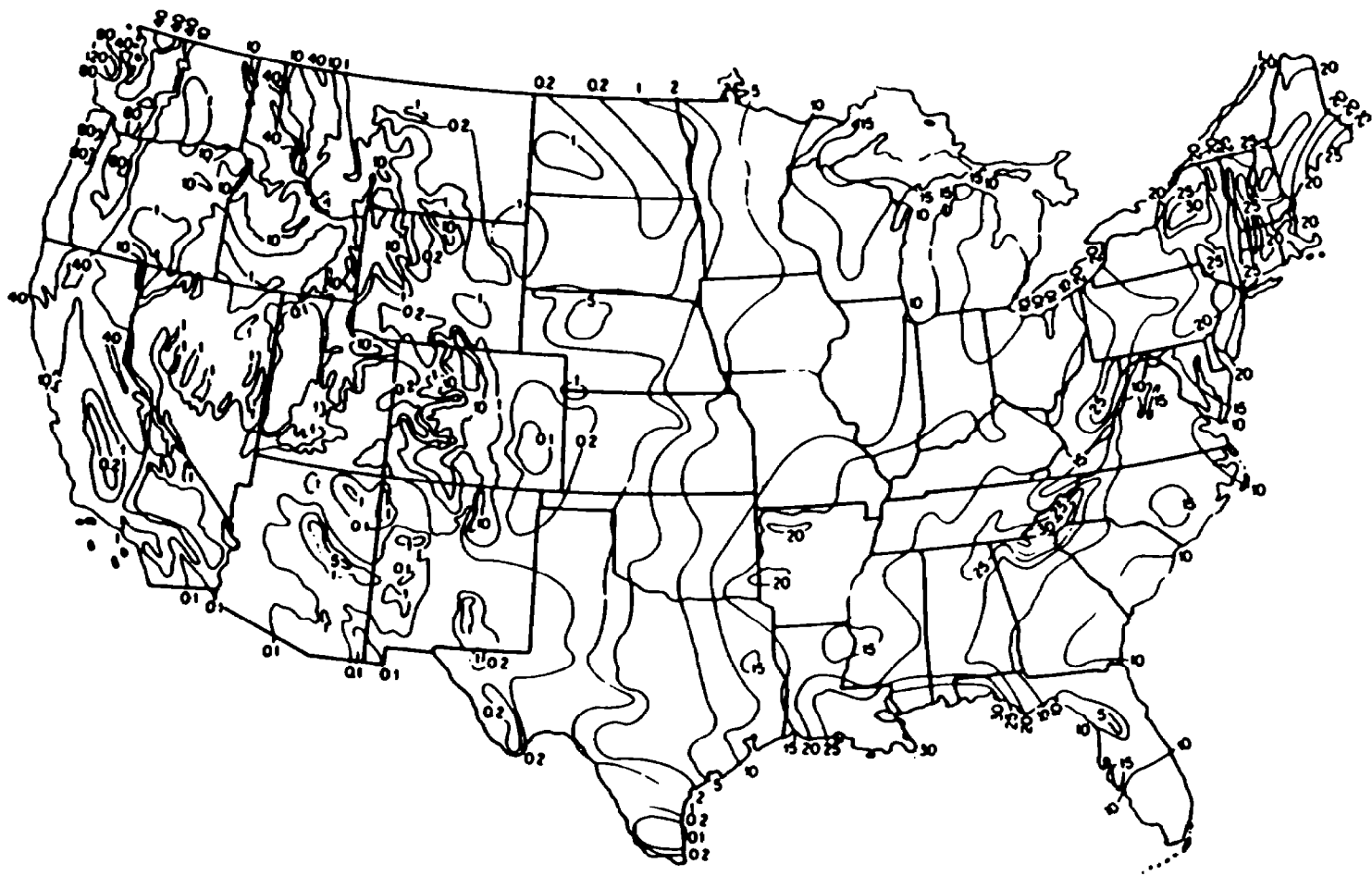
FIGURE III-6 AVERAGE ANNUAL STREAMFLOW IN INCHES (1IN = 2.54CM)
(LANGBEIN ET AL, 1949)

Noting that:

$$1 \text{ mg/l} = 0.001 \text{ kg/m}^3$$
$$1 \text{ km}^2 = 10^6 \text{m}^2$$

annual runoff is

$$0.254 \ (50) \ 10^6 = 12.7 \ 10^6 \text{m}^3.$$

Background loads are

BOD: $\quad 3 \ (0.001)(12.7) \ 10^6 = 38,100 \text{ kg/yr}$

Phosphorus: $\quad 0.011(0.001)(12.7) \ 10^6 = 140 \text{ kg/yr}.$

─────── END OF EXAMPLE III-1 ───────────

3.3 NONPOINT SOURCE MODE.

The nonpoint source loading process is illustrated in Figure III-7. Precipitation, in the form of rain or snowmelt, comes in contact with a "waste" product located on the land surface or within the soil. Portions of the waste are transported in runoff and percolation to streams and groundwater aquifers. Nonpoint source wastes are any potential pollutant which comes in contact with drainage. Examples include chemicals in urban dust and road litter, agricultural fertilizers, pesticides and animal manures, road de-icing salts, sanitary landfill wastes, eroded soil, mining slag piles, septic tank effluents, lawn chemicals and toxic wastes in lagoons and land disposal facilities.

Nonpoint source pollution is associated with random hydrologic events. Combined with the dispersed nature of drainage patterns, this randomness produces waste loads .nich are difficult to monitor, and hence most loading estimates are obtained from mathematical models. The foundations of all nonpoint source models, including the loading functions discussed herein, are equations to predict water movement, especially runoff and percolation. These equations are supplemented by methods to calculate sediment movement, and together the two components describe nonpoint source transport, since pollutants are either dissolved in a water flux or attached to sediment. The third model component is a procedure to estimate the dissolved and solid-phase (sediment-attached) concentrations of the pollutant. In the loading functions, these concentrations are obtained empirically or derived from simple mass balances. In more analytical, and hence complex models, concentrations are obtained from mechanistic descriptions of chemical and biological processes.

Both average annual and single event loads can be estimated by nonpoint source loading functions. The former are useful when the effects of pollution are determined by long-term mass loads to a water body. Groundwater quality problems are often of this type. Also, several simple lake eutrophication models require annual phosphorus loads as input. Conversely, major storm events exert the most significant impacts on streams and rivers, and estimates of single event nonpoint source loads are necessary.
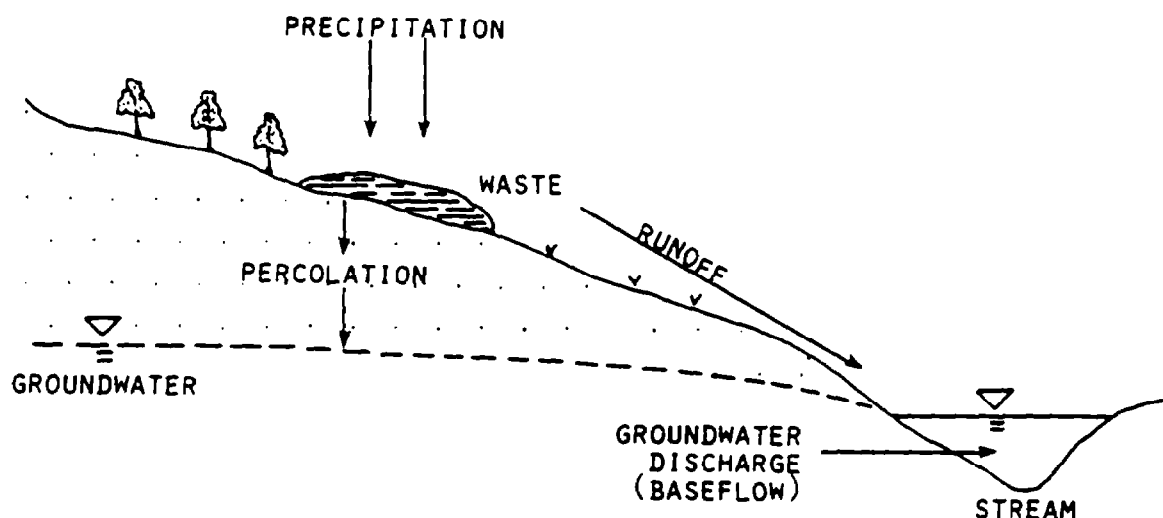
FIGURE III-7 THE NONPOINT SOURCE LOADING PROCESS

The most comprehensive estimates of nonpoint source loads are obtained from continuous simulation models such as HSPF, STORM, SWMM and CREAMS which have been developed under sponsorship of the U.S. Environmental Protection Agency, Army Corps of Engineers and Department of Agriculture. Since these models require computer facilities and extensive data structures, they are beyond the scope of this manual. Nevertheless, the simulation models are based on the same computational concepts presented in this chapter, particularly those used for single event loading functions.

Succeeding sections of this chapter present loading functions for rural runoff, irrigation return flows, urban runoff and groundwater.

3.4 RURAL RUNOFF LOADS

Nonpoint source waste loads to surface waters in rural areas include runoff from cropland (including pasture and range), forests, barnyards and feed lots, waste land application and storage facilities, construction sites and mining operations. Cropland and forest runoff are emphasized in this section, since these nonpoint sources are widespread, and their associated loading functions have been most extensively developed. Runoff loads from the other sources can in principle be estimated by procedures similar to the loading functions used for cropland and forest, but data are often lacking to implement the calculations.

3.4.1 Source Areas

Nonpoint source waste loads in runoff can be estimated for several different spatial scales. The most fundamental unit of analysis is a source area, which is a land area with sufficiently homogeneous soil and pollutant characteristics so that

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runoff loads can be considered uniform. A farmer's field is often considered a single source area and associated runoff loads are sometimes referred to as "edge-of-field" loads. Larger scales of analysis consist of aggregations of source areas or watersheds. Waste loads are transported from source areas by rivulets, ditches, streams and other drainage paths to eventually exit the watershed in streamflow. During this transit, portions of the wastes may be removed from the water flux by settling, adsorption, filtering or biochemical processes. The total watershed waste load in streamflow consists of these attenuated runoff sources plus waste loads from groundwater discharge.

Pollutants in runoff may be in dissolved and solid-phase forms, with the latter consisting of particulate material, or pollutants that are attached to sediment. The general loading function forms are:

$$\text{Dissolved pollutant waste load} = \text{Runoff water volume} \times \text{Dissolved pollutant concentration} \qquad (III-1)$$

$$\text{Solid-phase pollutant wasteload} = \text{Sediment flux} \times \text{Solid-phase pollutant concentration (concentration in sediment)} \qquad (III-2)$$

Sections 3.4.2, 3.4.3 and 3.4.4 describe methods for computing runoff volumes, sediment flux and pollutant concentrations, respectively.

3.4.2 Runoff

3.4.2.1 SCS Curve Number Equation

The U.S. Soil Conservation Service's curve number equation (CNE) is a standard procedure for estimating storm runoff (Mockus, 1972; Ogrosky and Mockus, 1964). The equation is:

$$Q = (P-0.2S)^2/(P+0.8S) \text{ for } P \geq 0.2S \qquad (III-3)$$

where

Q = runoff (cm)

P = precipitation (rainfall + snowmelt, cm)

S = water retention parameter (cm).

The 0.2S is an initial precipitation abstraction, and hence if $P < 0.2S$, Q is assumed to be zero.

The retention parameter S is computed from dimensionless curve numbers (CN) which are functions of soils, cover, management and antecedent moisture:

$$S = (2540/CN) - 25.4 \qquad\qquad (III-4)$$

The general form of the equation is shown in Figure III-8.

Although the CNE is most frequently applied to rainfall runoff, it may be used for snowmelt conditions. Snowmelt water can be estimated by the degree-day equation:

$$M = 0.45T \qquad\qquad (III-5)$$

where

        M = snowmelt water (cm)

        T = mean air temperature ($°C$).

If $T<0$, $M=0$. Also, M must not exceed the water content of the accumulated snowpack. The degree-day factor (0.45) is an average value (Stewart et al., 1976) and should be replaced by a location-specific value when available.

Since daily weather data are used for Equations III-3 and III-5, calculated runoff is the total runoff for a specific day.

3.4.2.2 Curve Number Selection

Curve numbers describe the hydrologic condition of land surface at the time of a precipitation event. The combined effects of soils, management and cover are shown in Table III-1 for "average" antecedent moisture conditions. Most soils in the United States have been classified in one of four hydrologic groups. Listings are available in Mockus (1972) Ogrosky and Mockus (1964) and Soil Conservation Service (1975). The qualifiers "good," "fair" or "poor" in Table III-1 indicate the extent to which cover and soil management conditions will minimize runoff. For example, continuous growth of a corn silage on the same site every year will deplete soil organic matter and encourage runoff. Conversely, corn grain in a rotation with hay or under no-till conditions will minimize runoff. Similarly, clear-cutting of woods accompanied by extensive disturbance of the soil surface by log skidding is a "poor" management practice.

The "woods" category in Table III-1 may be used for vegetated forest areas. Runoff for roads, logging trails and landings should be based on curve numbers for the "roads and right-of-way" category. Those curve numbers are also appropriate for construction sites.

The fourth, and most important factor in curve number selection is the wetness of the soil. If precipitation falls on soil that has been inundated by previous storms, infiltration is much less and runoff is much greater than would be the case for dry soil. Three different antecedent moisture conditions are specified for the CNE: I (dry), II (average), and III (wet). Antecedent moisture is approximated by the five-day antecedent precipitation, which is the total precipitation (rain +
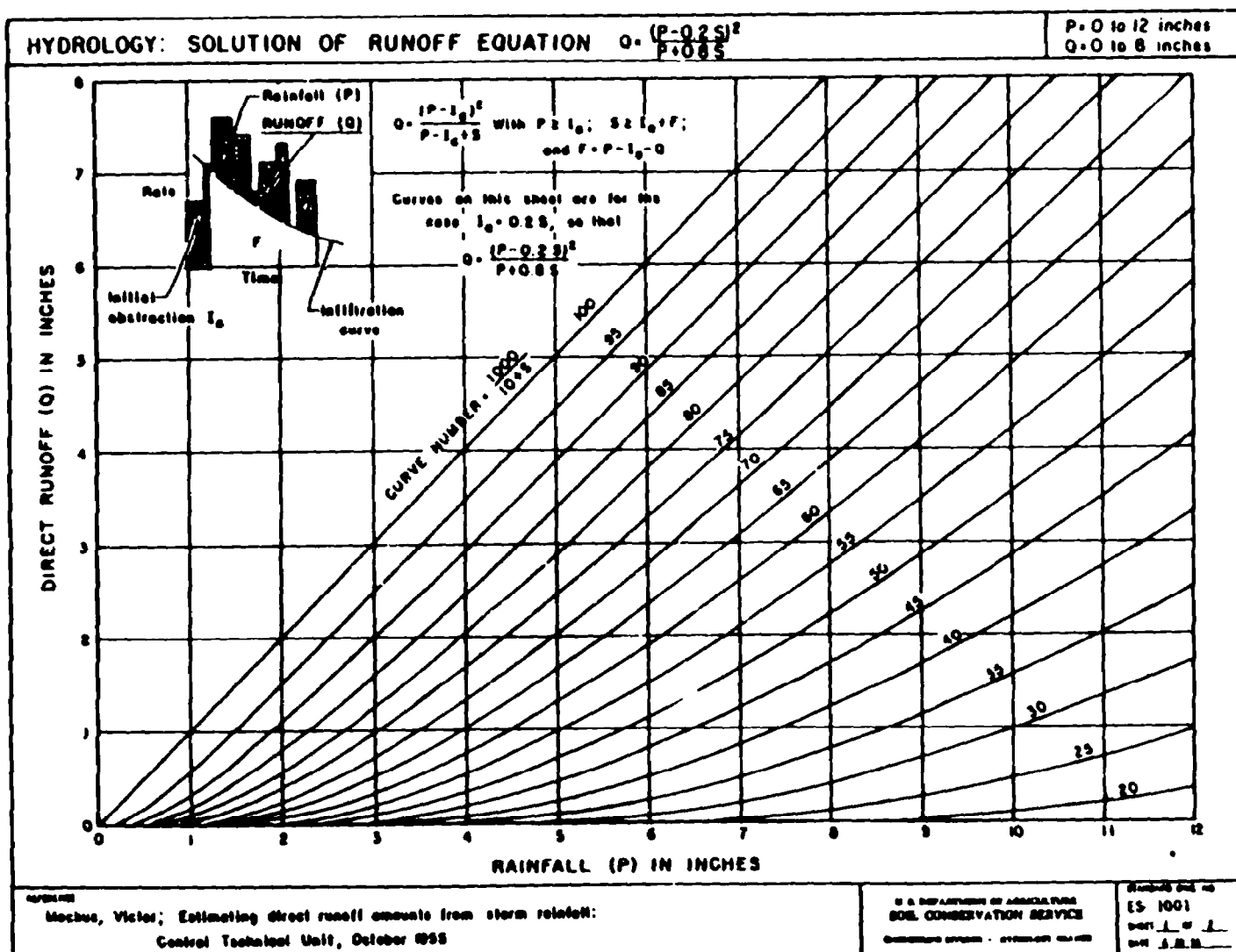
FIGURE III-8 SCS CURVE NUMBER RUNOFF EQUATION (1in = 2.54cm)

TABLE III-1

RUNOFF CURVE NUMBERS FOR AVERAGE ANTECEDENT MOISTURE CONDITIONS

(Mockus, 1972)

Land use or cover	Treatment or Practice	Hydrologic Condition	Hydrologic Soil Group*			
			A	B	C	D
Fallow	Straight row	--	77	86	91	94
Row crops	Straight row	Poor	72	81	88	91
	Straight row	Good	67	78	85	89
	Contoured	Poor	70	79	84	88
	Contoured	Good	65	75	82	86
	Terraced	Poor	66	74	80	82
	Terraced	Good	62	71	78	81
Small grain	Straight row	Poor	65	76	84	88
	Straight row	Good	63	75	83	87
	Contoured	Poor	63	74	82	85
	Contoured	Good	61	73	81	84
	Terraced	Poor	61	72	79	82
	Terraced	Good	59	70	78	81
Close-seeded legumes or rotation meadow	Straight row	Poor	66	77	85	89
	Straight row	Good	58	72	81	85
	Contoured	Poor	64	75	83	85
	Contoured	Good	55	69	76	83
	Terraced	Poor	63	73	80	83
	Terraced	Good	51	67	76	80
Pasture or range		Poor	68	79	86	89
		Fair	49	69	79	84
		Good	39	61	74	80
	Contoured	Poor	47	67	81	88
	Contoured	Fair	25	59	75	83
	Contoured	Good	6	35	70	79
Meadow (permanent)		Good	30	58	71	78
Woods		Poor	45	66	77	83
		Fair	36	60	73	79
		Good	25	55	70	77
Farmsteads		--	59	74	82	86
Roads and right-of-way (hard surface)		--	74	84	90	92

*Soil Group	Description
A	Lowest Runoff Potential: Includes deep sands with very little silt and clay, also deep, rapidly permeable loess.
B	Moderately Low Runoff Potential: Mostly sandy soils less deep than A, and loess less deep or less aggregated than A, but the group as a whole has above-average infiltration after thorough wetting.
C	Moderately High Runoff Potential: Comprises shallow soils and soils containing considerable clay and colloids, though less than those of group D. The group has below-average infiltration after presaturation.
D	Highest Runoff Potential: Includes mostly clays of high swelling per cent, but the group also includes some shallow soils with nearly impermeable subhorizons near the surface

snowmelt) in the five days preceding a storm. Approximate limits for the three antecedent moisture conditions are given in Table III-2. Different limits are specified for growing and dormant season since evapotranspiration dries the soil much more rapidly during the growing season. In absence of more specific information, the growing season may be assumed to consist of months for which average air temperature is 10°C or above. Antecedent precipitation is an inadequate criterion during snowmelt, however, and for such events condition III is always assumed (Haith and Tubbs, 1981).

The curve numbers for condition II, or CN2 are given in Table III-1. The curve numbers for the other two conditions, I and III respectively, can be obtained from the equations given by Hawkins (1978):

$$CN1 = CN2/(2.334-0.01334CN2) \tag{III-6}$$

$$CN3 = CN2/(0.4036 + 0.0059CN2) \tag{III-7}$$

TABLE III-2

ANTECEDENT MOISTURE LIMITS FOR CURVE NUMBER SELECTION

(Ogrosky and Mockus, 1964)

Antecedent Moisture Condition	5-Day Antecedent Precipitation (cm)	
	Dormant Season*	Growing Season
I	<1.3	<3.6
II	1.3-2.8	3.6-5.3
III	>2.8	>5.3

*During snowmelt, condition III is always assumed regardless of antecedent precipitation.

——————————————— EXAMPLE III-2 —·——·—·——·——·— —————————

Cropland Runoff

A three-day rainstorm falls on a 30-ha soybean field during early August. The crop is continuously grown (no rotation) in straight rows. The soil is in hydrologic group B. The relevant precipitation is as follows:

Date	August 1	2	3	4	5	6	7	8	9
Rain (cm)	0	0	0	0	0	3.8	5.1	0.3	0

Determine the runoff from this storm.

Solution:

The crop is a row crop planted in straight rows and in poor hydrologic condition. From Table III-1, the curve number for condition 2 is CN2 = 81 for soil group B. Solving Equations III-6 and III-7 for CN1 and CN3, we have CN1 = 64.6 and CN3 = 91.9.

The three-day storm begins on August 6. On that day, 5-day antecedent precipitation is 0; hence the soil is in the driest antecedent moisture condition. Thus:

$$CN = CN1 = 64.6$$

and from Equation III-4:

$$S = (2540/64.6) - 25.4$$
$$= 13.9 \text{ cm.}$$

Since precipitation exceeds initial abstraction, $0.2S = 2.78$ cm, runoff occurs as predicted by Equation III-3:

$$Q = (3.8-2.78)^2/(3.8 + 0.8(13.9))$$
$$= 0.07 \text{ cm.}$$

On August 7, 5-day antecedent precipitation is 3.8 cm, which during the growing season corresponds to CN = CN2 = 81 (Table III-2). Thus:

$$S = (2540/81) - 25.4$$
$$= 5.96 \text{ cm.}$$

Rain exceeds $0.2S = 1.19$ cm, and

$$Q = (5.1 - 1.19)^2/(5.1 + 0.8(5.96))$$
$$= 1.55 \text{ cm.}$$

On the final day, 5-day antecedent precipitation is $3.8 + 5.1 = 8.9$ cm, CN = CN3 = 91.9 and S = 2.24 cm. Since the 0.3 cm of rain does not exceed the initial abstraction of 0.2 (2.24) = 0.45 cm, no runoff occurs.

The storm summary is as follows:

Day	Rainfall (cm)	Runoff (cm)
8/6	3.8	0.07
8/7	5.1	1.55
8/8	0.3	0
Total	9.2	1.62

The 1.62 cm of runoff over the 30-ha field can be converted to runoff volume (m^3) by noting that 1 ha = 10,000 m^2, and hence 1 cm on 1 ha = 0.01 (10,000) = 100 m^3. This runoff volume is 1.62(30)(100) = 4860 m^3.

This example illustrates three important characteristics of runoff:

● Runoff is a nonlinear function of precipitation; i.e., runoff is not a constant portion of precipitation.

● Runoff is generally a small fraction of precipitation, particularly during the growing season.

● Runoff is dramatically dependent on antecedent moisture conditions.

— — — — — — — — — — — END OF EXAMPLE III-2 — — — — — — — — — — — — —

3.4.2.3 Annual Runoff

The CNE is only applicable to individual storm events, and this is a limitation in nonpoint source studies for which annual waste loads are required. In such cases annual runoff estimates are necessary. The only way to produce such estimates is to use Equation III-3 to calculate runoff for each storm in a year, and sum the resulting values for the year. If an average annual runoff is needed, the process must be repeated for each of a number of years. The repeated use of Equation III-3 for all storms in a multi-year period is not difficult (see for example Haith and Tubbs, 1981), but it is a continuous simulation modeling process that can only be implemented on a computer.

Average annual runoff for row crops has been calculated by Stewart et al. (1976) for the eastern United States. A simulation model based on the CNE was run using 10-25 years of daily weather data from 52 locations. The simulation runs were based on straight row corn in good hydrologic condition on the four different soil groups. Fallow or bare soil conditions were assumed during the spring. Results of the simulations are shown in Figure III-9. The four soil groups correspond to CN2 = 67, 78, 85 and 89. These runoff values should generally be appropriate for any row crop. Runoff for situations with curve numbers falling between any two curve numbers can be determined by linear interpolation.
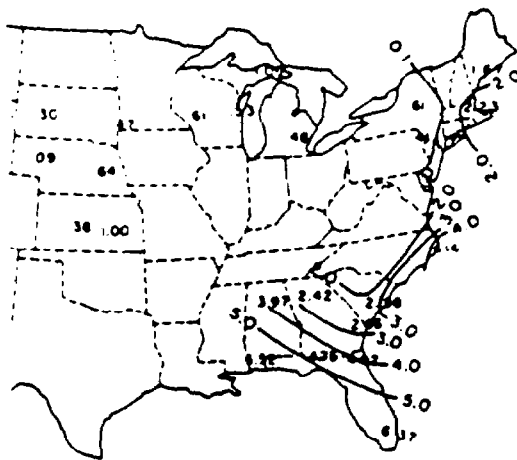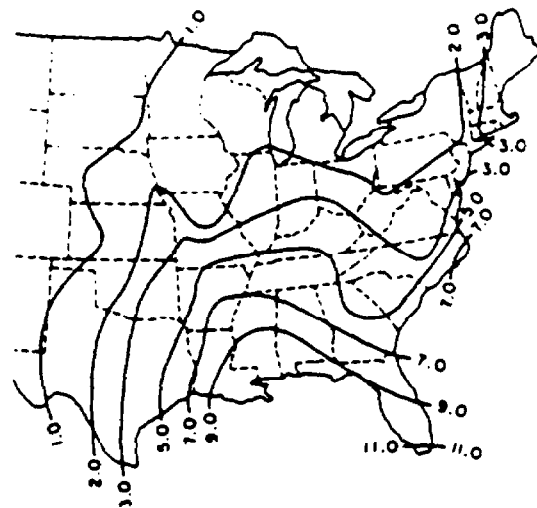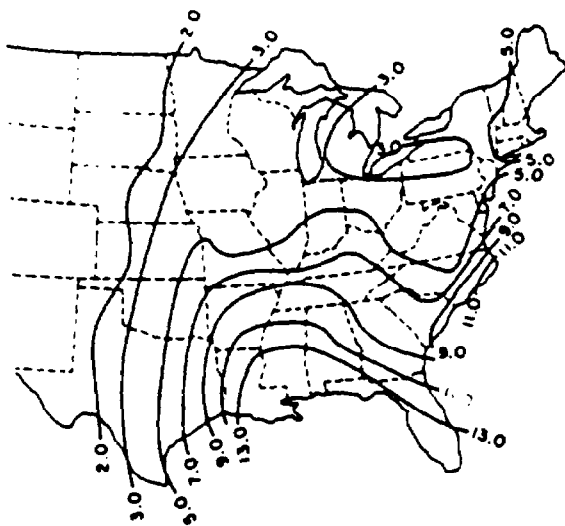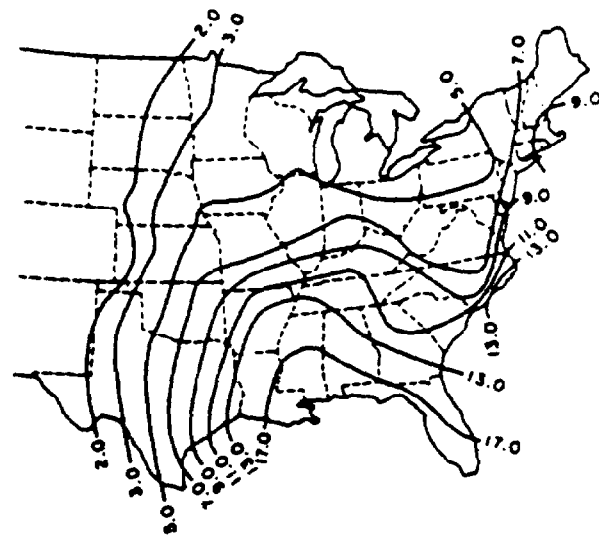
FIGURE III-9 MEAN ANNUAL ROW CROP RUNOFF IN INCHES
FOR SELECTED CURVE NUMBERS. A; CN2=67,
B: CN2=78; C: CN2=85; D: CN2=89. (1 IN
= 2.54CM) (STEWART ET AL, 1976)

3.4.2.4 Watershed Runoff

Runoff from a source area such as a farmer's field or logging road is given by Equation III-3. Runoff from an entire watershed is the sum of runoff from all source areas within the watershed. If we define:

Q_k = runoff from source area k (cm)

A_k = area of source area k (ha)

AT = total watershed area (ha)

a_k = fraction of watershed covered by source area k = A_k/AT

then watershed runoff Q(cm) is:

$$Q = \sum_k a_k Q_k \qquad (III-8)$$

Watershed runoff volume $V(m^3)$ is:

$$V = 100 \sum_k A_k Q_k$$
$$= 100 \, AT \sum_k a_k Q_k \qquad (III-9)$$

Equation III-8 or III-9 require computation of runoff Q_k from each source area. An alternative and simpler procedure is to determine a weighted average curve number:

$$CN = \sum_k a_k CN_k \qquad (III-10)$$

and compute watershed runoff directly from Equations III-3 and III-4. In Equation III-10 CN_k is the curve number for source area k.

The second procedure (average curve number) generally produces slightly lower watershed runoff estimates than Equation III-8 due to the nonlinear nature of the CNE. In any case, note that watershed runoff is only one component of streamflow. Additional components include groundwater discharge and point sources.

3.4.3 Erosion and Sediment

Erosion is the removal of soil particles by wind and water, and sediment is the particulate matter which is carried and eventually deposited by wind and water. Our concern here is with water pollution, and the prediction of sediment loads or yields in streamflow. Upstream erosion of soil surfaces and stream channels is the source of streamflow sediment yields. However, watershed sediment yield, as measured in streamflow at the outlet of the watershed, is generally substantially less than the

total upstream erosion since much of the transported sediment has been deposited or filtered from the water. Near a sediment source, nearly all eroded soil becomes a sediment mass flux. For example the sediment yield in runoff from a corn field is approximately equal to the eroded soil mass from the field. However, as the runoff travels from the field in drainage ditches and stream channels, portions of the sediment are removed, until only a fraction remains to exit the watershed.

Erosion of the land surface by sheet and rill erosion is the major source of solid-phase pollutants in surface waters, and most of this section is accordingly devoted to prediction of this sediment source. Although channel erosion may also be a significant component of sediment yield, it is not generally considered a pollution hazard and will not be considered in the following discussion.

3.4.3.1 The Universal Soil Loss Equation

The Universal Soil Loss Equation (USLE) is an empirical equation which was developed to predict average annual soil loss by sheet and rill erosion from source areas (Wischmeier and Smith, 1978). The equation, which was obtained by statistical analyses of over 10,000 plot-years of erosion field research data is:

$$X = 1.29 \ E(K)(1s)C(P) \qquad\qquad (III-11)$$

where

X = soil loss (t/ha; 1 t = 1 tonne = 1000 kg = 2205 lb)

E = rainfall/runoff erosivity index (10^2 m-tonne-cm/ha-hr)

K = soil erodibility (t/ha per unit of E)

$1s$ = topographic factor

C = cover/management factor

P = supporting practice factor.

The three factors 1s, C, P are dimensionless. The 1.29 is a conversion constant to obtain metric units.

The USLE is an important component of loading functions for runoff waste loads because its parameters have been evaluated for a wide range of conditions and many important pollutants are transported on eroded soil. For example, most organochlorine pesticides are very strongly adsorbed to soil particles. Procedures for determining the USLE parameters are presented in the following subsections.

3.4.3.1.1 Rainfall/Runoff Erosivity

The erosivity term E is related to rainfall intensity. Average annual values for the United States have been computed by Wischmeier and Smith (1978) and are given in Figures III-10 and 11. The values of E in these figures are in English units (10^2 ft-tons-in/ac-hr) and can be converted to the metric units of Equation III-11 by multiplying by 1.735; i.e. E (metric) = 1.735 E (English, Figures III-10,

FIGURE III-10 AVERAGE ANNUAL EROSIVITY INDICES (ENGLISH UNITS)
FOR EASTERN U.S. (WISCHMEIER AND SMITH, 1978)
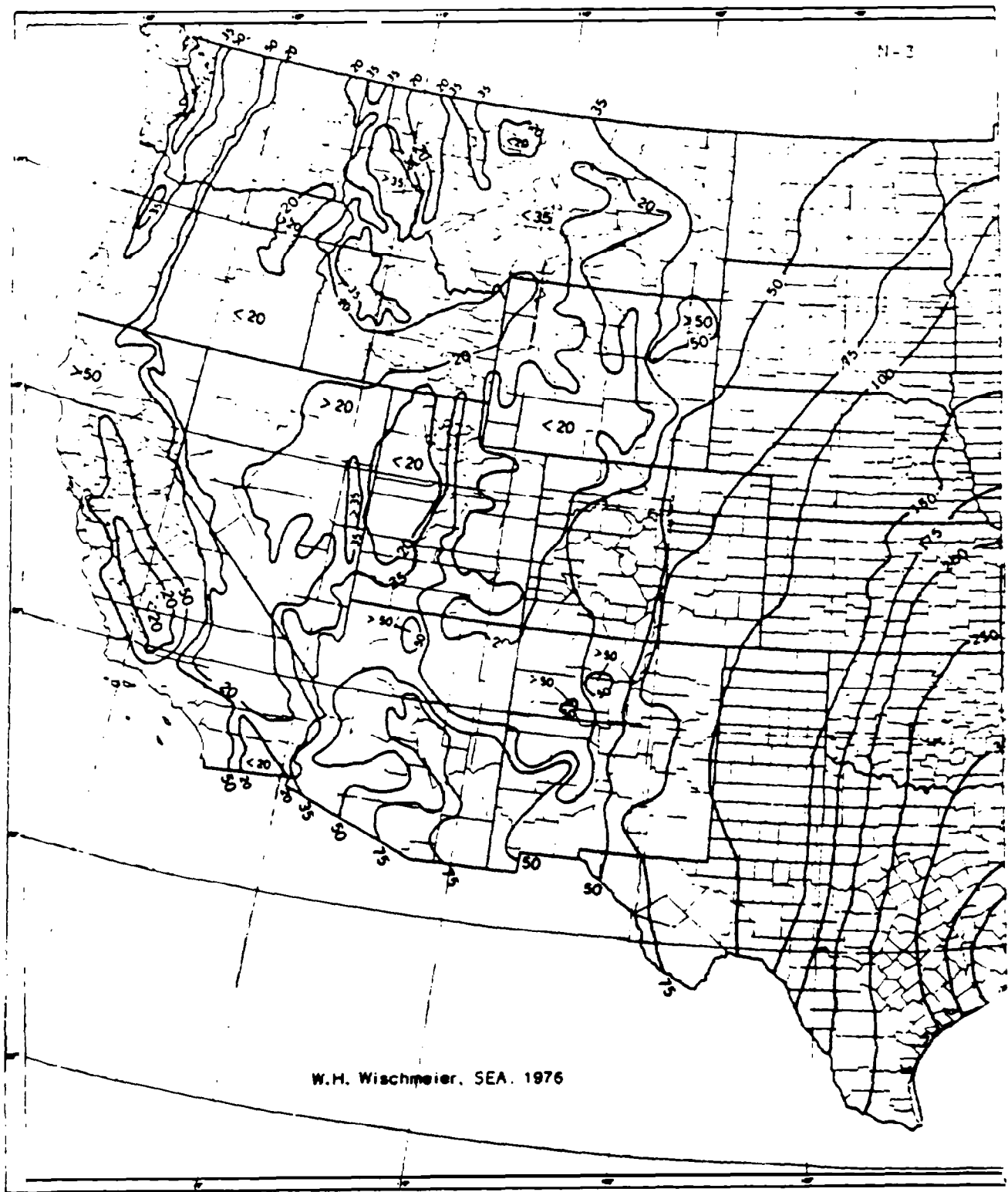
FIGURE III-11 AVERAGE ANNUAL EROSIVITY INDICES (ENGLISH UNITS)
FOR WESTERN U.S. (WISCHMEIER AND SMITH, 1978)

11). For example the erosivity for northern Maine is $E = 1.735 (75) = 130$.

It can be seen from Figure III-10 that the intense rainstorms of the Southeast produce the highest levels of erosivity in the United States. In contrast, erosivity in much of the western mountain region (Figure III-11) is less than 10 percent of the southeast values.

3.4.3.1.2 Soil Erodibility

Typical values of K are given in Table III-3 as a function of soil texture and organic matter content. Values for specific soils are available from local Soil and Water Conservation Districts and state offices of the Soil Conservation Service.

3.4.3.1.3 Topographic Factor

The topographic factor ls, is related to the angle of slope θ and slope length x (m) by:

$$ls = (0.045x)^b (65.41 \sin^2\theta + 4.56 \sin \theta + 0.065) \qquad (III-12)$$

The slope angle θ is obtained from percent slope, s by:

$$\theta = \tan^{-1}(s/100) \qquad (III-13)$$

For example, a slope of s = 8 percent has a slope angle of $\theta = 4.6°$. The exponent in Equation III-12 is given by b = 0.5 for s > 5, b = 0.4 for $3.5 \leq s \leq 4.5$, b = 0.3 for $1 \leq s \leq 3$, and b = 0.2 for $s \leq 1$ (Wischmeier and Smith, 1978).

Research data support Equation III-12 for $x \leq 100$ m and $s \leq 18$, although in practice it is often applied beyond these limits.

3.4.3.1.4 Cover/Management Factor

The cover/management factor C describes the protection of the soil surface by plant canopy, crop residues, mulches, etc. The maximum C value is 1.0, corresponding to no protection. Cropland C values change dramatically during the year in response to planting operations, crop growth and harvest. Although C values have been determined for each of these stages (Wischmeier and Smith, 1978), generalized annual values such as those given in Table III-4 are more suitable for loading functions.

Wischmeier and Smith (1978) have also developed C factors for construction sites; pasture, range and idle land; undisturbed forests; and mechanically prepared woodland sites. These C values are given in Tables III-5 through III-8. Note that cover factors are so small for undisturbed forest and pasture or range with good ground cover that these erosion sources can generally be neglected in water quality studies.

TABLE III-3

SOIL ERODIBILITY, K

(Stewart et al, 1975)

Texture	Organic Matter		
	0.5%	2%	4%
Sand	0.05	0.03	0.02
Fine sand	0.16	0.14	0.14
Very fine sand	0.42	0.36	0.28
Loamy sand	0.12	0.10	0.08
Loamy fine sand	0.24	0.20	0.16
Loamy very fine sand	0.44	0.38	0.30
Sandy loam	0.27	0.24	0.19
Fine sandy loam	0.35	0.30	0.24
Very fine sandy loam	0.47	0.41	0.33
Loam	0.38	0.34	0.29
Silt loam	0.48	0.42	0.33
Silt	0.60	0.52	0.42
Sandy clay loam	0.27	0.25	0.21
Clay loam	0.28	0.25	0.21
Silty clay loam	0.37	0.32	0.26
Sandy clay	0.14	0.13	0.12
Silty clay	0.25	0.23	0.19
Clay		0.13-0.29	

TABLE III-4

GENERALIZED VALUES OF THE COVER AND MANAGEMENT FACTOR, C,

IN THE 37 STATES EAST OF THE ROCKY MOUNTAINS (Stewart et al, 1975)

Line no	Crop, rotation, and management [3]	Productivity level [2]	
		High	Mod
		C value	
Base value continuous fallow, tilled up and down slope		1.00	1.00
CORN			
1	C, RdR, fall TP, conv (1)	0.54	0.62
2	C, RdR, spring TP, conv (1)	50	59
3	C, RdL, fall TP, conv (1)	42	52
4	C, RdR, wc seeding, spring TP, conv (1)	40	49
5	C, RdL, standing, spring TP, conv (1)	38	48
6	C, fall shred stalks, spring TP, conv (1)	35	44
7	C(silage)-W(RdL, fall TP) (2)	31	35
8	C, RdL, fall chisel, spring disk, 40-30% rc (1)	24	30
9	C(silage), W wc seeding, no-till pl in c-k W (1)	20	24
10	C(RdL)-W(RdL, spring TP) (2)	20	26
11	C, fall shred stalks, chisel pl, 40-30% rc (1)	19	26
12	C-C-C-W-M, RdL, TP for C, disk for W (5)	17	23
13	C, RdL, strip till row zones, 55-40% rc (1)	16	24
14	C-C-C-W-M-M, RdL, TP for C, disk for W (6)	14	20
15	C-C-W-M, RdL, TP for C, disk for W (4)	12	17
16	C, fall shred, no-till pl, 70-50% rc (1)	11	18
17	C-C-W-M-M, RdL, TP for C, disk for W (5)	087	14
18	C-C-C-W-M, RdL, no-till pl 2d & 3rd C (5)	076	13
19	C-C-W-M, RdL, no-till pl 2d C (4)	068	11
20	C, no-till pl in c-k wheat, 90-70 rc (1)	062	14
21	C-C-C-W-M-M, no-till pl 2d & 3rd C (6)	061	11
22	C-W-M, RdL, TP for C, disk for W (3)	055	095
23	C-C-W-M-M, RdL, no-till pl 2d C (5)	051	094
24	C-W-M-M, RdL, TP for C, disk for W (4)	039	074
25	C-W-M-M-M, RdL, TP for C, disk for W (5)	032	061
26	C, no-till pl in c-k sod, 95-80% rc (1)	017	053
COTTON [4]			
27	Cot, conv (Western Plains) (1)	0.42	0.49
28	Cot, conv (South) (1)	34	40
MEADOW			
29	Grass & Legume mix	0.004	0.01
30	Alfalfa, lespodeza or Sericea	020	
31	Sweet clover	025	
SORGHUM, GRAIN (Western Plains) [4]			
32	RdL, spring TP, conv (1)	0.43	0.53
33	No-till pl in shredded 70-50% rc	11	18

TABLE III-4 (Continued)

Line no	Crop, rotation, and management[3]	Productivity level[2]	
		High	Mod
		C value	
SOYBEANS[4]			
34	B. RdL, spring TP, conv (1)	0 48	0 54
35	C-B, TP annually, conv (2)	43	51
36	B, no-till pl	22	28
37	C-B, no-till pl, fall shred C stalks (2)	18	22
WHEAT			
38	W-I, fall TP after W (2)	0 38	
39	W-I, stubble mulch, 500 lbs rc (2)	32	
40	W-F, stubble mulch, 1000 lbs rc (2)	21	
41	Spring W, RdL, Sept TP, conv (N & S Dak) (1)	23	
42	Winter W, RdL, Aug TP, conv (Kans) (1)	19	
43	Spring W, stubble mulch, 750 lbs rc (1)	15	
44	Spring W, stubble mulch, 1250 lbs rc (1)	12	
45	Winter W, stubble mulch, 750 lbs rc (1)	11	
46	Winter W, stubble mulch, 1250 lbs rc (1)	10	
47	W-M, conv (2)	054	
48	W-M-M, conv (3)	026	
49	W-M-M-M, conv (4)	021	

[1] This table is for illustrative purposes only and is not a complete list of cropping systems or potential practices. Values of C differ with rainfall pattern and planting dates. These generalized values show approximately the relative erosion-reducing effectiveness of various crop systems, but locationally derived C values should be used for conservation planning at the field level. Tables of local values are available from the Soil Conservation Service.

[2] High level is exemplified by long-term yield averages greater than 75 bu. corn or 3 tons grass-and-legume hay, or cotton management that regularly provides good stands and growth.

[3] Numbers in parentheses indicate number of years in the rotation cycle. No (1) designates a continuous one-crop system

[4] Grain sorghum, soybeans, or cotton may be substituted for corn in lines 12, 14, 15, 17-19, 21-25 to estimate C values for sod-based rotations.

Abbreviations defined

B	- soybeans	F	- fallow
C	- corn	M	- grass & legume hay
c-k	- chemically killed	pl	- plant
conv	- conventional	W	- wheat
cot	- cotton	wc	- winter cover

lbs rc	- pounds of crop residue per acre remaining on surface after new crop seeding
% rc	- percentage of soil surface covered by residue mulch after new crop seeding
70-50% rc	- 70% cover for C values in first column; 50% for second column
RdR	- residues (corn stover, straw, etc.) removed or burned
RdL	- all residues left on field (on surface or incorporated)
TP	- turn plowed (upper 5 or more inches of soil inverted, covering residues)

TABLE III-5

C FACTOR VALUES FOR CONSTRUCTION SITES

(Wischmeier and Smith, 1978)[1]

Type of mulch	Mulch Rate	Land Slope	Factor C	Length limit [2]
	Tons per acre	Percent		Feet
None	0	all	1.0	—
Straw or hay,	1.0	1-5	0.20	200
tied down by	1.0	6-10	.20	100
anchoring and				
tacking	1.5	1-5	.12	300
equipment [3]	1.5	6-10	.12	150
Do.	2.0	1-5	.06	400
	2.0	6-10	.06	200
	2.0	11-15	.07	150
	2.0	16-20	.11	100
	2.0	21-25	.14	75
	2.0	26-33	.17	50
	2.0	34-50	.20	35
Crushed stone,	135	<16	.05	200
¼ to 1½ in	135	16-20	.05	150
	135	21-33	.05	100
	135	34-50	.05	75
Do.	240	<21	.02	300
	240	21-33	.02	200
	240	34-50	.02	150
Wood chips	7	<16	.08	75
	7	16-20	.08	50
Do.	12	<16	.05	150
	12	16-20	.05	100
	12	21-33	.05	75
Do.	25	<16	.02	200
	25	16-20	.02	150
	25	21-33	.02	100
	25	34-50	.02	75

[1] Developed by an interagency workshop group on the basis of field experience and limited research data.

[2] Maximum slope length for which the specified mulch rate is considered effective. When this limit is exceeded, either a higher application rate or mechanical shortening of the effective slope length is required.

[3] When the straw or hay mulch is not anchored to the soil, C values on moderate or steep slopes of soils having K values greater than 0.30 should be taken at double the values given in this table.

TABLE III-6

C FACTOR VALUES FOR PERMANENT PASTURE, RANGE AND IDLE LAND

(Wischmeier and Smith, 1978)[1]

Vegetative canopy		Cover that contacts the soil surface						
Type and height[2]	Percent cover	Type[4]	Percent ground cover					
			0	20	40	60	80	95+
No appreciable canopy		G	0.45	0.20	0.10	0.042	0.013	0.003
		W	.45	.24	.15	.091	.043	.011
Tall weeds or short brush with average drop fall height of 20 in	25	G	.36	.17	.09	.038	.013	.003
		W	.36	.20	.13	.083	.041	.011
	50	G	.26	.13	.07	.035	.012	.003
		W	.26	.16	.11	.076	.039	.011
	75	G	.17	.10	.06	.032	.011	.003
		W	.17	.12	.09	.068	.038	.011
Appreciable brush or bushes, with average drop fall height of 6½ ft	25	G	.40	.18	.09	.040	.013	.003
		W	.40	.22	.14	.087	.042	.011
	50	G	.34	.16	.08	.038	.012	.003
		W	.34	.19	.13	.082	.041	.011
	75	G	.28	.14	.08	.036	.012	.003
		W	.28	.17	.12	.078	.040	.011
Trees, but no appreciable low brush. Average drop fall height of 13 ft	25	G	.42	.19	.10	.041	.013	.003
		W	.42	.23	.14	.089	.042	.011
	50	G	.39	.18	.09	.040	.013	.003
		W	.39	.21	.14	.087	.042	.011
	75	G	.36	.17	.09	.039	.012	.003
		W	.36	.20	.13	.084	.041	.011

[1] The listed C values assume that the vegetation and mulch are randomly distributed over the entire area.

[2] Canopy height is measured as the average fall height of water drops falling from the canopy to the ground. Canopy effect is inversely proportional to drop fall height and is negligible if fall height exceeds 33 ft.

[3] Portion of total-area surface that would be hidden from view by canopy in a vertical projection (a bird's-eye view).

[4] G: cover at surface is grass, grasslike plants, decaying compacted duff, or litter at least 2 in deep.

W: cover at surface is mostly broadleaf herbaceous plants (as weeds with little lateral-root network near the surface) or undecayed residues or both.

TABLE III-7

C FACTOR VALUES FOR UNDISTURBED FOREST LAND

(Wischmeier and Smith, 1978)

Percent of Area Covered by Canopy of Trees and Undergrowth	Percent of Area Covered by Duff (litter) at least 5 cm deep	Factor C
100-75	100-90	0.0001-0.001
70-45	85-75	0.002-0.004
40-20	70-40	0.003-0.009

3.4.3.1.5 Supporting Practice Factor

The supporting practice factor P measures the effect of traditional soil conservation practices on cropland erosion. Values of the P factor are given in Table III-9. Note that two different types of practice factors apply to terracing. For example, for a double terrace (n=2) on a 6 percent slope, $P = 0.5/\sqrt{2} = 0.35$. The value indicates the amount of erosion from the soil surface. However, approximately 80 percent of the eroded soil is trapped in the terraces channel and does not leave the source area. Hence, for purposes of estimating nonpoint source loads, the practice factor is $0.2(0.35) = 0.07$.

3.4.3.2 Single Event Erosion Estimates

Although the USLE was developed for average annual erosion estimates, nonpoint source studies often require waste loads for specific storm events. When this is the case, the erosivity term E in Equation III-11 must be determined for the storms in question. Three different methods may be used to obtain these erosivities.

Method 1: Direct computation from rainfall intensities.

The most analytical approach involves the use of rainfall intensity data directly to compute storm kinetic energy and maximum intensities. This procedure, as described in Wischmeier and Smith (1978) is generally too cumbersome for screening studies.

Method 2: Design storms.

Wischmeier and Smith (1978) have analyzed rainfall data throughout the United States to determine frequencies of E values. The results are given in Table III-10, and may be used to determine the soil erosion associated with storms of various

TABLE III-8

C FACTOR VALUES FOR MECHANICALLY PREPARED WOODLAND SITES

(Wischmeier and Smith, 1978)

Site preparation	Mulch cover[1]	Soil condition[2] and weed cover[3]							
		Excellent		Good		Fair		Poor	
		NC	WC	NC	WC	NC	WC	NC	WC
	Percent								
Disked, raked, or bedded[4]	None	0.52	0.20	0.72	0.27	0.85	0.32	0.94	0.36
	10	.33	.15	.46	.20	.54	.24	.60	.26
	20	.24	.12	.34	.17	.40	.20	.44	.22
	40	.17	.11	.23	.14	.27	.17	.30	.19'
	60	.11	.08	.15	.11	.18	.14	.20	.15
	80	.05	.04	.07	.06	.09	.08	.10	.09
Burned[5]	None	.25	.10	.26	.10	.31	.12	.45	.17
	10	.23	.10	.24	.10	.26	.11	.36	.16
	20	.19	.10	.19	.10	.21	.11	.27	.14
	40	.14	.09	.14	.09	.15	.09	.17	.11
	60	.08	.06	.09	.07	.10	.08	.11	.08
	80	.04	.04	.05	.04	.05	.04	.06	.05
Drum chopped[5]	None	.16	.07	.17	.07	.20	.08	.29	.11
	10	.15	.07	.16	.07	.17	.08	.23	.10
	20	.12	.06	.12	.06	.14	.07	.18	.09
	40	.09	.06	.09	.06	.10	.06	.11	.07
	60	.06	.05	.06	.05	.07	.05	.07	.05
	80	.03	.03	.03	.03	.03	.03	.04	.04

[1] Percentage of surface covered by residue in contact with the soil.

[2] Excellent soil condition—Highly stable soil aggregates in topsoil with fine tree roots and litter mixed in.

Good—Moderately stable soil aggregates in topsoil or highly stable aggregates in subsoil (topsoil removed during raking), only traces of litter mixed in.

Fair—Highly unstable soil aggregates in topsoil or moderately stable aggregates in subsoil, no litter mixed in.

Poor—No topsoil, highly erodible soil aggregates in subsoil, no litter mixed in.

[3] NC—No live vegetation.

WC—75 percent cover of grass and weeds having an average drop fall height of 20 in. For intermediate percentages of cover, interpolate between columns.

[4] Modify the listed C values as follows to account for effects of surface roughness and aging:

First year after treatment: multiply listed C values by 0.40 for rough surface (depressions >6 in); by 0.65 for moderately rough; and by 0.90 for smooth (depressions <2 in).

For 1 to 4 years after treatment: multiply listed factors by 0.7.

For 4+ to 8 years: use table 6.

More than 8 years: use table 7.

[5] For first 3 years: use C values as listed.

For 3+ to 8 years after treatment: use table 6.

More than 8 years after treatment: use table 7.

TABLE III-9

PRACTICE FACTORS (P) USED IN UNIVERSAL SOIL LOSS EQUATION

(Stewart et al, 1975)

Practice	Land slope (percent)				
	1.1-2	2.1-7	7.1-12	12.1-18	18.1-24
	(Factor P)				
Contouring (P_c)	0.60	0.50	0.60	0.80	0.90
Contour strip cropping (P_{sc})					
R-R-M-M[1]	0.30	0.25	0.30	0.40	0.45
R-W-M-M	0.30	0.25	0.30	0.40	0.45
R-R-W-M	0.45	0.38	0.45	0.60	0.68
R-W	0.52	0.44	0.52	0.70	0.90
R-O	0.60	0.50	0.60	0.80	0.90
Contour listing or ridge planting (P_{cl})	0.30	0.25	0.30	0.40	0.45
Contour terracing (P_t)[2]	[3] $0.6/\sqrt{n}$	$0.5/\sqrt{n}$	$0.6/\sqrt{n}$	$0.8/\sqrt{n}$	$0.9/\sqrt{n}$
No support practice	1.0	1.0	1.0	1.0	1.0

[1] R = rowcrop, W = fall-seeded grain, O = spring-seeded grain, M = meadow. The crops are grown in rotation and so arranged on the field that rowcrop strips are always separated by a meadow or winter-grain strip.

[2] These P_t values estimate the amount of soil eroded to the terrace channels and are used for conservation planning. For prediction of off-field sediment, the P_t values are multiplied by 0.2.

[3] n = number of approximately equal-length intervals into which the field slope is divided by the terraces. Tillage operations must be parallel to the terraces.

return periods. Note that the English units E values given in Table III-10 must be multiplied by 1.735 to obtain the metric E used in Equation III-11.

Method 3: Erosivities from daily rainfall data.

Richardson et al. (1983) developed a regression equation for erosivity based on daily rainfall data. Converting their results to the units of E in Equation III-11, the expected values of E for a daily rainfall R (cm) is:

$$E = 6.46a \ R^{1.81} \qquad\qquad (III-14)$$

The coefficient "a" varies with location and season. Richardson et al. (1983) determined cool season (October-March) and warm season (April-September) coefficients for the locations shown in Figure III-12.

TABLE III-10

EXPECTED MAGNITUDES OF SINGLE-STORM EROSIVITY INDICES (ENGLISH UNITS)

(Wischmeier and Smith, 1978)

Location	Index values normally exceeded once in—				
	year 1	years 2	years 5	years 10	years 20
Alabama:					
Birmingham	54	77	119	140	170
Mobile	97	122	151	177	194
Montgomery	62	86	118	145	172
Arkansas:					
Fort Smith	43	65	101	132	167
Little Rock	41	69	115	158	211
Mountain Home	33	44	68	87	105
Texarkana	51	73	105	132	163
California:					
Red Bluff	13	21	34	49	65
San Luis Obispo	11	15	22	28	34
Colorado:					
Akron	22	36	63	87	118
Pueblo	17	31	60	88	127
Springfield	31	51	84	112	152
Connecticut:					
Hartford	23	33	38	44	79
New Haven	31	47	73	96	122
District of Columbia	39	57	84	108	136
Florida:					
Apalachicola	87	124	180	224	272
Jacksonville	92	123	166	201	236
Miami	93	134	200	253	308
Georgia:					
Atlanta	49	67	92	112	134
Augusta	34	52	74	94	118
Columbus	61	81	108	131	152
Macon	53	72	99	122	146
Savannah	82	128	203	272	358
Watkinsville	52	71	99	120	142
Illinois:					
Cairo	39	63	101	135	173
Chicago	33	49	77	101	129
Dixon Springs	39	56	82	105	130
Moline	39	50	89	116	143
Rantoul	27	39	56	69	83
Springfield	34	52	73	94	117
Indiana:					
Evansville	26	38	54	71	86
Fort Wayne	24	33	45	54	65
Indianapolis	29	41	60	75	90
South Bend	26	41	65	86	111
Terre Haute	42	57	78	96	113
Iowa:					
Burlington	37	48	63	72	81
Charles City	33	47	68	85	103
Clarinda	35	46	66	79	94
Des Moines	31	45	67	86	105
Dubuque	43	63	91	114	140
Rockwell City	31	49	76	101	129
Sioux City	46	58	84	105	131

Location	Index values normally exceeded once in—				
	year 1	years 2	years 5	years 10	years 20
Kansas:					
Burlingame	37	51	69	83	100
Coffeyville	47	69	101	126	159
Concordia	33	53	86	116	154
Dodge City	31	47	76	97	124
Goodland	26	37	53	67	80
Hays	25	51	76	97	121
Wichita	41	61	93	121	150
Kentucky:					
Lexington	30	44	80	114	151
Louisville	31	43	59	72	85
Middlesboro	28	38	52	63	73
Louisiana:					
New Orleans	104	149	214	278	338
Shreveport	55	73	99	121	141
Maine:					
Caribou	14	20	28	34	44
Portland	16	27	42	44	82
Skowhegan	18	27	40	51	63
Maryland:					
Baltimore	41	59	84	109	133
Massachusetts:					
Boston	17	27	43	57	73
Washington	29	35	41	45	50
Michigan:					
Alpena	14	21	32	41	50
Detroit	21	31	45	56	68
East Lansing	19	26	36	43	51
Grand Rapids	24	28	34	38	43
Minnesota:					
Duluth	31	34	53	72	93
Fosston	17	26	39	51	63
Minneapolis	25	35	51	65	78
Rochester	41	58	83	105	129
Springfield	24	37	60	80	102
Mississippi:					
Meridian	69	92	125	151	176
Oxford	48	64	86	103	120
Vicksburg	57	78	111	134	161
Missouri:					
Columbia	43	58	77	93	107
Kansas City	38	43	63	78	93
McCredie	35	55	89	117	151
Rolla	43	63	91	115	140
Springfield	37	51	70	87	102
St. Joseph	45	62	86	106	126
Montana:					
Great Falls	4	8	14	20	26
Miles City	7	12	21	29	38
Nebraska:					
Antioch	19	26	36	45	53
Lincoln	36	51	74	92	112
Lynch	26	37	54	67	82
North Platte	25	36	59	78	99
Scribner	38	53	76	96	116
Valentine	18	28	45	61	77

TABLE III-10 (Continued)

Location	Index values normally exceeded once in—				
	year 1	years 2	years 5	years 10	years 20
New Hampshire:					
Concord	18	27	45	62	79
New Jersey:					
Atlantic City	39	55	77	97	117
Marlboro	39	57	83	111	136
Trenton	29	46	76	102	131
New Mexico:					
Albuquerque	4	6	11	15	21
Roswell	10	21	34	45	53
New York:					
Albany	18	26	38	47	56
Binghamton	16	24	36	47	58
Buffalo	15	23	34	49	61
Marcellus	16	24	38	49	62
Rochester	13	23	38	54	75
Solomons	15	21	32	40	47
Syracuse	15	24	38	51	65
North Carolina:					
Asheville	28	40	58	72	87
Charlotte	41	63	100	131	164
Greensboro	37	51	74	92	113
Raleigh	53	77	110	137	168
Wilmington	59	87	129	167	206
North Dakota:					
Devils Lake	19	27	37	47	57
Fargo	20	31	54	77	103
Williston	11	16	23	33	41
Ohio:					
Cincinnati	17	26	46	59	69
Cleveland	22	25	53	71	86
Columbiana	20	26	35	41	48
Columbus	27	40	60	77	94
Coshocton	27	45	77	108	143
Dayton	21	30	44	57	70
Toledo	16	26	42	57	74
Oklahoma:					
Ardmore	46	71	107	141	179
Cherokee	44	59	80	97	113
Guthrie	47	70	105	134	163
McAlester	54	82	127	165	209
Tulsa	47	69	100	127	154
Oregon:					
Portland	6	9	13	15	18
Pennsylvania:					
Franklin	17	24	35	45	54
Harrisburg	19	25	35	43	51
Philadelphia	28	39	55	69	81
Pittsburgh	23	32	45	57	67
Reading	28	39	55	66	81
Scranton	23	32	44	53	63
Puerto Rico:					
San Juan	57	87	131	167	216
Rhode Island:					
Providence	23	34	53	66	83

Location	Index values normally exceeded once in—				
	year 1	years 2	years 5	years 10	years 20
South Carolina:					
Charleston	74	106	154	196	248
Clemson	51	73	106	133	163
Columbia	41	59	85	106	132
Greenville	44	63	96	124	153
South Dakota:					
Aberdeen	23	25	53	73	92
Huron	19	27	40	50	61
Isabel	15	24	34	52	67
Rapid City	12	20	34	46	64
Tennessee:					
Chattanooga	34	49	72	93	114
Knoxville	25	41	66	93	122
Memphis	43	55	70	82	91
Nashville	35	49	66	83	99
Texas:					
Abilene	31	49	79	103	138
Amarillo	27	47	88	112	130
Austin	51	88	125	169	218
Brownsville	73	113	181	245	312
Corpus Christi	57	79	114	146	171
Dallas	53	82	126	166	213
Del Rio	44	67	108	144	182
El Paso	6	9	15	19	24
Houston	82	127	208	275	357
Lubbock	17	29	53	77	103
Midland	23	35	52	69	85
Nacogdoches	77	103	138	164	194
San Antonio	57	82	122	155	193
Temple	53	78	123	162	206
Victoria	59	83	116	146	178
Wichita Falls	47	63	86	106	123
Vermont:					
Burlington	15	22	25	47	55
Virginia:					
Blacksburg	23	31	41	48	56
Lynchburg	31	45	66	83	102
Richmond	44	63	86	102	125
Roanoke	23	33	48	61	73
Washington:					
Spokane	3	4	7	8	11
West Virginia:					
Elkins	23	31	42	51	60
Huntington	18	27	49	69	97
Parkersburg	20	31	44	61	76
Wisconsin:					
Green Bay	18	26	38	49	59
LaCrosse	44	67	99	125	154
Madison	29	42	61	77	95
Milwaukee	25	35	50	62	74
Rice Lake	29	45	70	92	119
Wyoming:					
Casper	4	7	9	11	14
Cheyenne	9	14	21	27	34

COOL SEASON (OCT.-MAR.)

WARM SEASON (APR.-SEPT.)
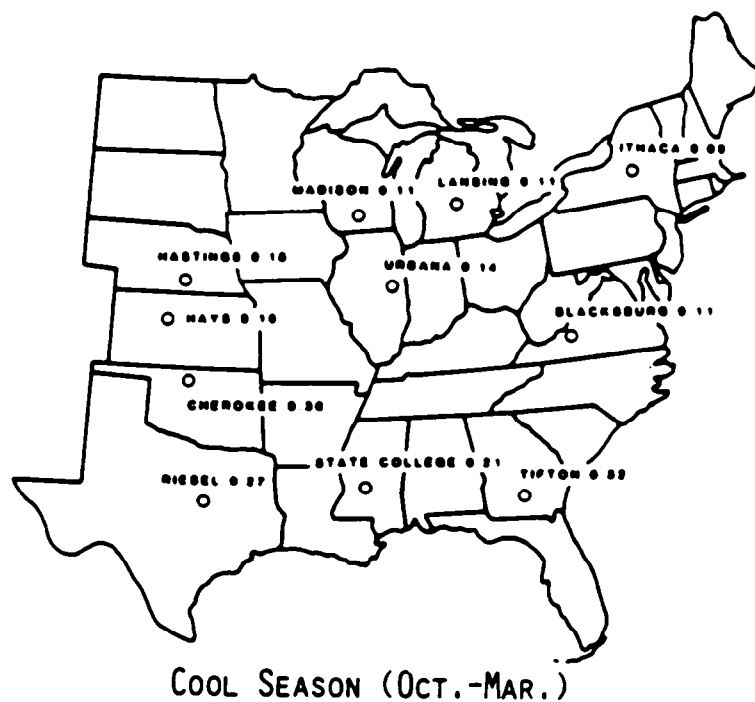
FIGURE III-12 VALUES OF "A" FOR EQUATION III-14
(RICHARDSON ET AL, 1983)

When cropland erosion estimates are made for single storm events, the cover/management factor should in principle be selected for the crop stage corresponding to the time of year in which the storm occurs. The procedures for estimating seasonal C values as described in Wischmeier and Smith (1978) require crop development information which is usually not available in screening studies, and hence the annual C values given in Table III-4 are often used for single event estimates.

──────────────── EXAMPLE III-3 ────────────────

Soil Erosion Computations

Compare annual soil erosion values in central Michigan and southern Louisiana for a corn field with the following characteristics:

- Soil: silt loam, 4% organic matter
- Slope: 6%, 100 m length
- Moderate productivity, residues left, fall turn-plowed conventional management

For both locations, determine annual soil erosion with no conservation practices and with contouring.

Solution:

Soil erosion is determined by Equation III-11:

$$X = 1.29 \, E \, (K) \, (ls) \, C \, (P)$$

From Figure III-10, erosivities (in English units) for the two locations are approximately 100 (Michigan) and 500 (Louisiana). Multiplying by the metric conversion 1.735, we have E = 174 and 868. Other parameters are:

$K = 0.33$ (Table III-3)

$C = 0.52$ (Table III-4, line 3).

From Table III-9, P = 0.5 for contouring and 1.0 with no practices.

The 6 percent slope corresponds to $\theta = \tan^{-1}(0.06) = 3.43°$ (Equation III-13) and the ls factor from Equation III-12 is:

$$ls = [0.045(100)]^{0.5} \, (65.41 \sin^2 3.43 + 4.56 \sin 3.43 + 0.065)$$
$$= 1.21.$$

Thus 1.29 (K)(ls)C(P) = 0.268 without contouring and 0.134 with contouring. Soil erosion for the two locations and practices:

	No practice	Contouring
Michigan	46.6 t/ha	23.3 t/ha
Louisiana	232.6 t/ha	116.3 t/ha

──────────────── END OF EXAMPLE III-3 ────────────────

3.4.3.3 Watershed Sediment Yield

3.4.3.3.1 Annual Yields

Watershed sediment yield due to surface erosion is:

$$Y = S_d \sum_k X_k A_k \qquad (III-15)$$

where

$\quad$ Y $\quad$ = $\quad$ annual sediment yield (tonnes/yr)

$\quad$ X_k $\quad$ = $\quad$ erosion from source area k as given by Equation III-11 (t/ha)

$\quad$ A_k $\quad$ = $\quad$ area of source area k (ha)

$\quad$ S_d $\quad$ = $\quad$ watershed sediment delivery ratio.

The sediment delivery ratio S_d is a factor which accounts for the attenuation of sediment through deposition and filtering as it travels from source areas to the watershed outlet. Although a number of different relationships have been proposed for S_d, the simple function of watershed drainage area given in Figure III-13 remains the most generally accepted procedure.

3.4.3.3.2 Seasonal Yields

Equation III-15 is appropriate for annual sediment yields and should not be used to determine event or seasonal watershed sediment yields. Large watershed sediment yields often do not coincide with major erosion periods. For example, in the eastern United States, most soil erosion is caused by late spring and summer intense rainstorms, but most sediment discharge occurs during late winter and early spring runoff. The reason for this is that runoff during erosive periods is often insufficient to transport eroded soil far from a source area. Subsequent large events "flush" portions of the accumulated sediment from the watershed drainage network.

Although general procedures are not available for estimating seasonal sediment yields, the following approach produced satisfactory results for an 850 km^2 watershed in upstate New York (Haith et al., 1984).

Sediment yield in month m, Y_m (tonnes), is assumed to be proportional to $Q_m^{1.2}$ where Q_m is the watershed runoff (cm) during month m. The annual sediment yield Y, as given in Equation III-15, is likewise proportional to QT, where

$$QT = \sum_{m=1}^{12} Q_m^{1.2} \qquad (III-16)$$
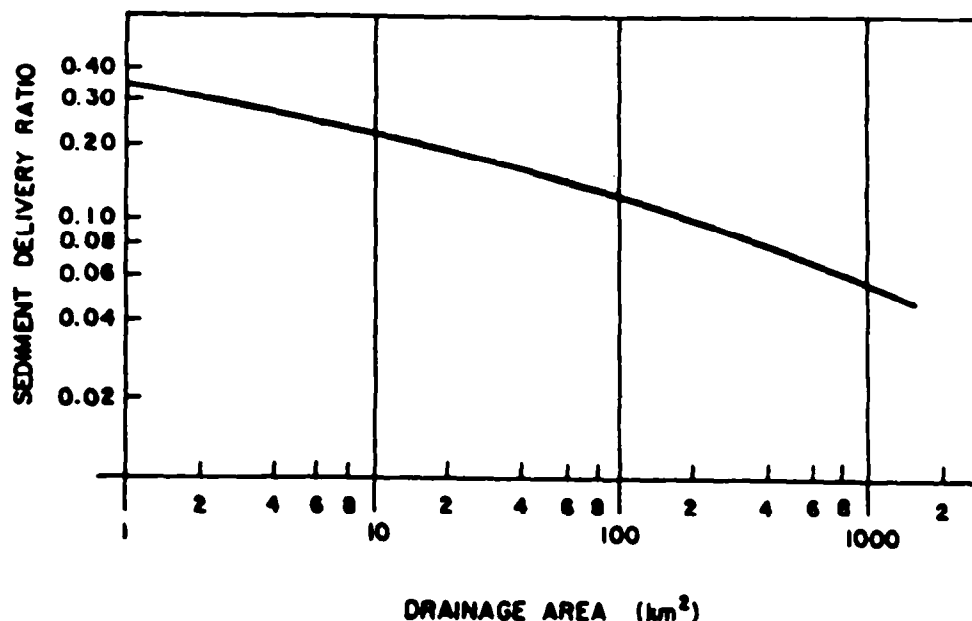
FIGURE III-13 SEDIMENT DELIVERY RATIO AS A FUNCTION OF
WATERSHED DRAINAGE AREA (VANONI, 1975)

Thus:

$$Y_m/Y = Q_m^{1.2}/QT$$

or

$$Y_m = Q_m^{1.2} Y/QT \qquad \text{(III-17)}$$

Equation III-17 was used to estimate monthly sediment yields over a 25-month
period for the 850 km^2 West Branch Delaware River Basin in upstate New York.
Comparisons with measured sediment yields indicated that the estimated mean monthly
sediment yield was within 12 percent of the observed value. Based on correlations
between monthly estimated and observed sediments yields, Equation III-17 explained 92
percent of the observed monthly variations (Haith et al., 1984).

3.4.4 Chemical Loading Functions for Rural Runoff

As suggested in Section 3.4.1, loading functions for rural runoff are equations
that multiply dissolved and solid-phase pollutant concentrations by volume or mass
fluxes of runoff water or sediment, respectively (Equations III-1 and III-2).
Procedures for calculating runoff and sediment yield were described in Sections 3.4.2
and 3.4.3. It now remains to outline procedures for determining pollutant concen-
trations in runoff and sediment.

The principal pollutants in rural runoff are nutrients (nitrogen and phosphorus), heavy metals and synthetic organic pesticides. Although most of these chemicals have both solid and dissolved phases it is convenient to divide them into three categories, based on their main transport phase in runoff:

- Solid phase; chemicals which are strongly associated with sediment.
- Dissolved phase; chemicals which are dissolved in runoff.
- Distributed phase; significant chemical quantities are transported in both solid-phase and dissolved forms.

Loading functions for the first two c..egories are straightforward; empirical estimates are used for the chemical concentrations. Runoff of distributed-phase chemicals is more difficult to model since dissolved and solid-phase concentrations are influenced by adsorption equilibrium phenomena.

Solid-phase chemicals include organic nitrogen, particulate phosphorus and heavy metals. The assignment of metals to this category is arbitrary, since dissolved forms are often present under acidic conditions. However, it is assumed here that the primary sources of metals in rural runoff are metal-based pesticides which are tightly bound to soil particles (Weber, 1975).

The dissolved chemical group includes only inorganic nitrogen and soluble phosphorus. Inorganic nitrogen in drainage is mostly nitrate-nitrogen, and this ion does not adsorb to soil particles. Phosphorus is a special case. Most phosphorus in runoff is solid-phase, but dissolved phosphorus is directly available to plants and algae and hence cannot be neglected in eutrophication studies. The loading functions for solid-phase and dissolved phosphorus are operational means of describing complex soil chemistry. There is a continuous set of reactions that relate fixed, adsorbed and soluble phosphorus forms. Although it is possible to model this behavior (Donigian and Crawford, 1976; Knisel, 1980; Tubbs and Haith, 1981), such models are neither simple nor especially accurate.

Distributed-phase chemicals include most organic pesticides. Models for runoff of these chemicals are considerably more complex than the solid-phase and dissolved chemical loading functions. Indeed, the term "loading function" is used advisedly, since models of these adsorbed chemicals are comparable to the continuous simulation models discussed in Section 3.3.

3.4.4.1 Loading Functions for Solid-Phase Chemicals (Organic Nitrogen, Particulate Phosphorus, Heavy Metals)

The loading function for solid-phase chemicals in runoff from a source area is:

$$LS = 0.001 \ Cs \ X \qquad\qquad (III-18)$$

where

LS = solid-phase chemical load in runoff (kg/ha)

Cs = concentration of chemical in eroded soil (sediment) (mg/kg)

X = soil loss (t/ha).

The "0.001" in Equation III-18 is a dimensional conversion constant. Soil loss is given by the Universal Soil Loss Equation (Equation III-11) on either an annual or single event basis. In determining a source area's contribution to watershed chemical loading, LS must be modified by a sediment delivery ratio (Section 3.4.4.1.2).

Equation III-18 is often considered to be an estimate of _total_ chemical load rather than just the solid-phase portion. The assumption is essentially correct for heavy metals since they are tightly bound to soil particles. Moreover since most soil nitrogen is in the solid-phase organic form and most soil phosphorus is particulate, solid-phase nutrient loads will generally be a very large portion of total loads.

3.4.4.1.1 Solid-Phase Chemical Concentrations

The concentration Cs is best determined by direct measurement. Samples may be taken of sediment depositions in fields and drainage ditches. These samples are subsequently analyzed for total concentrations of heavy metals, organic nitrogen or particulate phosphorus in the sediment. Streamflow suspended solids samples in rural watersheds free of point sources and urban drainage may also be used. When sediment sampling is infeasible, procedures described in the following subsections may be used to obtain approximate concentration estimates.

3.4.4.1.1.1 Organic Nitrogen and Particulate Phosphorus

Nitrogen and phosphorus concentrations in eroded soil are generally larger than comparable concentrations in uneroded or _in situ_ soil. This is due to the selective nature of the erosion process. Lighter organic matter and clay particles are more readily eroded than heavier sand and silt. Since nutrients tend to be associated with these light particles, sediment is "enriched" with nutrients compared to the soil from which it originates. A sediment nutrient concentration can thus be related to the comparable concentration in soil by an enrichment ratio:

$$Cs = en \ Ci \qquad\qquad (III-19)$$

where

en = nutrient enrichment ratio

Ci = nutrient concentration in _in situ_ soil (mg/kg).

Soil nutrient concentrations are sometimes available from soil surveys or extension specialists. Nitrogen concentrations may be inferred from soil organic

matter percentages by assuming that organic matter is 5 percent nitrogen (Brady, 1974). Thus, for nitrogen $C_i \approx 0.05(\% \text{ OM}/100)10^6 = 500 \ (\% \text{ OM})$, where % OM is percent organic matter in the soil.

Very rough estimates of soil nutrient concentrations can be obtained from the general maps shown in Figures III-14 and 15. Figure III-15 indicates soil content of P_2O_5 which is 44 percent phosphorus. To use Figures III-14 and 15, we note that 1% = 10,000 mg/kg, and hence for

Nitrogen: $C_i = (\% \text{ N})10^4$

Phosphorus: $C_i = 0.44 \ (\% \ P_2O_5)10^4$.

Although these nutrient concentrations are for total nitrogen and phosphorus, they may be used for organic nitrogen and particulate phosphorus since these nutrient forms are so dominant in the soil.

Nutrient enrichment ratios are in principle event-specific, since they are related to the degree of erosion which occurs during a storm. With very small storms, only the finest soil particles are eroded, and the enrichment ratio is high. Conversely, large storms erode all soil particles, and the enrichment ratio approaches one. Based on analyses of many field studies of nutrient transport, Menzel (1980) suggested the relationship:

$$en = 7.39/\text{Sed}^{0.2} \qquad\qquad\qquad (III\text{-}20)$$

in which Sed is the sediment discharge (kg/ha) during the storm event. Equation III-20 gives values of en ranging from 2.94 at Sed = 100 kg/ha to 1.35 at Sed = 5000 kg/ha.

Equation III-20 can be used directly for single storm loading estimates by letting Sed = 1000 X, since the units of soil loss X are tonnes/ha. The equation is not suitable for annual loads. For these loads, a midrange value of en = 2.0 is appropriate (Haith and Tubbs, 1981). In summary:

$$en = \begin{cases} 2.0 \text{ for annual loads} \\ 7.39/(1000 \ X)^{0.2} \text{ for single event loads} \end{cases} \qquad (III\text{-}21)$$

For very large soil losses (X > 22 t/ha), Equation III-21 will give en < 1.0 for an event. When this occurs, en should be set equal to 1.0.

3.4.4.1.1.2 Heavy Metals

The U.S. Geological Survey has analyzed soil samples from 863 sites in the United States for heavy metals. The results, as summarized by McElroy et al. (1976), are given in Table III-11. These concentrations may be used directly as Cs in Equation III-18 since 1 ppm = 1 mg/kg, and it may be assumed that no metals enrichment of sediment occurs (McElroy et al., 1976).
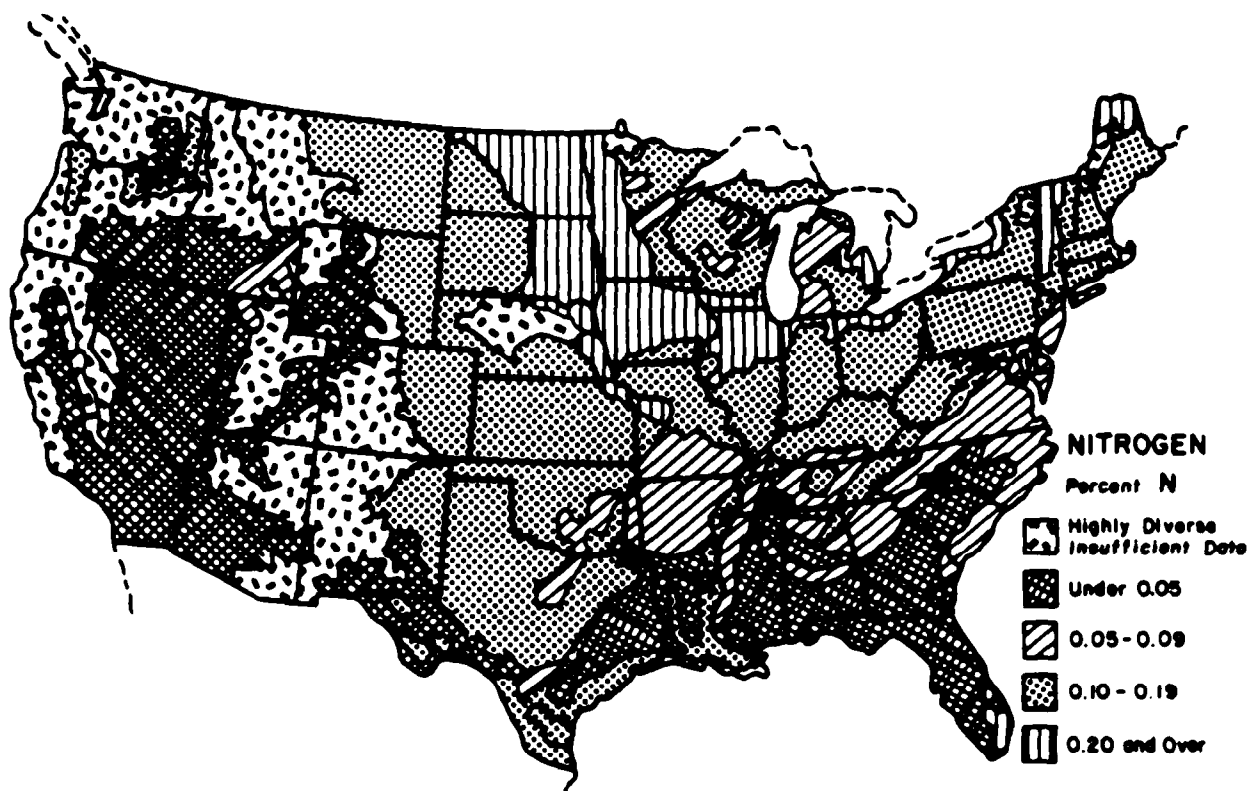
FIGURE III-14 NITROGEN IN SURFACE FOOT OF SOIL (PARKER, ET AL, 1946)
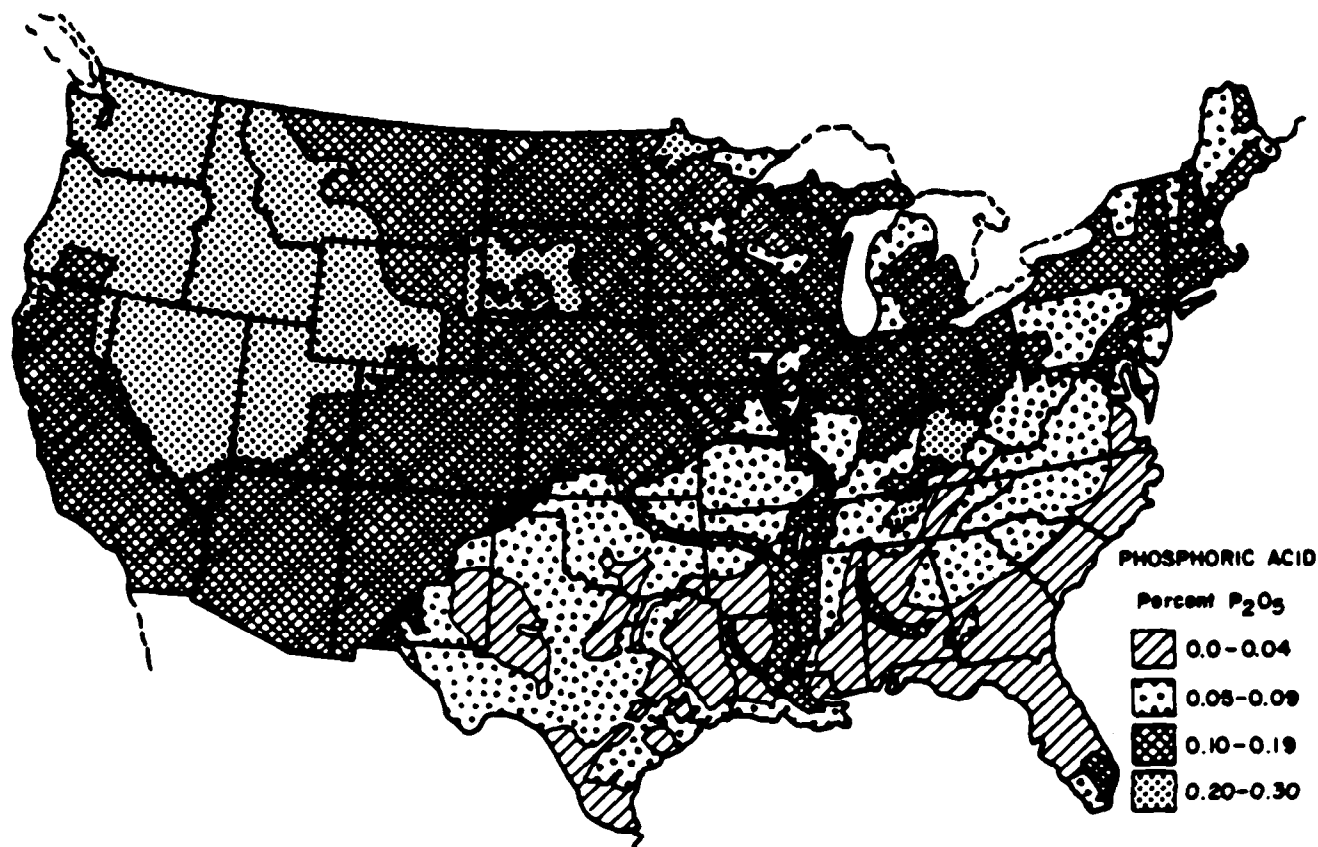
FIGURE III-15 PHOSPHORUS (AS P_2O_5) IN THE SURFACE FOOT OF SOIL
(NOTE: P_2O_5 IS 44% PHOSPHORUS) (PARKER ET AL, 1946)

TABLE III-11

HEAVY METAL CONCENTRATIONS IN SURFICIAL MATERIALS IN THE UNITED STATES

(McElroy et al, 1976)

Element	Arithmetic analysis Average (ppm)	Arithmetic analysis Range (ppm)	Geometric means Conterminous U.S. (ppm)	Geometric means West of 97th meridian (ppm)	Geometric means East of 97th meridian (ppm)
Arsenic	--	< 1,000	--	--	--
Barium	554	15-5,000	430	560	300
Cadmium	--	< 20	--	--	--
Cerium	86	< 150-300	75	74	78
Chromium	53	1-1,500	37	38	36
Cobalt	10	< 3-70	7	8	7
Copper	25	< 1-300	18	21	14
Iron	25,000	100-100,000	18,000	20,000	15,000
Gallium	19	< 5-70	14	18	10
Germanium	--	< 10	--	--	--
Gold	--	< 20	--	--	--
Hafnium	--	< 100	--	--	--
Indium	--	< 10	--	--	--
Lanthanum	41	< 30-200	34	35	33
Lead	20	< 10-700	16	18	14
Manganese	560	< 1-7,000	340	389	285
Molybdenum	< 3	< 3-7	--	--	--
Neodymium	45	< 70-300	39	36	44
Nickel	20	< 5-700	14	16	13
Niobium	13	< 10-100	12	11	13
Palladium	--	< 1	--	--	--
Platinum	--	< 10	--	--	--
Rhenium	--	< 30	--	--	--
Scandium	10	< 5-50	8	9	7
Strontium	240	< 5-3,000	120	210	51
Tantalum	--	< 200	--	--	--
Tellurium	--	< 2,000	--	--	--
Thallium	--	< 50	--	--	--
Thorium	--	< 200	--	--	--
Titanium	3,000	300-15,000	2,500	2,100	3,000
Uranium	--	< 500	--	--	--
Vanadium	76	< 7-500	56	66	46
Ytterbium	4	< 1-50	3	3	3
Yttrium	29	< 10-200	24	25	23
Zinc	54	< 25-2,000	44	51	36
Zirconium	240	< 10-2,000	200	170	250
Total	30,099		21,991	23,858	19,263

Note: "--" indicates all analyses showed element to be below detectable limits.

3.4.4.1.2 Watershed Loads of Solid-Phase Chemicals

The annual watershed load of a solid-phase chemical in rural runoff is the sum of the attenuated runoff loads from all source areas in the watershed. Since these chemicals travel with sediment, attenuation (i.e., transport loss) is described by the sediment delivery ratio, S_d:

$$WLS = S_d \sum_k LS_k A_k \qquad (III-22)$$

$$= 0.001 \, S_d \sum_k Cs_k X_k A_k$$

where

WLS = annual watershed solid-phase chemical load in rural runoff (kg/yr)

LS_k = solid-phase chemical load in runoff from source area k (kg/ha)

A_k = area of source area k (ha)

Cs_k = solid-phase chemical concentration in eroded soil (sediment) from source k (mg/kg)

X_k = soil loss from source area k (t/ha).

Single event loads cannot be estimated by Equation III-22 due to the sediment transport variations discussed in Section 3.4.3.3.2. However, seasonal loads may be calculated by assuming them to be proportional to seasonal sediment yields. From Equation III-17, we know that the ratio of monthly watershed sediment yield Y_m to annual yield Y is:

$$Y_m/Y = Q_m^{1.2}/QT \qquad (III-17)$$

where Q_m is watershed runoff in month m(cm) and QT is given by Equation III-16. Thus if WLS is the annual chemical load given by Equation III-22, then WLS_m, the load (kg) in month m, is:

$$WLS_m = (Y_m/Y)WLS \qquad (III-23)$$

In many watersheds, the concentration of a chemical in sediment is relatively uniform, and hence Cs_k the same for all source areas. For this case, Equation III-23 reduces to:

$$WLS_m = (Y_m/Y) \, 0.001 \, S_d \, Cs \sum_k X_k A_k$$
$$= (Y_m/Y) \, 0.001 \, Cs \, Y$$

or

$$WLS_m = 0.001 \, Cs \, Y_m \qquad (III-24)$$

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Thus when soil chemical concentrations are uniform, monthly chemical loads can be obtained directly from monthly sediment loads.

— EXAMPLE III-4 —

Watershed Sediment and Phosphorus Loads

The West Branch Delaware River is an 85,000 ha watershed in south-central New York that drains into Cannonsville Reservoir. Soil erosion is a major phosphorus source to the reservoir. Major land uses contributing erosion are as follows:

Land Use	Area (ha)	Mean K(ls)CP
Corn	3,430	0.214
Hay	13,085	0.012
Pasture	5,093	0.016
Inactive Agricultural	3,681	0.017
Logging Roads	20	0.217

Determine:

a) Average annual sediment yield (tonnes/yr)

b) Average annual solid-phase phosphorus input to the reservoir (kg/yr)

Solution:

a) Average annual sediment yield is given by Equations III-15 and III-11:

$$Y = S_d \sum_k X_k A_k \qquad \text{(III-15)}$$

$$X_k = 1.29 \, E \, (K) \, (ls) \, C \, (P) \qquad \text{(III-11)}$$

There are five different source areas, each with their associated K (ls) C (P) values. Rainfall/runoff erosivity is approximately 125 (Figure III-10). Converting to metric units:

$$E = 1.735(125) = 217.$$

Soil erosion X_k, from each source area is:

- Corn: 1.29(217) 0.214 = 59.9 t/ha
- Hay: 1.29(217) 0.012 = 3.4 t/ha
- Pasture: 4.5 t/ha
- Inactive Agriculture: 4.8 t/ha
- Logging Roads: 60.7 t/ha

The sediment delivery ratio S_d is approximately 0.065 for an 850 km^2

watershed (Figure III-13). Sediment yield is:

$$Y = 0.065 [59.9(3430) + 3.4(13,085) + 4.5(5,093)$$
$$+ 4.8(3681) + 60.7(20)]$$
$$= 18,960 \text{ tonnes/yr}$$

b) Phosphorus load is:

$$LS = 0.001 \ S_d \sum_k Cs_k \ X_k \ A_k \qquad (III-22)$$

Since no other information is available, phosphorus concentrations are obtained from Figure III-15. New York soils are 0.10 - 0.19 percen $_2O_5$. Using a mid-range value of 0.15 percent and recalling that P_2O_5 is 44 percent phosphorus, we obtain a soil phosphorus level of:

$$C_i = 0.44(0.15) \ 10^4$$
$$= 660 \text{ mg/kg}$$

Using an enrichment ratio of 2.0 (Equation III-21), $Cs = 2.0 \ (660) = 320$ mg/kg.

We must assume that Cs is the same for all source areas and hence:

$$LS = 0.001 \ C_s \ S_d \sum_k X_k \ A_k$$
$$= 0.001 \ Cs \ Y$$
$$= 0.001(1320)(18,960) = 25,000 \text{ kg/yr}.$$

-- --- -- --- --- --- --- -- END OF EXAMPLE III-4 -- --- -- --- --- --- --- --- --

3.4.4.2 Loading Functions for Dissolved Chemicals (Inorganic Nitrogen and Soluble Phosphorus)

The loading function for dissolved nutrients in runoff from a source area is:

$$LD = 0.1 \ Cd \ Q \qquad (III-25)$$

where

LD = dissolved chemical load in runoff (kg/ha)

Cd = concentration of dissolved chemical in runoff (mg/l)

Q = runoff from source area (cm).

The "0.1" in Equation III-25 is a dimensional conversion constant. For event loads, Q is given by Equation III-3. The loading function may also be used for annual loads provided annual runoff values such as those shown in Figure III-9 are available.

3.4.4.2.1 Dissolved Nutrient Concentrations

Concentrations of dissolved nutrients in runoff vary with soil cover. Representative concentrations are given in Table III-12. Concentrations for fallow, corn, small grains, hay and pasture are flow-weighted average concentrations measured in runoff over several years from large field sites in South Dakota (Dornbush, et al., 1974). Forest concentrations are the National Eutrophication Survey values for inorganic nitrogen and orthophosphorus given in Figures III-4 and 5 for 90% forested watersheds.

In the northern U.S., cropland which has manure left on the soil surface, particularly during snowmelt, is likely to have significantly higher dissolved nutrient concentrations in runoff than unmanured cropland. The concentrations for manured fields given in Table III-12 should be used for snowmelt runoff from fields which have received winter applications of manure.

Although the representative concentrations given in Table III-12 should be replaced by local data whenever possible, such data are unavailable in most water quality screening studies. However, since the concentrations in Table III-12 are comparable to other values reported in the literature (see for example Baker, 1980), it is unlikely that use of the representative concentrations would produce large errors in loading estimates.

EXAMPLE III-5

Single Event Runoff, Sediment and Nitrogen Load

During the growing season a 7.0 cm rainstorm falls on the Louisiana cornfield described in Example III-3. The field has an area of 10 ha and is planted in straight rows. The soil is in hydrologic Group B and is in poor hydrologic condition. This storm was preceded by 5.5 cm of rain four days previously. From Example III-3, the soil has an organic matter content of 4 percent and the USLE parameters for this field are:

$$K = 0.33, \ ls = 1.21, \ C = 0.52 \ \text{and} \ P = 1.0$$

Determine:

    a)   Storm runoff (cm)

    b)   Soil loss (tonnes)

    c)   Solid-phase and dissolved nitrogen in runoff (kg).

Solution:

    a)   Runoff is given by the Curve Number Equation (Equation III-3). The curve number for straight row, poor hydrologic condition, soil B is $CN2 = 81$ (Table III-1). According to Table III-2, the preceding 5.5 cm of

TABLE III-12

REPRESENTATIVE DISSOLVED NUTRIENT CONCENTRATIONS IN RURAL RUNOFF

Soil Cover	Nitrogen (mg/l)	Phosphorus (mg/l)
Fallow[a]	2.6	0.10
Corn[a]	2.9	0.26
Small Grains[a]	1.8	0.30
Hay[a]	2.8	0.15
Pasture[a]	3.0	0.27
Inactive Agriculture[b]		
Eastern U.S.	1.6	0.14
Midwest	1.5	0.14
West	1.5	0.14
Forest[c]		
Eastern U.S.	0.19	0.006
Midwest	0.06	0.009
West	0.07	0.012
Snowmelt Runoff from Manured Fields[d]		
Fallow	12.2	1.9
Corn	12.2	1.9
Small Grains	25.0	5.0
Hay	36.0	8.7

[a]Dornbush et al (1974)

[b]Average of pasture and forest

[c]Omernik (1977). See Figures III-4,5

[d]Gilbertson et al (1979). These concentrations are associated with winter manure spreading.

rain places the field in antecedent moisture condition III, and hence the relevant curve number is CN = CN3. From Equation III-7:

CN3 = 81/[0.4036 + 0.0059(81)] = 91.9

The retention parameter (Equation III-4) is:

S = 2540/91.9 - 25.4 = 2.24 cm

Runoff Q is:

$Q = [7 - 0.2(2.24)]^2/[7 + 0.8(2.24)]$

= 4.9 cm

b) Soil loss is given by the USLE:

$$X = 1.29(K)(ls)C(P) \qquad (III-11)$$

where in this case E is the event erosivity given by Equation III-14:

$$E = 6.46 \ a \ R^{1.81}$$

The nearest location for the "a" value is State College, Mississippi (Figure III-12), which has a warm season value of $a = 0.51$. Erosivity is thus:

$$E = 6.46(0.51)(7)^{1.81} = 112$$

Soil loss is:

$$X = 1.29(112)0.33(1.21)0.52(1)$$
$$= 30 \ t/ha$$

Over 10 ha, the loss is $30(10) = 300$ tonnes.

c) Solid-phase nitrogen loss (kg/ha) is:

$$LS = 0.001 \ Cs \ X \qquad \text{(III-18)}$$

where

$$Cs = en \ Ci \qquad \text{(III-19)}$$

and

$$en = 7.39/(1000X)^{0.2} \qquad \text{(III-21)}$$

As described in Section 3.4.4.1.1.1, soil nitrogen concentration Ci (mg/kg) can be estimated by assuming that organic matter is 5 percent nitrogen. The field's 4 percent organic matter gives a nitrogen concentration of:

$$Ci = 0.05(0.04)10^6 = 2000 \ mg/kg$$

The enrichment ratio for the storm is:

$$en = 7.39/[1000(30)]^{0.2} = 0.94$$

Since this is less than 1.0, we set $en = 1.0$, and the solid-phase nitrogen concentration in sediment is:

$$Cs = 1.0 \ Ci = 2000 \ mg/kg$$

The solid-phase nitrogen load is:

$$LS = 0.001(2000)(30) = 60 \ kg/ha$$

or 600 kg for the 10 ha field.
The dissolved nitrogen load is:

$$LD = 0.1 \; CdQ \tag{III-25}$$

where from Table III-12, Cd = 2.9 mg/l for corn. Hence:

LD = 0.1(2.9)(4.9) = 1.4 kg/ha

or 14 kg for the 10-ha field.

───────────── END OF EXAMPLE III-5 ─────────────────────

3.4.4.2.2 Watershed Loads of Dissolved Chemicals

Since all runoff from watershed source areas is transported to the watershed outlet (see Section 3.4.2.4), it is assumed that dissolved nutrient loads are not attenuated. Watershed load is thus the sum of the source area loads:

$$WLD = 0.1 \sum_{k} Cd_k \; Q_k \; A_k \tag{III-26}$$

where

WLD = annual or event watershed dissolved chemical load in rural runoff (kg)

Cd_k = dissolved chemical concentration in runoff from source area k (mg/l)

Q_k = runoff from source area k (cm)

A_k = area of source area k (ha).

3.4.4.3 Loading Functions for Distributed Phase Chemicals (Pesticides)

Runoff of pesticides can be described by the same general loading functions used for nutrients and metals (Equations III-18 and III-25). However, the estimation of dissolved and solid-phase concentrations is more difficult for pesticides. All pesticides are adsorbed to some extent by soil particles, and hence dissolved and solid-phase concentrations cannot be determined independently. Also, these concentrations are dynamic, since pesticides are decomposed or decayed by photochemical, chemical, and microbiological process. Decay rates are often sufficiently high that most of a pesticide will have decomposed within several weeks of application. A final complicating factor is the large number of pesticide compounds currently in use, each with its own properties and characteristic behavior in the soil.

It follows that pesticide concentrations in runoff cannot be estimated by simple empirical methods, since they depend on the relative timing of applications and storm events, and the specific adsorption and degradation properties of the pesticide. However relatively simple equations can be used to describe the adsorption and decay phenomena, and calculations can be made for each storm event following a pesticide application. The following subsections describe such a model and also provide model

parameters for a large number of pesticides. The model estimates pesticide load runoff events from a source area; i.e., a small catchment with uniform soil, hydrologic and chemical characteristics. Methods are not available to aggregate these source area loads into total watershed load.

3.4.4.3.1 Pesticide Runoff Model

The pesticide runoff model developed by Haith (1980) is based on a pesticide mass balance of the surface centimeter of soil. On day t after a pesticide application P_0 (g/ha) to the surface soil layer, the pesticide content is:

$$P_t = P_0 \exp(-k_s t) + \Delta P_t \tag{III-27}$$

where

$\quad P_t$ = pesticide in surface centimeter on day t (g/ha)

$\quad k_s$ = pesticide decay rate (day^{-1})

$\quad \Delta P_t$ = additional pesticide application (if any) on day t (g/ha).

Equation III-27 is a standard exponential or first-order decay model. If a previous storm and/or pesticide application was made on some day τ prior to day t, then:

$$P_t = P_\tau^+ \exp[k_s(t-\tau)] + \Delta P_t \tag{III-28}$$

where

$\quad P_\tau^+$ = pesticide content after storm event or application on day τ (g/ha).

Total pesticide P_t is divided into adsorbed (solid-phase) and dissolved forms based on a linear adsorption equilibrium relationship.

$$P_t = A_t + D_t \tag{III-29}$$

and

$$a_t = K_D d_t \tag{III-30}$$

where

$\quad A_t$ = adsorbed (solid-phase) pesticide in surface centimeter on day t (g/ha)

$\quad D_t$ = dissolved pesticide in surface centimeter on day t (g/ha)

$\quad a_t$ = adsorbed pesticide concentration on soil particles (mg/kg)

$\quad d_t$ = dissolved pesticide concentration in solid water (mg/l)

$\quad K_D$ = pesticide partition or distribution coefficient (1/kg).

If a rainfall or snowmelt event sufficient to fill the surface layer's volumetric

available water capacity w (cm/cm) occurs on day t, then D_t is given by 100 w d_t and A_t is 100b a_t where b is the surface soil bulk density (g/cm^3). Substituting these relationships into Equations III-29 and III-30 produces:

$$A_t = [1/(1 + w/K_D b)]P_t \qquad (III-31)$$

and

$$D_t = [1/(1 + K_D b/w)]P_t \qquad (III-32)$$

If runoff occurs on day t, portions of A_t and D_t will be removed by water and sediment movement. The solid-phase loss is the product of adsorbed concentration and soil loss. Since $a_t = A_t/100b$, we have

$$PX_t = (A_t/100b)X_t \qquad (III-33)$$

where

PX_t = solid-phase pesticide in runoff on day t (g/ha)

X_t = soil loss (sediment) in runoff on day t (t/ha).

Dissolved pesticide losses are distributed into runoff, percolation and a residual which remains in the surface layer after a storm. These components are assumed proportional to the distribution of rainfall R_t (cm) plus snowmelt M_t (cm) into runoff, percolation, and available soil water. Considering only events for which $R_t + M_t > w$, runoff loss of dissolved pesticide is:

$$PQ_t = [Q_t/(R_t + M_t)] D_t \qquad (III-34)$$

where

PQ_t = dissolved pesticide in runoff on day t (g/ha)

Q_t = runoff on day t (cm).

Assuming that the surface layer is dry prior to the event, percolation loss of dissolved pesticide from the layer is $[(R_t + M_t - Q_t - w)/(R_t + M_t)]D_t$, and dissolved pesticide remaining in the soil after the event is $[w/(R_t + M_t)] D_t$. Pesticide remaining in the surface layer is:

$$P_t^+ = P_t - PX_t - [1-w/(R_t + M_t)] D_t \qquad (III-35)$$

Equations III-33 and III-34 are the basic loading functions for solid-phase and dissolved pesticide in runoff. For the solid-phase loads, X_t in Equation III-33 is the eroded soil from the source area as given by the Universal Soil Loss Equation, (Equation III-11). The remainder of Equation III-33, $A_t/100$ b, is

the pesticide concentration in eroded soil or sediment. In the dissolved pesticide loading function, Equation III-34, Q_t is runoff from the source area determined by the Curve Number Equation (Equation III-3), and $D_t/(R_t + M_t)$ is the dissolved pesticide in runoff. These loading functions are of the same form as the solid-phase and dissolved chemical loading functions of Sections 3.4.4.1 and 3.4.4.2.

3.4.4.3.2 Computational Steps

The pesticide runoff model is implemented by a set of sequential computations:

1. The day of initial pesticide application is designated t = 0 and P_o is set equal to the application to the surface centimeter (g/ha).

2. On each day t = 1,2,.... following application, a check is made to see if an "event" occurs. An event is either (i) a new pesticide application or (ii) a precipitation (rain + melt) amount exceeding the soil's available water capacity. If no event occurs, the computations proceed to the next day. If there is an event, the current pesticide content of the soil is determined by Equation III-28.

3. If $R_t + M_t > w$, then pesticide leaching will occur, and the following steps are required:

   a. Dissolved pesticide D_t is obtained from Equation III-32.

   b. Runoff Q_t is computed by Equation III-3. If $Q_t = 0$, go to step e.

   c. Dissolved pesticide runoff PQ_t is determined from Equation III-34.

   d. Adsorbed (solid-phase) pesticide runoff PX_t is obtained from Equation III-33 with soil loss X_t given by Equation III-11 and adsorbed pesticide A_t given by Equation III-31.

   e. Soil pesticide level is updated to P_t^+ by Equation III-35. Note that Equation III-35 may predict substantial pesticide losses in percolation even if no runoff occurs and hence PX_t and PQ_t are both zero.

These computational steps are repeated for subsequent days following a storm until the surface pesticide level P_t becomes negligible. Often the combined effects of decay and leaching will remove virtually all pesticide from the surface layer within several weeks of application.

3.4.4.3.3. Data for the Pesticide Runoff Model

Four types of data are required for pesticide runoff calculations: daily weather records, Universal Soil Loss Equation parameters and runoff curve numbers, soil properties and pesticide parameters. The first two categories have been discussed in previous sections. The soil properties needed are available water capacity (w) and bulk density (b). These parameters are often given in county soil surveys.

Representative values of w and b for several soil textures are given in Table III-13. These data are mean bulk densities for 207 soils and mean available water capacities for 154 soils reported by Baes and Sharp (1983).

Pesticide application rates, timing, and mode of application cannot be generalized. This information can only be obtained from local or regional pest control specialists. Mode of application refers to surface applied versus soil incorporated pesticide. The model describes pesticide behavior into the surface centimeter of soil and hence the application P_0 or ΔP_t are the chemical additions to that surface layer. For example, if 3000 g/ha of pesticide is applied to the soil and incorporated to a depth of 5 cm (2 in.), the application rate for the surface layer is 3000/5 = 600 g/ha (assuming complete mixing in the soil). Conversely, if the pesticide is left on the soil surface, the entire 3000 g/ha is contained in the surface centimeter.

3.4.4.3.3.1 Pesticide Partition Coefficients

Pesticide adsorption is generally considered to be related to soil organic matter. A general relationship given by Rao and Davidson (1980) is:

$$K_D = K_{OC} \, (\%OC/100) \qquad (III-36)$$

where

K_{OC} = pesticide partition coefficient for organic carbon

$\%OC$ = organic carbon of the soil, measured as a %.

Table III-14 lists K_{OC} values which have been summarized by Rao and Davidson (1982) from a number of studies. The table entries are means and coefficients of variation (standard deviation/mean, as a percent). The mean values can be used to estimate a partition coefficient for any soil. For example, the K_D value for atrazine in a soil with 2 percent organic carbon is:

$$K_D = 163 \, (2/100) = 3.26$$

Soil organic matter percentage, $\%OM$, is often more readily available than $\%OC$. In such cases, $\%OC$ may be estimated as 59 percent of organic matter (Brady, 1974):

$$\%OC = 0.59 \, (\%OM) \qquad (III-37)$$

When K_{OC} values are unavailable, they may be indirectly measured by the octanol-water partition coefficient K_{OW}. Rao and Davidson (1980) derived the regression equation:

$$\log K_{OC} = 1.029 \log K_{OW} - 0.18$$

or

TABLE III-13

MEAN BULK DENSITIES AND AVAILABLE WATER CAPACITIES

(Bass and Sharp, 1983)

Soil Type	Bulk Density b (g/cm3)	Available Water Capacity w (cm/cm)
Silt Loam	1.33	0.22
Clay and Clay Loam	1.30	0.14
Sandy Loam	1.50	0.14
Loam	1.42	0.19

TABLE III-14

ORGANIC CARBON PARTITION COEFFICIENTS FOR SELECTED PESTICIDES

(Rao and Davidson, 1982)

Pesticide	Number of Soils	K_{oc} Mean (%CV)	Pesticide	Number of Soils	K_{oc} Mean (%CV)
AMETRYNE	32	388.4(57.1)	LINURON	33	862.8(72.3)
AMIBEN	12	189.6(149.7)	MALATHION	20	1796.9(65.9)
ATRAZINE	56	163.0(49.1)	METHYL PARATHION	7	5101.5(113.6)
BROMACIL	2	72.0(102.1)	METHYL UREA	5	58.8(15.1)
CARBOFURAN	5	29.4(30.0)	METOBROMURON	4	271.5(37.1)
CHLOROBROMURON	5	995.6(55.1)	MONOLINURON	10	284.3(55.2)
CHLORONEB	1	1652.9(—)	MONURON	18	183.5(60.8)
CHLOROXURON	5	4343.3(28.8)	NEBURON	5	3110.5(23.5)
CHLOROPROPHAM	36	816.3(—)	p-CHLOROANILINE	5	561.5(33.6)
CHLORTHIAMID	6	98.3(27.5)	PARATHION	4	10650.3(74.6)
CIODRIN	3	74.8(59.1)	PHENYL UREA	5	76.3(12.3)
DDT	2	243118.0(65.0)	PICLORAM	26	25.5(138.5)
DICAMBA	5	2.2(73.5)	PROMETONE	29	524.3(143.6)
DICHLOBENIL	34	224.4(77.4)	PROMETRYNE	38	614.3(99.1)
DIMETHYL AMINE	5	434.9(19.8)	PROPAZINE	36	153.5(37.0)
DIPROPETRYNE	5	1180.8(74.9)	SIMAZINE	147	138.4(12.6)
DISULFOTON	20	1603.0(144.2)	TELONE (cis)	6	798.1(44.3)
DIURON	84	382.6(72.4)	TELONE (trans)	6	1379.0(45.4)
FENURON	10	42.2(84.7)	TERBACIL	4	41.2(42.2)
LINDANE	3	1080.9(13.0)	THIMET	4	3255.2(49.5)
			TRITHION	4	46579.7(80.2)
2,4-D	9	19.6(72.4)			
2,4-D AMINE	3	109.1(30.2)			
2,4,5-T	4	80.1(45.3)			

$$K_{OC} = 0.66 \, K_{OW}^{1.029} \qquad \qquad (III-38)$$

Values of K_{OW} for selected pesticides are given in Table III-15.

3.4.4.3.3.2 Pesticide Decay Rates

Pesticide decomposition in the soil is related to moisture, temperature and pH. Unfortunately, the only information usually available is a simple pesticide half-life, which is the mean number of days required for 50% of the original pesticide to decompose in the soil. Decay rate k_s can be obtained from half-life using Equation III-27 (with $\Delta P_t = 0$). Since at $t =$ half-life, $P_t = 0.5 \, P_0$:

$$P_t = 0.5 \, P_0 = P_0 \exp \, (-k_s t)$$

and half-life is given by:

$$t = -\ln(0.5)/k_s$$

or

$$k_s = 0.69/\text{Half-life (days)} \qquad \qquad (III-39)$$

Mean decay coefficients from Rao and Davidson (1982) are given in Table III-16 for 32 pesticides. Three different rates are given for many of these chemicals. When available, the "field" coefficient should be used, since it in principle most closely corresponds to actual runoff conditions. The starred (*) lab rates are the second choice, since they also measure decomposition of the original compound. The remaining lab rates attempt to describe the complete decay of the pesticide and its decomposition products. These "total decay" rates may be used if a very conservative runoff estimate is described, but the nature, toxicity and fate of most intermediate pesticide decomposition products are so poorly understood that it is probably misleading to model them with a simple first-order decay rate.

The mean decay coefficients given in Table III-16 are supplemented by the specific k_s values given in Table III-17. The latter were summarized from a large number of decay studies by Nash (1980). Since the coefficients in Table III-17 are often unique to specific soil types, pH and organic matter contents, they are perhaps less useful in screening studies than the mean values in Table III-16. However, many commonly-used pesticides are not listed in Table III-16, and in such cases the data in Table III-17 may be the best available information.

TABLE III-15

OCTANOL-WATER PARTITION COEFFICIENTS FOR SELECTED PESTICIDES

(Rao and Davidson, 1982)

Pesticide	K_{ow}	Pesticide	K_{ow}
A. INSECTICIDES		PROPOXUR	2.80000E+01
		RONNEL	7.58580E+04
ALDICARB	5.00000E+00	TERBUFOS	1.67000E+02
ALTOSID	1.76000E+02	TOXAPHENE	1.69500E+03
CARBARYL	6.51000E+02		
		B. HERBICIDES	
CARBOFURAN	2.07000E+02		
CHLORDANE	2.10800E+03	ALACHLOR	4.34000E+02
CHLORPYRIFOS	2.05900E+03	ATRAZINE	2.12000E+02
CHLORPYRIFOS	6.60000E+04	ATRAZINE	2.26000E+02
CHLÓRPYRIFOS	1.28825E+05	BIFENOX	1.74000E+02
CHLORPYRIFOS, METHYL	1.97000E+03	BROMACIL	1.04000E+02
CHLORPYRIFOS, METHYL	2.04170E+04	CHLORAMBEN	1.30000E+01
DDD	1.15000E+05	CHLOROPROPHAM	1.16000E+03
DDE	7.34450E+04	DALAPON	5.70000E+00
DDE p,p	4.89779E+05	DALAPON, NA SALT	1.00000E+00
DDT	3.70000E+05	DICAMBA	3.00000E+00
DDT p,p	1.54882E+06	DICHLOBENIL	7.87000E+02
DDVP	1.95000E+02	DIURON	6.50000E+02
DIALIFOR	4.89780E+04	MONURON	1.33000E+02
DIAZINON	1.05200E+03	MSMA	8.00000E-04
DICHLOFENTHION	1.38038E+05	NITROFEN	1.24500E+03
DICIFOL	3.46100E+03	PARAQUAT .2HCL	1.00000E+00
DIELDRIN	4.93000E+03	PICLORAM	2.00000E+00
DINOSEB	1.98000E+02	PROPACHLOR	4.10000E+01
ENDRIN	1.61900E+03	PROPANIL	1.06000E+02
ETHOXYCHLOR	1.18000E+03	SIMAZINE	8.80000E+01
FENITROTHION	2.29900E+03	TERBACIL	7.80000E+01
HCB	1.66000E+06	TRIFLURALIN	1.15000E+03
HEPTACHLOR	7.36600E+03	2,4-D	4.16000E+02
LEPTOFOS	4.12200E+03	2,4-D	4.43000E+02
LEPTOPHOS	2.04174E+06	2,4-D	6.46000E+02
LINDANE	6.43000E+02	2,4,5-T	7.00000E+00
MALATHION	2.30000E+02	2,4,5-T, BUTYL ESTER	6.40000E+04
MALATHION	7.76000E+02	2,4,5-T OCTYL ESTER	9.09000E+02
METHOMYL	1.20000E+01		
METHOXYCHLOR	2.05000E+03	**C. FUNGICIDES**	
METHOXYCHLOR	1.20000E+05		
METHYL PARATHION	2.07600E+03	BENOMYL	2.64000E+02
PARATHION	6.45500E+03	CAPTAN	3.30000E+01
PERMETHRIN	7.53000E+02	PCP	1.42900E+04
PHORATE	8.23000E+02		
PHOSALONE	1.99530E+04		
PHOSMET	6.76000E+02		

TABLE III-16

MEAN FIRST ORDER DECAY COEFFICIENTS FOR SELECTED PESTICIDES

(Rao and Davidson, 1982)

Pesticide		Rate Coeff. (day^{-1})		Pesticide		Rate Coeff. (day^{-1})	
		Mean	%CV			Mean	%CV
A. HERBICIDES				**B. INSECTICIDES**			
2,4-D	Lab.*	0.066	74.2	PARATHION	Lab.*	0.029	48.3
	Lab.	0.051	23.5		Field	0.057	101.8
	Field	3.6	83.3				
				METHYL PARATHION	Lab.*	0.16	-
2,4,5-T	Lab.	0.029	51.7		Field	0.046	-
	Lab.*	0.035	82.9				
				DIAZINON	Lab.*	0.023	108.7
ATRAZINE	Lab.*	0.019	47.4		Lab.	0.022	-
	Lab.	0.0001	70.4				
	Field	0.042	33.3	FONOFOS	Lab.*	0.012	-
SIMAZINE	Lab.*	0.014	71.4	MALATHION	Lab.*	1.4	71.4
	Field	0.022	95.5				
				PHORATE	Lab.*	0.0084	-
TRIFLURALIN	Lab.*	0.008	65.5		Field	0.01	30.0
	Lab.* (anaerobic)	0.025	-				
	Lab. (chain)	0.0013	-	CARBOFURAN	Lab.*	0.047	87.2
	Field	0.02	65.0		Lab.	0.0013	-
					Lab.* (anaerobic)	0.026	50.0
BROMACIL	Lab.*	0.0077	49.4		Field	0.016	87.5
	Lab.	0.0024	116.2	CARBARYL	Lab.*	0.037	56.8
	Field	0.0038	100.0		Lab. (Chain)	0.0063	101.6
					Field	0.10	79.2
TERBACIL	Lab.*	0.015	33.3				
	Lab.	0.0045	124.0	DDT	Lab.*	0.00013	130.8
	Field	0.006	55.0		Lab.* (anaerobic)	0.0035	82.9
LINURON	Lab.*	0.0096	19.8	ALDRIN and			
	Field	0.0034	41.2	DIELDRIN	Lab.*	0.013	-
					Field	0.0023	100.0
DIURON	Lab.	-	-				
	Field	0.0031	58.1	ENDRIN	Lab.*		
					(anaerobic)	0.03	53.3
DICAMBA	Lab.*	0.022	80.2		Field (aerobic)	0.0015	-
	Lab. (ring)	0.0022	-		Field (anaerobic)	0.0053	-
	Lab. (chain)	0.0044	-				
	Field	0.093	16.1	CHLORDANE	Field	0.0024	104.2
PICLORAM	Lab.*	0.0073	58.9	HEPTACHLOR	Lab.*	0.011	-
	Lab.	0.0008	111.3		Field	0.0046	119.6
	Field	0.033	51.5				
				LINDANE	Lab.*	0.0026	-
DALAPON	Lab.*	0.047	-		Lab. (anaerobic)	0.0046	-
TCA	Lab.*	0.059	103.4	**C. FUNGICIDES**			
	Field	0.073	-				
				PCP	Lab.*	0.02	60.0
GLYPHOSATE	Lab.*	0.1	121.0		Lab. (anaerobic)	0.07	44.3
	Lab.	0.0086	93.0		Field	0.05	-
PARAQUAT	Lab.*	0.0016	-				
	Field	0.00015	-	CAPTAN	Field	0.231	-

*These rates are based on the disappearance of solvent- extractable parent compound under aerobic incubation conditions, unless stated otherwise.

TABLE III-17

FIRST ORDER PESTICIDE DECAY COEFFICIENTS FOR SELECTED PESTICIDES AND SOIL CONDITIONS

(Nash, 1984)

Pesticide	Soil Type	pH	om/ (%)	Crop or conditions	Application rate (kg/ha)	k_s
				FUNGICIDES		
BAS 3460f————Potting Soil				Agonis Flexuosa		0.0822
Benomyl————Potting Soil				Agonis Flexuosa		.1486
Benomyl	sl					.0058
Benomyl	l					.0023
				HERBICIDES		
Alachlor						.0384
Amitrole						.0768
Arsenic acid						<.0064
Asulam————Regina	c	7.7	4.2	14 May		.0986
Asulam————Regina	c			12 July		.0619
Asulam————Regina	c	7.7	4.2	30 July		.0310
Atrazine	sl	4.8	1.0			.0131
Atrazine————Regina	c	6.6	2.0			.0063
Atrazine						.0064
Atrazine————Norfolk	sl	6.8			~5.2	.0133
Atrazine————Decatur	cl	6.4			~5.2	.0149
Benefin						.0053-.0077
Benefin						.0077-.0070
Bifenox————Potting soil mixture				Various	1.7	.142
Butralin						.0128
Butralin						.0077
Cyanazine						.0064
Di-Allate————Weyburn	l	6.5	6.5	None	2.6	.0138
Di-Allate————Weyburn	l	7.0	4.5	Laboratory	.65	.0248
Di-Allate————Regina	c	7.5	4.0	Laboratory	.65	.0180
Di-Allate————Regina	c	7.8	4.2	None	2.2	.0110
Dicamba————Asquithse		7.5	3.2	5% moisture	.25	.0197
Dicamba————Asquithse		7.5	3.2	10% moisture	.25	2/ .2140
Dicamba————Holtfort	sic	5.2	11.7	Various moisture	.25	2/ >.2140
Dicamba————Regina	c	7.7	4.2	25% moisture	.25	.0486
Dicamba————Regina	c	7.7	4.2	35% moisture	.25	.0902
Dicamba————Ouachita	cl		3.3	Forest	.3	.0217
				HERBICIDES		
Dicamba————Ouachita	cl		2.6	Grass	.3	.0407
Dicamba————Cross Timbers	l		3.6	Forest	.3	.0267
2,4-D————Cross Timbers	l		3.6	Forest	.6	.1733
2,4-D acid————Cross Timbers	l					>.0768
2,4-D————Cross Timbers	l		3.3	Forest	.6	.1386
2,4-D salt						.0768
2,4-D————Ouachita	cl		2.6	Grass	.6	.1733
2,4-D ester						>.0768
2,4-D isooctyl ester.	Neff	sil	3.2	Laboratory 30°C	15	.2546
2,4-D	Neff	sil	3.2	Laboratory 10°C	15	.2731
2,4-D amine————Neff	Neff	sil	3.2	Laboratory carboxyl-^{14}C	12.5	.1457
2,4-D amine————Neff	Neff	sil	3.2	Laboratory carboxyl-^{14}C	12.5	.1008
2,4-D isooctyl ester & amine.	Neff	sil	3.2	Laboratory carboxyl-^{14}C	12.5	.0951
2,4-D isooctyl ester & amine.	Neff		3.2	Laboratory carboxyl-^{14}C	12.5	.0555
2,4-D isooctyl ester & amine.			3.2	Laboratory Ring-^{14}C	12.5	.0852

TABLE III-17 (Continued)

Pesticide	Soil Type	pH	OM[1]	Crop or conditions	Application rate	k_s
			(%)	HERBICIDES	(kg/ha)	
2,4-D isooctyl ester + amine.			3.2	Laboratory Ring[14]C	12.5	0.0257
Dichlorprop------Ouachita	sl		3.3	Forest	.6	.0578
Dichlorprop------Ouachita	sl		2.8	Grass	.6	.0866
Dichlorprop------Cross Timbers	l		3.8	Forest	.6	.0693
Dinitramine						.0193
Dinitramine						.0193
Diuron-----------Norfolk	cl	6.8			~5.2	.0064
Diuron-----------Decatur	cl	6.4			~5.2	.0072
EPTC------------Regina	c	7.5	4.0	Laboratory	.65	.0220
EPTC------------Weyburn	l	7.0	4.5	Laboratory	.65	.0248
Fluchloralin						[2].0070
Fluchloralin						[2].0045
Isopropalin------Daummer	sic	6.7	5.1	Various		.0023-.0036
Isopropalin------Eisne	sil	7.2	1.6			[2].0054 .0040
Isopropalin------Ochley	sil	4.7	2.9	Sorghum	1.68	.0304
Isopropalin------Ochley	sil	4.7	2.9	Sorghum	3.36	.0214
Isopropalin------Bloomfield	fs	6.3	.6	Sorghum	1.12	.0275
Karbutilate------cl		6.3	2.2	Rangeland		.0057-.0282
Karbutilate------lc		6.2	1.1	Rangeland		.0118
Linuron				Cropped		[2].0104-.0231
Linuron-----------ls				Non-cropped		.0047
Linuron-----------cl		7.0	2.0	Carrots	.85	[2].0280
Linuron-----------cl		7.0	2.0	None	3.4	[2].0039
Linuron-----------0-5 cm		7.0	2.0	None	3.4	[2].0061
MCPA-----------Coarse cl		7.0	2.0	Barley	1.7	[2].1221
MCPA-----------Coarse cl		7.0	2.0	None	3.4	[2].1070
Metribuzin						[2].0298
Metobromuron-----------sl		4.8	1.0			.0231
Metobromuron-----------sl		6.5	2.0			.0248
Monolinuron						.00216
Monuron-----------Ramona sl				Various	2.24	.0060
Monuron-----------Ramona sl					4.48	.0075
Neburon-----------Ramona sl				Various	2.24	.0073
Neburon-----------Ramona sl				Various	4.48	.0059
Nitralin						.0062-.0086
Nitralin						.0096-.0086
Nitralin-----------Ochley sil		4.7	2.9	Sorghum	1.12	.0110
Nitralin-----------Ochley sil		4.7	2.9	Sorghum	1.12	.0079
Nitralin-----------Ochley sil		4.7	2.9	Sorghum	2.24	.0090
Nitralin-----------Ochley sil		4.7	2.9	Sorghum	2.24	.0024
Nitralin-----------Bloomfield fs		6.3	.6	Sorghum	.56	.0155
Nitralin-----------Bloomfield fs		6.3	.6	Sorghum	1.12	.0091
Oryzalin-----------Bloomfield fs						[2].0054-.0083
Oryzalin						.0144-.0056
Pebulate-----------Regina c		7.5	4.0	Laboratory	.65	.0396
Pebulate-----------Weyburn l		7.0	4.5	Laboratory	.65	.0396
Picloram------Scot l, oxbows cl				Various		.0025 [2].0083 [2].0056

TABLE III-17 (Continued)

Pesticide	Soil			Crop or conditions	Application rate	k_s
	Type	pH	OM			
			(%)	HERBICIDES	(kg/ha)	
Pebulate————————Regina c	7.5	4.0		Laboratory	.65	0.0396
Pebulate————————Weyburn l	7.0	4.5		Laboratory	.65	.0396
Picloram——————Scot l, oxbows cl				Various		.0025
Picloram——————————Various						2/.00772
Picloram——————Nova Scotia cl					4.8	.0044
Picloram—————————Somerset sl	4.8	2.9		Fallow	4.48	.0050
Picloram——————————Fanin cl	6.3	1.9		Orchard grass	2.24	.0354
Picloram————————Chandler f sl	5.5	1.7		Orchard grass	2.24	.0258
Picloram—————————Chester l	5.8	1.9		Orchard grass	2.24	.0268
Picloram—————————Chester l	5.8	1.9		Orchard grass	4.48	.0269
Picloram————————Various	Various				.05	2/.004
Picloram————————Ouachita cl			3.3	Forest	.6	3/.0019
Picloram————————Ouachita cl			2.8	Grass	.6	.0048
Picloram——————Cross Timbers l			3.8	Forest	.6	.0028
Profluralin						2/.0047
Profluralin						2/.0051
Pometryne————————————sl	7.0	2.0				.0238
Propazine————————————sl	4.8	1.0				.0108
Propazine	6.5	2.0				.0056
Propyzamide———————c to sl				Lettuce		.0061- 4/.0158
Silvex—————————Ouachita sl			3.3	Forest	.6	.0330
Silvex—————————Ouachita sl			2.8	Grass	.6	.0495
Silvex—————————Cross Timbers l			3.8	Forest	.6	.0462
Simazine	7	2		None	3.4	4/.0074
Simazine————————0 to 5 cm	7	2		None	3.4	.0083
Simazine————————————sl	4.8	1.0				.0116
Simazine————————————sl	6.5	2.0				.0082
Simazine				Cropped		.0539
Simazine				Noncropped		.062
Simazine————————————sl	7.0	2.0				.0187
Tebuthiuron——————Various				Corn	.025	.0024
Tebuthiuron—— Houston Black c, Udic Pellustert				In surface runoff water.	2.24	.0060
Tebuthiuron—— Houston Black Udic Pellustert				In surface pellets.	2.24	.0427
Tebuthiuron—— Houston Black Udic Pellustert				In surface broadcast spray.	2.24	.0201
Tebuthiuron—— Houston Black Udic Pellustert				In pellets	2.24	.0517
Tebuthiuron—— Houston Black Udic Pellustert				In surface band pellets.	2.24	.0624
Tebuthiuron—— Houston Black Udic Pellustert				Broadcast in soil spray.	2.24	.0069
Triallate——————Regina c	7.5	4.0		Laboratory	.65	.0090
Triallate——————Weyburn l	7.0	4.5		Laboratory	.65	.0110
Triallate——————Coarse sl	7.0	2.0		Barley	1.7	3/.0144
Triallate——————Coarse sl	7.0	2.0		None	3.4	3/.0067
Triallate——————Weyburn l	6.5	6.5		None	2.8	.0068
Triallate——————Regina c	7.8	4.2		None	2.2	.0053
2,4,5-T————————Ouachita sl			3.3	Forest	.6	.0289
2,4,5-T————————Ouachita sl			2.8	Grass	.6	.0330
2,4,5-T————————Cross Timbers l			3.8	Forest	.6	.0330
2,4,5-T————————Fanin cl	6.3	1.9		Orchard grass	2.24	3/.0508
2,4,5-T————————Chandler fls	5.5	1.7		Orchard grass	2.24	.0495

TABLE III-17 (Continued)

Pesticide	Soil			Crop or conditions	Application rate	$t_{\frac{1}{2}}$
	Type	pH	OM			
			(%)	HERBICIDES	(kg/ha)	
2,4,5-T——Chester l		5.8	1.9	Orchard grass	2.24	1/0.0416
2,4,5-T——Chester l		5.8	1.9	Orchard grass	4.48	.0414
Trifluralin						2/.0037-
Trifluralin						.0047
Trifluralin						2/.0051-
						.0044
Trifluralin——Cecil sl		6.5	.6	Soybeans		.0175
Trifluralin——Wet soil				None		.0956
Trifluralin——Dry soil				None		4/.0189
Trifluralin——Ochley sil		4.7	2.9	Sorghum	.84	.0145
Trifluralin——Ochley sil		4.7	2.9	Sorghum	.84	.0117
Trifluralin——Ochley sil		4.7	2.9	Sorghum	1.68	.0104
Trifluralin——Ochley sil		4.7	2.9	Sorghum	1.68	.0026
Trifluralin——Bloomfield fs		6.3	.6	Sorghum	.56	.0155
Trifluralin——Bloomfield fs		6.3	.6	Sorghum	1.12	.0091
Vernolate——Regina c		7.5	4.0	Laboratory	.65	.0396
Vernolate——Weyburn l		7.0	4.5	Laboratory	.65	.0396
				INSECTICIDES		
Aldicarb——Beaumont c		5.4			130	.00273
Aldicarb——Houston c		7.8			130	.0087
Aldicarb——Houston cl		7.5	.25	Shandi	.5	3/.0991
Aldicarb——Houston cl		7.5	.25	Shandi	1.0	.0420
Aldicarb——Houston cl		7.5	.25	Orange	2.8-22.4	.0322-
Aldrin						<.0032
Aldrin——Ulysses sil				Fallow	2.24	.0264
Aldrin——Knox sil				Fallow	2.24	.0259
Aldrin——Caleryville muck				Fallow	2.24	4/.0014
Aldrin——Marietta sl				Fallow	2.24	.0138
Aldrin——Fox fsl				Fallow	2.24	.0256
Aldrin——Miami sil				Fallow	2.24	.0258
Aldrin——Muck				Fallow	2.24	4/.0066
Aldrin——Carrington sil		Nondisked		Fallow	4.5	2/.0101
Aldrin——Carrington sil		Disked		Fallow	4.5	2/.0136
Aldrin——Udaipur cl		7.8	1.6	Various	3.0	.0149
						x̄ of 19
						x̄ of 19
Aldrin——Jobner		8.6	.26	Various	3.0	.0165
						x̄ of 19
Aldrin——Muck					22.4	.0061
Aldrin——Miami sil					22.4	.0096
Aldrin——Composite					22.4	.0038
Aldrin (Dieldrin)——Carrington sil		Nondisked			4.5	4/.0006
Aldrin (Dieldrin)——Carrington sil		Disked			4.5	4/.0008
Aldrin (Dieldrin)——Carrington sil		Disked		Granules	5.6	4/.0012
Aldrin (Dieldrin)——Carrington sil				Spray		4/.0017
Alton——Sultan sil		6.3	3.4	Corn granules	2.24	.0032
Azinphosmethyl		8.4				.0239
Azinphosmethyl——Orchard sl		6.6-7.8	3.4			4/,5/.0026
Azinphosmethyl——Orchard sl		6.6-7.8	3.4			5/,5/.0014
Azinphosmethyl——Gila sil					.018	.0633
Azinphosmethyl——Nacho sil						.0273
Azinphosmethyl——Linne c						.0516
Azinphosmethyl——Madera sl						.0086
Azinphosmethyl——Lawoen sl						.0119
Azinphosmethyl——Santa Lucia sill						.0235

TABLE III-17 (Continued)

Pesticide	Soil Type	pH	OM (%)	Crop or conditions	Application rate (kg/ha)	k_s
				INSECTICIDES		
Azinphosmethyl----Windy 1						0.0074
Azinphosmethyl-------fsl						.0101
Azinphosmethyl------sicl						.0458
Azinphosmethyl-------c						.0505
Azinphosmethyl-------sl						.0211
BHC						.0021
BHC--------------Udaipur	7.8	1.6	Various	5.0		.0140
BHC						$\bar{x}$ of 19
BHC--------------Jobner sl	8.6	.26	Various	5.0		.0098
						$\bar{x}$ of 19
BHC alpha----------Berwick sl			Vegetables	7.4 BHC	5/	.0006
BHC beta----------Berwick sl			Vegetables	7.4 BHC	2/	.00015
BHC gamma----------Berwick sl			Vegetables	7.4 BHC	2/	.00042
BHC delta----------Berwick sl			Vegetables	7.4 BHC	2/	.00036
Bromophos----------Composite						.0198
Carbaryl						.0768
Carbaryl----------Udaipur cl	7.8	1.6	Various	15.0		.1196
						$\bar{x}$ of 8
Carbaryl----------Jobner sl	8.6	.26	Various	15.0		.0969
						$\bar{x}$ of 8
Carbofuran						.0768
Carbofuran----------Take sil	8.5			10.0		.0079
CGA-12223----------sil	4.8	1.0				.0385
CGA-12223 2/----------sil	6.5	2.2				.0693
Chlordane----------Berwick sl				2.0	2/	.00072
Chlordane----------Composite						.0020
Chlorfenvinphos						.0055
Diazinon----------Composite						.0330
Diazinon----------Sultan sil	6.7	3.1	25°C			.0151
Diazinon----------Sultan sil	6.7	3.1	15°C			.0067
Diazinon----------Sultan sil	4.3	3.1				.0242
Diazinon----------sl	4.8	1.0				.0239
Diazinon----------sl	6.5	2.0				.0239
Diazinon----------sl	6.5	2.0				.0248
Diazinon----------Puyallup sl	5.0	2.1				.0189
Diazinon----------Puget sil	5.4	3.0				.0260
Diazinon----------Chehalis cl	5.6	7.2				.0166
Diazinon----------Organic	5.4	40				.0171
Dieldrin--------Carrington sil	Nondisked		Fallow	4.5	2/	.0142
Dieldrin--------Carrington sil	Disked		Fallow	4.5	2/	.0187
Dieldrin					3/	.0003
Dieldrin----------Imperial sc	7.8	1.0		20.0		.0002
Dieldrin----------Holtville fsl	7.8	.5		20.0		.0001
Dieldrin----------Composite						.0008
Dioxacarb----------sl	4.8	1.0				.0248
Dioxacarb----------sl	6.5	2.0				.3465
Dioxathion----------fsl						.0156
Dioxathion----------sicl						0128
Dioxathion----------c						.0141
Dioxathion----------sl						.0229
p,p'-DDT----------Ulysses sil	6.9	1.8	Fallow	9.4	3/	.0008
p,p'-DDT----------Knox sil	6.8	.8	Fallow	9.4	3/	.0005
p,p'-DDT--------Celeryville muck	4.9	74.5	Fallow	9.4		.0021
p,p'-DDT----------Marietta sl	6.0	2.0	Fallow	9.4	3/	.0014
p,p'-DDT----------Fox fsl	7.2	.8	Fallow	9.4		.0009
p,p'-DDT----------Miami sil	7.1	3.6	Fallow	9.4	3/	.0004
p,p'-DDT----------Muck	6.8	40.0	Fallow	1.0		.0009
p,p'-DDT--------Commerce sil				24.4		.0037

TABLE III-17 (Continued)

Pesticide	Soil Type	pH	OM	Crop or conditions	Application rate	k_s
			(%)		(kg/ha)	
				INSECTICIDES		
p,p'-DOT--------Carrington sil	Nondisked				4.5	[2/]0.0024
p,p'-DOT--------Carrington sil	Disked			Fallow	4.5	[2/].0048
p,p'-DOT--------Miami sil				Fallow	11.6	.0003
p,p'-DOT--------Carrington sil	Disked/non-disked			Fallow	4.5	[4/].0002
p,p'-DOT--------Muck					11.2	.0011
p,p'-DOT--------Miami sil					11.2	.0029
p,p'-DOT--------Berwick sl				37 DOT		[2/].00016
p,p'-DOT--------Composite						.0007
o,p'-DOT--------Berwick sl						[2/].00029
Dimethoate-------Composite						.0990
Disulfoton				Various		.1604
Endosulfan-------Various					1.3	.0162
Ethion-----------Mocho sil						.0014
Ethion-----------Linne c						.0012
Ethion-----------Madera sl						.0009
Ethion-----------Lovean sl						.0015
Ethion-----------Santa Lucia sil						.0014
Ethion-----------Windy l						.0015
Ethion-----------fsl						[1/].0009
Ethion-----------sicl						.0022
Ethion-----------c						.0032
Ethion-----------sl						.0025
Fenitrothion-------sl	4.8	1.0				.0578
Fenitrothion-------sl	6.5	2.0				.1155
Fonofos-----------Taka sil	8.5				10	.0158
Heptachlor--------Composite						.0021
Heptachlor--------Composite						.0025
Heptachlor--------Composite						.0028
Hexachlorobenzene--Chaveda				Zoysia		[2/].0006
Isobenzan--------Composite						.0060
Lindane----------Imperial sc	7.8	1.0			20	.0022
Lindane---------- Holtville fsl	7.8	.5			20	.0026
Lindane----------Composite						.0017
Lindane----------Gila sil	7.7	.6		None		[2/].0046
Lindane----------Miami sil					11.6	.0011
Lindane----------Muck					11.2	.0014
Lindane----------Miami sil					11.2	.0048
Lindane----------Ulysses sil				Fallow	1.12	.0147
Lindane----------Knox sil				None	11.2	.0264
Lindane------Coloryville muck				None	11.2	.0074
Lindane----------Marietta sl				None	11.2	.0263
Lindane----------Fox fsl				None	11.2	.0264
Lindane----------Miami sil				None	11.2	.0139
Lindane----------Muck				None	11.2	[1/].0059
Malathion--------Poygan sicl	7.2			None		2.9173
Malathion--------Kovama c	6.4			None		2.4618
Malathion--------Ella ls	3.6			None		1.2681
Malathion--------Freestone sl	5.3	1.1		None		.4152
Malathion--------Oholona c	7.4	3.1		None		1.9832
Malathion--------Trinity l	7.2	4.7		None		1.9026
Mecarbam--------Composite						.0495
Methidathion--------sl	4.8	1.0				.0108
Methidathion--------sl	6.5	2.0				.0495
Methoxychlor	4.8	1.0				.0046
Methoxychlor	6.5	2.0				.0033
Methyl Parathion-Carrington l				Radishes	5.6	.2207
Naviphos--------Sacramento s	5.4	.4			13	.2936
Parathion-------Carrington l				Radishes	5.6	.0248
Parathion						.056
Parathion--------Mocho sil	>7	.6		None		[2/].0046
Parathion--------Waipur cl	7.8	1.6		Various	10	.1239

TABLE III-17 (Continued)

Pesticide	Soil			Crop or	Application	k_s
	Type	pH	OM	conditions	rate	
			(%)	INSECTICIDES	(kg/ha)	
Parathion--------Jobner sl	8.6	.26		Various	10	x̄ of 8 / 0.0727
Parathion--------Mocho sil						x̄ of 7 / 3/.1371
Parathion----------Linne c						.1306
Parathion--------Madera sl						1/.0944
Parathion--------Laveen sl						3/.1150
Parathion-------Santa Lucia sil						.0866
Parathion-----------fsl	6.8	0.8				.0654
Parathion-----------sicl	7.3	2.1				3/.0891
Parathion-----------c	7.3	2.3				.2962
Parathion-----------sl	7.6	1.8				.2614
Phenthoate----------fls	6.8	.8				.2865
Phenthoate---------sicl	7.3	2.1				.0156
Phenthoate-----------c	7.3	2.3				.0141
Phenthoate----------sl	7.6	1.8				.0229
Phorate-------Sacramento muck					13	.0040
Phorate-------Sacramento peat					13	2/.0043
Phorate-------Sacramento peat					13	2/.0051
Phorate----------Take sil	8.5				10	1/.0363
Phorate--------Sacramento s					13	4/.0078
Phorate--------Sacramento c					13	.0277
Zinophos---------Sultan sil	6.7	3.1	25°C			3/.0223
Zinophos---------Sultan sil	6.7	3.1	15°C			.0164
Zinophos---------Sultan sil	5.5	3.1				.0144
Zinophos---------Sultan sil	8.1	3.1				.0244
Zinophos---------Sultan sil						.0096
Zinophos						.0133
Zinophos						.0206
Zinophos						.0075
				NEMATICIDES		
Dichlofenthion--Composite						.0031
Trichloronate---Composite						.0050

1/ Organic matter.
2/ Unknown.
3/ r = <-0.9.
4/ r = <-0.8.
5/ Emulsifiable concentrate formulation.
6/ Wettable powder formulation.
7/ Diethyl (1-iso-propyl-5-chloro-1,2,4-triazolyl-3) phosphorothioate.

Pesticide Runoff

Two pesticides, carbofuran and atrazine, have been applied to a cornfield at planting time. Carbofuran is an insecticide used to control corn rootworm and atrazine is a herbicide for weed control. Three days after each pesticide has been applied at 4000 g/ha, a 4.5 cm storm occurs which produces 0.2 cm of runoff and 0.6 t/ha of sediment. The soil has an organic matter content of 3%, bulk density of $b = 1.3$ g/cm^3 and available water capacity of $w = 0.2$. Determine the runoff losses of each pesticide.

Solution:

Partition coefficients K_D are determined from K_{OC} values in Table III-14 (Atrazine, $K_{OC} = 163$; Carbofuran, $K_{OC} = 29.4$):

$$K_D = K_{OC} \ (\%OC/100) \tag{III-36}$$

where

$\%OC = 0.59 \ \%OM$ (Equation III-37), or $\%OC = 0.59(3) = 1.77$

$K_D = 163(.0177) = 2.89$ (Atrazine)

$K_D = 29.4 \ (0.0177) = 0.52$ (Carbofuran)

Decay coefficients k_s (field values) are given in Table III-16:

$k_s = 0.042$ (Atrazine)

$k_s = 0.016$ (Carbofuran)

Total adsorbed and dissolved pesticide in the surface centimeter are given by Equations III-27, III-31, and III-32. Assuming the pesticide is left on the soil surface, initial levels for both pesticides are $P_o = 4000$ g/ha. For day $t = 3$:

Atrazine:

$P_3 = 4000 \exp \ [-0.042(3)] = 3526$ g/ha

$w/K_D b = 0.2/2.89(1.3) = 0.0532$

$A_3 = [1/(1 + 0.0532)] \ 3526 = 3348$ g/ha

$D_3 = [1/(1 + 1/0.0532)] \ 3526 = 178$ g/ha

Similarly, for Carbofuran:

$P_3 = 3813$ g/ha

$A_3 = 2942$ g/ha

$D_3 = 871$ g/ha

Solid-phase and dissolved losses are given by:

$$PX_3 = (A_3/100b)X_3 \qquad\qquad (III-33)$$

$$PQ_3 = [Q_3/(R_3 + M_3)]D_3 \qquad\qquad (III-34)$$

where

$X_3 = 0.6$ t/ha

$Q_3 = 0.2$ cm

$R_3 = 4.5$ cm

M_3, snowmelt, is obviously zero.

Atrazine:

$PX_3 = [3348/1.3(100)]0.6 = 15.5$ g/ha

$PQ_3 = (0.2/4.5)178 = 7.9$ g/ha

Carbofuran:

$PX_3 = [2942/1.3(100)] 0.6 = 13.6$ g/ha

$PQ_3 = (0.2/4.5) 871 = 38.7$ g/ha

In summary:

Losses in Runoff (g/ha)	Atrazine	Carbofuran
Solid-phase	15.5	13.6
Dissolved	7.9	38.7
Total	23.4	52.3

————————————— END OF EXAMPLE III-6 ——————————————

3.5 SALT LOADS IN IRRIGATION RETURN FLOWS

3.5.1 Description

Pollution of surface waters by salty irrigation drainage water is a problem in many arid regions. As shown in Figure III-16, water may be diverted from a river to water crops in an irrigation district. Portions of the diverted water are lost from the diversion canal through seepage and evaporation, and most of the remaining water is applied to crops in the irrigation district. Much of this applied water is consumed by plant evapotranspiration (ET) and the excess passes through the soil to be collected by tile drainage and returned to the river. This drainage water has a much higher salt concentration than the irrigated water. As the water moves through the soil, it retains its salt mass, but due to ET, the water volume is diminished.

Return flow salinity can be computed by assuming a steady-state condition in which:

Salts applied in irrigation = Salts removed in drainage

$$s_o I = sR$$

or

$$s = s_o I/R \qquad\qquad (III-40)$$

where

s_o = irrigation water salinity (mg/l)

s = return flow salinity (mg/l)

I = irrigation application (m^3/day)

R = return flow (m^3/day).

Salt concentration or salinity is measured either as dissolved solids (mg/l) or electrical conductivity (μmho/cm or mmho/cm). In the Western U.S., an average conversion factor is 1000 μmho/cm = 640 mg/l. Water fluxes, such as I and R refer to total water movement over the irrigation season and can be measured in length or volume units. For example, if I is given in centimeters, it is converted to cubic meters by $I(m^3)$ = $I(cm)$ 100 A, where A = irrigated area (ha).

When the irrigation diversion is taken from a river, as in Figure III-16, s_o is the salinity of the river water. The return flow salinity given by Equation III-40 obviously exceeds s_o since R « I. The river salinity after the return flow is:

$$s_o' = \frac{s_o (Q - D) + sR}{Q - D + R} \qquad\qquad (III-41)$$

where

s_o' = river salinity after return flow (mg/l)

Q = river flow prior to diversion (m^3/day)

D = irrigation diversion (m^3/day).

Since $s_o' > s_o$, the river is saltier for the next downstream user. As successive irrigation districts withdraw and return water, the river becomes progressively saltier until it is no longer suitable for municipal or agricultural use.

Variations of the salinity problem include pumping of irrigation water from aquifers and unsteady-state or transient leaching of soil salts. In the former case, s_o is the aquifer salinity. The salty drainage flow might be discharged to surface waters as in Figure III-16 or allowed to percolate through the soil, thus producing saltier groundwater. Transient salt leaching often occurs when soils are initially irrigated or reclaimed. Until a steady-state situation is reached, the
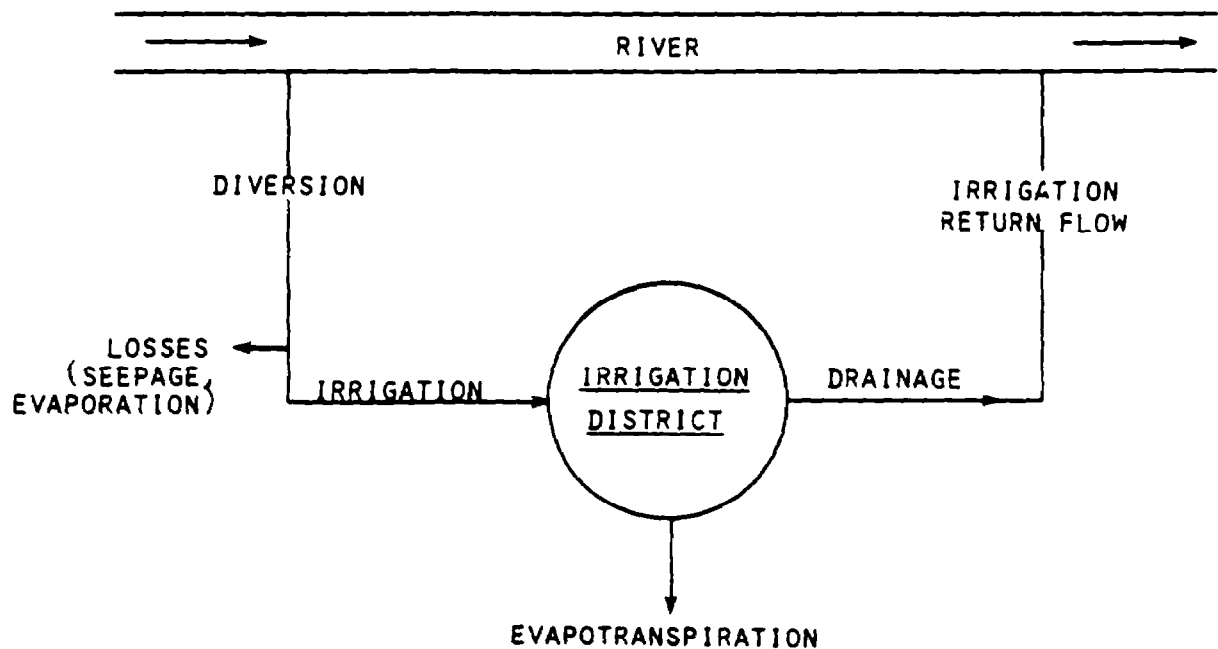
FIGURE III-16 COMPONENTS OF AN IRRIGATION SYSTEM

salt load in return flow may exceed the salts applied in irrigation.

3.5.2 Estimation of Return Flows

Equations III-40 and III-41 may be used directly when return flow volumes R are known. However, accurate return flow measurements are often unavailable and indirect estimates are necessary. A general procedure for computing return flows is shown in Figure III-17.

Design factors for irrigation systems incluuc irrigation efficiencies, diversions, leaching fractions and ET. Water losses in the diversion system are indicated by a delivery efficiency, E_d:

$$I = E_d D \tag{III-42}$$

To prevent salt buildup in soil which would injure plants, irrigation applications must exceed crop water needs so that applied salts may be washed from the soil in drainage. The leaching fraction is the fraction of irrigation application which is used to control salinity, or the ratio of drainage to irrigation. As shown in Figure III-17:

$$LF = (I - E)/I \tag{III-43}$$
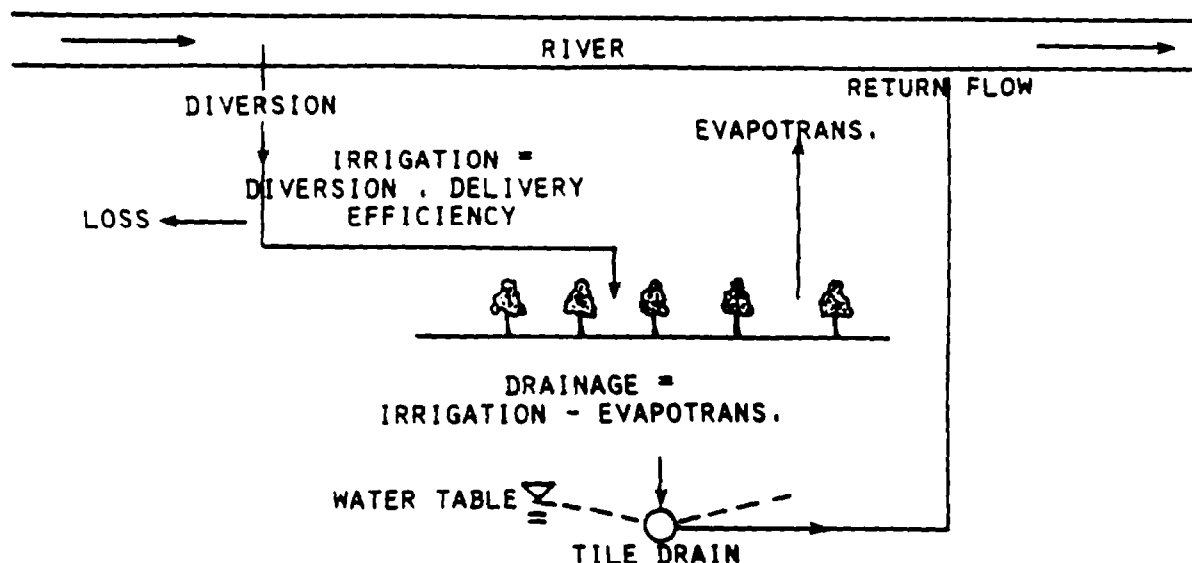
FIGURE III-17 COLLECTION OF IRRIGATION DRAINAGE

where

LF = irrigation leaching fraction

E = crop ET (m^3/day)

Since return flow (R) consists of the drainage water collected in tile drains, $R = I - E$ and $LF = R/I = R/E_d D$. Thus:

$$R = (LF)E_d D \qquad (III-44)$$

and rearranging Equation III-40:

$$s = s_0/LF \qquad (III-45)$$

If irrigation diversion D, delivery efficiency E_d and leaching fraction LF are known, return flow volume and salinity can be estimated by Equations III-44 and III-45. If LF is unknown, it can be determined from Equation III-43, provided E, crop ET, is available. Since E depends on crop mixture and local weather conditions, it is best obtained form local irrigation specialists. In the absence of such data, E may be estimated from potential ET. Potential ET, or PE, is a maximum ET which occurs when the soil is covered with a dense cover such as alfalfa and water is not limiting. Thus potential ET is a function of the atmosphere's ability to absorb water. Actual ET is generally less than PE, but by letting E = PE, we obtain a conservative overestimate of return flow salinity.

Potential ET can be determined from pan evaporation data or empirical equations. Figure III-18 shows average annual pan evaporation for the U.S. Potential ET is
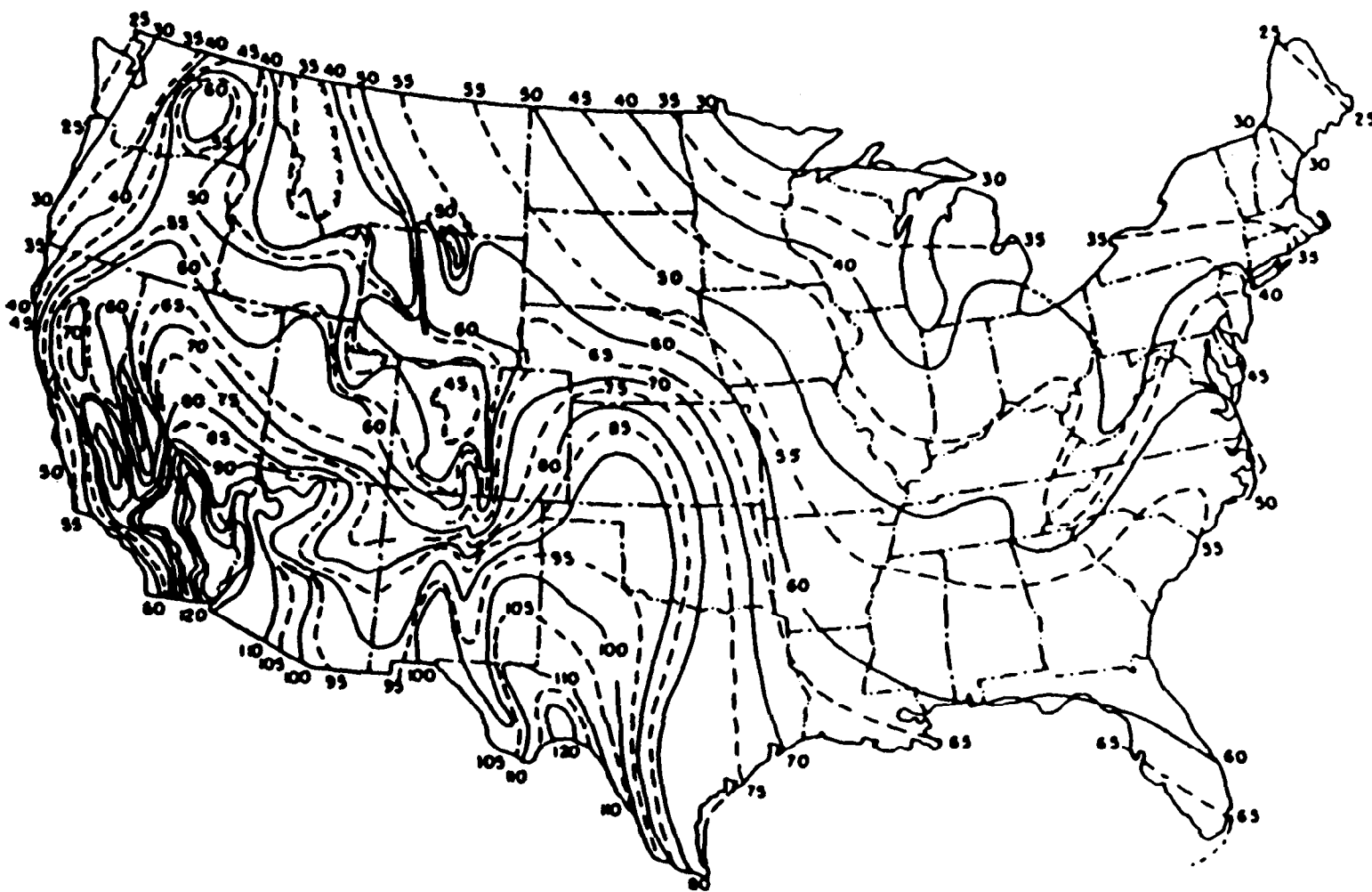
FIGURE III-18 MEAN ANNUAL PAN EVAPORATION IN INCHES (1IN = 2.54CM) (KOHLER ET AL, 1959)

approximately 70% of pan evaporation. To use the data from Figure III-18, we must assume that all annual PE occurs in the growing season. Growing season PE may also be estimated from Hamon's (1961) equation:

$$PE = (0.021 \ H^2 p)/(T + 273) \qquad (III-46)$$

where

PE = potential ET (cm/day)

H = mean number of daylight hours per day during period of interest

T = mean air temperature during period of interest (°C)

p = saturation water vapor pressure at temperature T (millibars).

Values of H and p are given in Tables III-18 and 19. The "period of interest" for irrigation studies is the irrigation season.

-- EXAMPLE III-7 --

Irrigation Return Flows

A 2000 ha irrigation district diverts an average of 350,000 m^3/day of water from a river in the irrigation season. During this time, the mean river flow is 1,000,000 m^3/day. The delivery system is 80 percent efficient and the district operates at an average leaching fraction of 0.3. The river water salinity is 200 mg/l.

Determine:

    a)   Return flow volume and salinity

    b)   River salinity downstream of the return flow.

Solution:

    Data for the problem:

        D = 350,000 m^3/day

        Q = 1,000,000 m^3/day

        s_o = 200 mg/l

        E_d = 0.8

        LF = 0.3

    a)   From equation III-44, return flow is:

        R = 0.3(9.8)(350,000)

          = 84,000 m^3/day

        with salinity given by Equation III-45:

        s = 200/0.3 = 667 mg/l

TABLE III-18

MEAN DAYLIGHT HOURS PER DAY

Latitude North	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
48	8.7	10.0	11.7	13.4	14.9	15.7	15.3	14.0	12.3	10.6	9.1	8.3
46	8.9	10.2	11.7	13.3	14.7	15.4	15.0	13.8	12.3	10.7	9.3	8.5
44	9.2	10.3	11.7	13.2	14.5	15.2	14.8	13.7	12.3	10.8	9.5	8.8
42	9.3	10.4	11.7	13.1	14.3	15.0	14.6	13.6	12.3	10.9	9.7	9.0
40	9.5	10.5	11.8	13.0	14.1	14.7	14.4	13.6	12.2	11.0	9.8	9.2
38	9.7	10.6	11.8	13.0	14.0	14.5	14.3	13.4	12.2	11.0	10.0	9.4
36	9.9	10.7	11.8	12.9	13.8	14.3	14.1	13.3	12.2	11.1	10.1	9.6
34	10.0	10.8	11.8	12.8	13.7	14.2	14.0	13.2	12.2	11.2	10.2	9.8
32	10.2	10.9	11.8	12.8	13.6	14.0	13.8	13.3	12.2	11.2	10.4	10.0
30	10.3	11.0	11.8	12.7	13.5	13.9	13.7	13.0	12.2	11.3	10.5	10.1
28	10.5	11.1	11.8	12.7	13.4	13.7	13.5	13.0	12.1	11.3	10.6	10.3
26	10.6	11.1	11.8	12.6	13.2	13.6	13.4	12.9	12.1	11.4	10.7	10.4
24	10.7	11.2	11.9	12.6	13.1	13.4	13.3	12.8	12.1	11.4	10.9	10.6

TABLE III-19

SATURATION VAPOR PRESSURE AS FUNCTION OF TEMPERATURE

(Jensen, 1973)

Temperature (°C)	Saturation Water Vapor Pressure (millibars)
0	6.1
2	7.1
4	8.1
6	9.4
8	10.7
10	12.3
12	14.0
14	16.0
16	18.2
18	20.6
20	23.4
22	26.4
24	29.8
26	33.6
28	37.8
30	42.4
32	47.5

3.6 URBAN RUNOFF LOADS

Nonpoint source pollution from urban runoff differs in several ways from its rural counterpart. Runoff rates are usually much higher in urban areas due to the distribution of _impervious_ surfaces (pavements, roofs, etc.). Urban runoff is collected in separate storm sewers or _combined sewers_. The later collect both runoff and sanitary wastewater. During a large runoff event, storm flow may exceed sanitary flows by one or more orders of magnitude. To avoid flooding from surcharged combined sewers, combined sewer "overflows" are discharged directly to receiving waters. These overflows are highly polluting since they contain runoff pollutants, raw sanitary sewage, and scoured wastewater solids which were previously deposited in the sewers.

Urban runoff quality is influenced by human activities; important determinants are land uses and population density. Land uses may be considered the "source areas" in an urban watershed; the total runoff load is the sum of runoff loads from each land use.

Sections 3.6.1 and 3.6.2 describe equations for determining annual and event pollutant loads. The annual loading functions are highly empirical, but provide estimates of pollutant loads from both separate storm sewers and combined sewer overflows. Conversely, the event loading functions are more analytical, but describe only runoff (i.e., separate storm sewer load).

Urban runoff and combined sewer overflow data are summarized by Huber, et al. (1979) and E. C. Jordan Co. (1984). Additional references on urban runoff computations include Novotny and Chesters (1980) and Kibler (1982).

3.6.1 Annual Urban Runoff and Combined Sewer Loads

General urban loading functions have been proposed by Heaney, et al. (1977), and Heaney and Huber (1979) of the form:

$$L_k = \alpha_k F_k Y_k P \tag{III-47}$$

where

L_k = annual load of pollutant due to runoff from land use k (kg/ha)

α_k = pollutant concentration factor (kg/ha-cm)

F_k = population density function

Y_k = street cleaning factor

P = annual precipitation (cm).

Total pollutant load from the urban area is:

$$L = \sum_k L_k A_k \qquad (III-48)$$

where

L = annual pollutant load due to runoff (kg)

A_k = area of land use k (ha).

Equation III-47 can be interpreted as a general loading function which multiplies a water flux (F_k P) by a concentration (α_k) and an attenuation ratio (Y_k).

Annual precipitation is obtained from local weather data or the general map shown in Figure III-19. Concentration factors for separate and combined severed land uses are given in Table III-20.

The population density function is as follows:

$$F_k = \begin{cases} 1.0, & \text{commercial and industrial} \\ 0.142 + 0.134\ PD^{0.54}, & \text{residential} \\ 0.142, & \text{other} \end{cases} \qquad (III-49)$$

where

PD = population density (persons/ha).

The street cleaning factor Y_k is based on street cleaning interval N_s (days):

$$Y_k = N_s/20 \quad \text{for } N_s < 20 \qquad (III-50)$$

For $N_s > 20$ days, no street cleaning effects are apparent and $Y_k = 1.0$. Because most pollution load in combined sewers is due to raw wastewater and sewer scour, street cleaning will not significantly reduce loads, and $Y_k = 1.0$ for combined sewers areas.
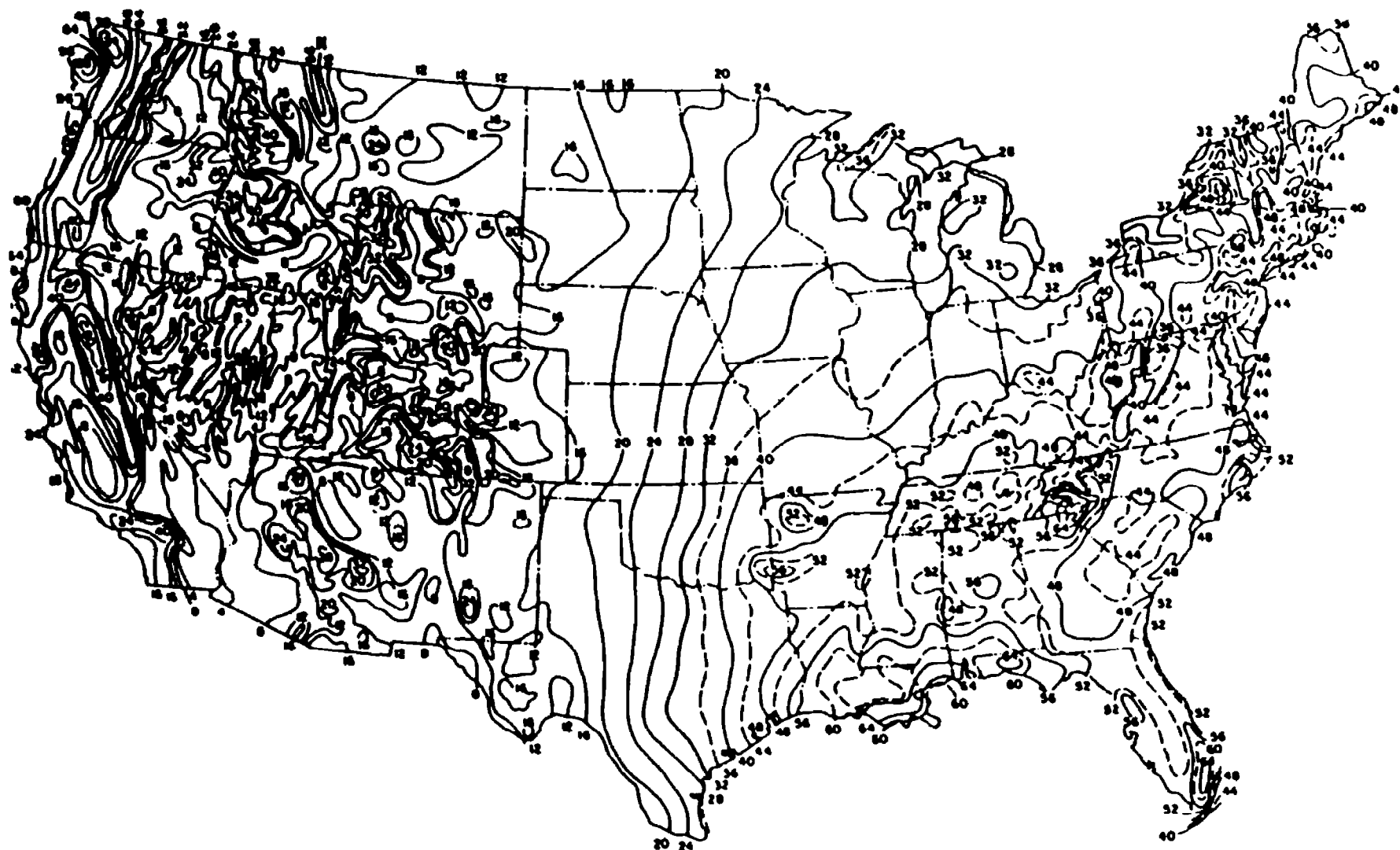
FIGURE III-19 MEAN ANNUAL PRECIPITATION IN INCHES (1IN = 2.54CM) (GILMAN, 1964)

TABLE III-20

POLLUTANT CONCENTRATION FACTORS FOR ANNUAL LOADING

FUNCTIONS (HEANEY AND HUBER, 1979)

Land Use	Pollutant (kg/ha-cm)				
	BOD_5	SS	VS	PO_4	N
Separate Sewers					
Residential	0.35	7.2	4.2	0.015	0.058
Commercial	1.41	9.8	6.2	0.033	0.131
Industrial	0.53	12.9	6.3	0.031	0.122
Other Developed	0.05	1.2	1.2	0.004	0.027
Combined Sewers					
Residential	1.45	29.7	17.2	0.061	0.239
Commercial	5.83	40.6	25.6	0.138	0.539
Industrial	2.21	53.0	26.2	0.291	0.504
Other Developed	0.21	4.9	4.8	0.018	0.066

--------------------- EXAMPLE III-8 ---------------------

Estimation of Annual Urban Pollutant Loads

Consider a city of 4000 hectares of which 20 percent is commercial, 10 percent industrial, 65 percent residential and 5 percent is in other developed areas. The residential population density is 25 persons/ha. Most of the city has separate sewers but approximately 30 percent of the residential area still has combined sewers. The streets are swept every five days in the commercial and industrial areas and are not swept in the residential areas. The mean annual precipitation is 105 cm. Determine the average annual loads of nitrogen and phosphate.

Solution:

The land use areas are:

Commercial: 800ha

Industrial: 400ha

Residential: 780ha, combined

              1820ha, separate

Other: 200ha

Loads from each land use are given by Equation III-47, with F_k from Equation III-49. The street cleaning factor is:

$$Y_k = 5/20 = 0.25$$

in commercial/industrial areas and $Y_k = 1.0$ in all other areas. The population function for residential areas is:

$$F_k = 0.142 + 0.134(25)^{0.54}$$
$$= 0.904$$

Loading calculations are summarized in the following table.

Land Use	F_k	Y_k	α_k (kg/ha-cm) N	PO_4	L_k (kg/ha) N	PO_4
Residential						
combined	0.904	1.0	0.239	0.061	22.69	5.79
separate	0.904	1.0	0.058	0.015	5.51	1.42
Commercial	1.0	0.25	0.131	0.033	3.44	0.87
Industrial	1.0	0.25	0.122	0.031	3.20	0.81
Other	0.142	1.0	0.027	0.004	0.40	0.06

Total annual loads are obtained by multiplying each load L_k by its respective area as in Equation III-48.

Nitrogen:

$$780(22.69) + 1820(5.51) + 800(3.44) + 400(3.20) + 200(0.40)$$
$$= 31,800 \text{ kg/yr}$$

Phosphate:

$$780(5.79) + 1820(1.42) + 800(0.87) + 400(0.81) + 200(0.06)$$
$$= 8100 \text{ kg/yr}$$

Over half the pollution load comes from the 780-ha combined sewer residential area.

─── END OF EXAMPLE III-8 ───

3.6.2 Event Loads in Urban Runoff

Event loading functions for urban runoff are based on general procedures proposed by Amy et al. (1974), many of which were incorporated in the U.S. Army Corps of

Engineers urban runoff model STORM (Hydrologic Engineering Center, 1977). The basic
loading function is similar to that used for solid-phase rural runoff loads (Equation
III-18). Sediment (also referred to as "dirt and dust" or simply "solids") in runoff
is multiplied by a pollutant concentration:

$$L = 10^{-6} C Y \qquad \text{(III-51)}$$

where

    L = pollutant load in urban runoff (kg/ha)

    Y = sediment washed off the urban area during a runoff event (kg/ha)

    C = pollutant concentration in sediment (ppm: μg/g, or mg/kg).

Although Equation III-51 is often used for both dissolved and solid-phase pollutants,
we would expect it to be more accurate for the latter.

    Sediment washoff is limited by the total sediment which has accumulated on land
surfaces:

$$Y = W X \qquad \text{(III-52)}$$

where

    X = accumulated sediment at the time of the storm (kg/ha)

    W = fraction of X which washes off during the storm.

The washoff function is derived by assuming that washoff rate is a
linear function of runoff rate and accumulated sediment (Amy et al., 1974; Alley,
1981):

$$\frac{dX(h)}{dh} = -uqX(h) \qquad \text{(III-53)}$$

or

$$X(h) = X(0) \exp \left[-u \int_{0}^{h} qdh \right] \qquad \text{(III-54)}$$

where

    X(h) = sediment remaining on the land surface at hour h after the beginning
of a storm (kg/ha)

    X(0) = accumulated sediment at the beginning of a storm (kg/ha)

    q = runoff rate (cm/hr)

    u = washoff coefficient (cm^{-1}).

The integral in Equation III-54 is the total storm runoff up to hour h. If we let h
equal storm duration then:

$$X(h) = X(0) \exp(-uQ) \qquad \text{(III-55)}$$

where

$\qquad$ Q = total storm runoff (cm).

The washoff coefficient is determined by assuming 90% of accumulated sediment will be washed off with 1.27cm (0.5in) of runoff (Amy et al., 1974). Hence 0.1 X(0) = X(0) exp [- 1.27u] or u = 1.8 cm^{-1}. The fraction of sediment washed off is:

$$W = \frac{X(0) - X(h)}{X(0)}$$

$$= 1 - \exp(-1.8Q) \qquad \qquad (III-56)$$

and Equation III-51 can be written:

$$L = 10^{-6} [1 - \exp(-1.8Q)] C X \qquad \qquad (III-57)$$

When this loading function is applied to an area with multiple land uses, either loads are weighted from each area:

$$L = \sum_k a_k L_k \qquad \qquad (III-58)$$

or weighted average concentrations and sediment accumulations are used:

$$CX = [\sum_k a_k X_k][\sum_k a_k C_k] \qquad \qquad (III-59)$$

where

$\qquad a_k$ = fraction of total area in land use k

$\qquad L_k$ = pollutant load from land use k (kg/ha) as given by Equation III-57

$\qquad X_k$ = accumulated sediment on land use k (kg/ha)

$\qquad C_k$ = pollutant concentration in sediment on land use k (mg/kg).

3.6.2.1 Runoff

Two alternative procedures are used in STORM to compute storm runoff. The first is the U.S. Soil Conservation Service's Curve Number Equation (Equation III-3) as described in Section 3.4.2. Appropriate urban curve numbers for average antecedent moisture conditions (CN2) are given in Table III-21.

The second option is based on runoff coefficients and depression storage:

$$Q = CR(P - DS) \qquad \qquad (III-60)$$

TABLE III-21

RUNOFF CURVE NUMBERS (ANTECEDENT MOISTURE CONDITION II)

FOR URBAN AREAS (SOIL CONSERVATION SERVICE, 1975)

Land Use Description		Hydrologic Soil Group			
		A	B	C	D
Open spaces, lawns, parks, golf courses, cemeteries, etc.					
Good condition: grass cover on 75% or more of the area		39	61	74	80
Fair condition: grass cover on 50% to 75% of the area		49	69	79	84
Commercial and business area (85% impervious)		89	92	94	95
Industrial districts (72% impervious)		81	88	91	93
Residential:					
Average lot size	Average % impervious				
1/8 acre or less	65	77	85	90	92
1/4 acre	38	61	75	83	87
1/3 acre	30	57	72	81	86
1/2 acre	25	54	70	80	85
1 acre	20	51	68	79	84
Paved parking lots, roofs, driveways, etc.		98	98	98	98
Streets and roads:					
Paved with curbs and storm sewers		98	98	98	98
Gravel		76	85	89	91
Dirt		72	82	87	89

where

P = storm precipitation (rainfall + snowmelt, cm)

DS = depression storage (cm)

CR = runoff coefficient.

Equation III-60 (which applies only for P > DS) suggests that precipitation must satisfy the available depression storage on plant surfaces and in mud puddles, pot holes, etc., before runoff will occur.

A conceptual view of this runoff process is shown in Figure III-20. Depression storage DS is at a maximum value DS^* when the land surface is completely dry, and the depression shown in Figure III-20 is empty. However, previous events may have partially filled depressions so that as in the figure, only a portion of DS^* remains to be filled.

Depressions are assumed to be emptied by evaporation, and a general mass balance is:

$$DS_{t+1} = DS_t + E_t - P_t \tag{III-61}$$

for

$$0 \leq DS_{t+1} \leq DS^* \tag{III-62}$$

where

DS_t = depression storage on day t (cm)

P_t = precipitation on day t (rain + snowmelt, cm)

E_t = evaporation on day t (cm)

DS^* = maximum depression storage (cm).

Evaporation may be assumed equal to potential evapotranspiration and determined as in Section 3.5.2.

The depression storage computation (Equations III-61,62) is a procedure for describing antecedent moisture conditions. When the Curve Number Equation is used, antecedent moisture is a function of 5-day antecedent precipitation. In Equation III-60, the water in storage on the land surface is the indicator of antecedent moisture.

Both maximum depression storage DS^* and the runoff coefficient CR are functions of the urban area's impervious surfaces:

$$CR = cr_i I + cr_p (1-I) \tag{III-63}$$

$$DS^* = ds_i I + ds_p (1-I) \tag{III-64}$$

PRECIPITATION
P
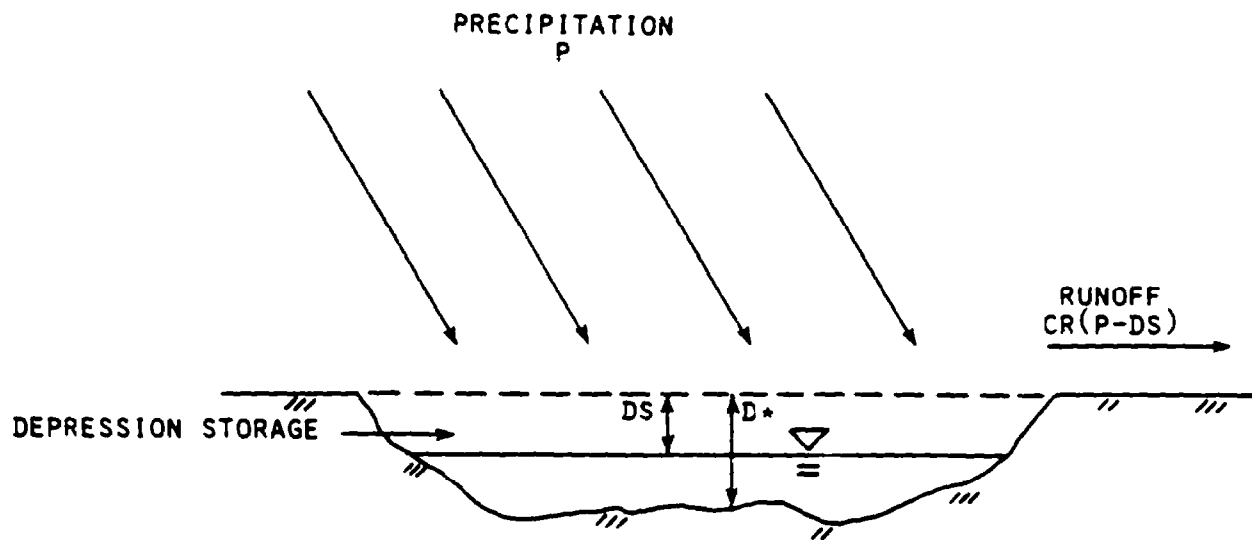
FIGURE III-20 CONCEPTUAL MODEL OF DEPRESSION STORAGE

where

I = fraction of the urban area which is impervious

cr_i, cr_p = runoff coefficients for impervious and pervious areas

ds_i, ds_p = maximum depression storage (cm) for impervious and pervious areas.

Default runoff coefficients used in STORM are cr_i = 0.90 and cr_p = 0.15 (Hydrologic Engineering Center 1977). Typical depression storage coefficients are ds_i = 0.15cm and ds_p = 0.60cm (Aron, 1982; Novotny and Chesters, 1980). These values may be used when more specific local data are unavailable.

Impervious fractions are best estimated directly from aerial photographs or land-use maps. When these are not available, regression equations based on population density are sometimes used. The equation given by Heaney and Huber (1979) can be approximated by:

$$I = 0.069 \ PD^{0.48}$$

(III-65)

where

PD = population density (persons/ha).

3.6.2.2 Sediment

Sediment and pollutant accumulation in urban areas is a complex process which depends on daily deposition from the atmosphere and other sources, removal by street

cleaning and washoff by runoff. In order to estimate C and X in Equation III-57, we must begin by determining the sediment or solids accumulation. This rate may be measured by monitoring of storm sewer suspended solids data. When these data cannot be obtained, average values from previous urban monitoring programs must be used.

Urban sediment data are often normalized with respect to the length of street curbing. This is because most of the dirt and dust which constitutes urban sediment collects in street gutters. Daily sediment buildup is:

$$x = z \, Cl \tag{III-66}$$

where

x = daily sediment buildup (kg/ha-day)

z = sediment accumulation rate (kg/km of curb per day)

Cl = curb length density (km/ha).

Curb length may be estimated as twice the total street lengths, and Cl is obtained by dividing curb length by area. Alternatively, the regression equation given by the American Public Works Association (1974) may be used (converted to metric units):

$$Cl = 0.31 - 0.27(0.93)^{PD} \tag{III-67}$$

Urban sediment accumulation rates from several sources are given in Table III-22. The rates given by Amy et al., (1974) and Sartor and Boyd (1972) are mean values based on data from a number of urban areas. The STORM rates are suggested default values for that model. Although the Sartor and Boyd (1972) rates are larger than the other two sets, they are generally comparable with the Amy et al., (1974) data. The Sartor and Boyd rates are recommended for use in Equation III-66 because they are conservative and consistent.

Sediment will accumulate at a daily rate x until the streets are cleaned or a runoff event occurs. The daily sediment mass balance is:

$$X_{t+1} = X_t + x - Y_t - S_t \tag{III-68}$$

where

X_t = accumulated sediment at beginning of day t (kg/ha)

Y_t = sediment removed in runoff on day t (kg/ha)

S_t = sediment removed by street cleaning on day t (kg/ha).

If a runoff event occurs on day t, then from Equations III-52 and 56:

TABLE III-22

URBAN SEDIMENT (SOLIDS) ACCUMULATION RATES

Land Use	Amy et al (1974)	Sartor & Boyd (1972)[a]	STORM[b]
	(all in kg/curbs-1 km-day)		
Residential	42	-	-
Single-family residential	-	48*	10
Multi-family residential	-	66*	34
Commercial	21	69*	49
Industrial	-	127*	68
Light industry	110	-	-
Heavy industry	57	-	-
Parks	-	-	22
Open space	3.4	-	-

*Recommended values

[a]Cited in Novotny and Chesters (1980)

[b]Hydrologic Engineering Center (1977)

$$Y_t = [1 - \exp(-1.8 Q_t)] \, X_t \qquad \text{(III-69)}$$

where

Q_t = runoff on day t (cm).

Conversely, if the streets are cleaned on day t:

$$S_t = e \, X_t \qquad \text{(III-70)}$$

where

e = street cleaning efficiency (fraction removed by cleaning).

It is assumed that streets are not cleaned on the same day that a runoff event occurs.

Sediment accumulations and removal are illustrated in the following example.

Urban Sediment Accumulation and Removal

A storm occurs on May 31 which removes all sediment from an urban area. Subsequent storms occur on June 9 and June 15 which produce 0.5cm and 1.1cm of runoff, respectively. On June 6, the streets are cleaned with an efficiency $e = 0.4$. The daily sediment buildup is $x = 80$ kg/ha. How much sediment is contained in the runoff from the June 15 storm?

Solution:

Letting May 31 be day $t = 0$, the next event is the cleaning on day 6 (June 6). Accumulated sediment is $X_6 = 6(80) = 480$ kg/ha.
Cleaning removes:

$$S_6 = 0.4(480) = 192 \text{ kg/ha}$$

and on June 7, remaining sediment is:

$$X_7 = X_6 - S_6 + x$$
$$= 480 - 192 + 80 = 368 \text{ kg/ha}.$$

For the June 9 runoff event, $X_9 = 368 + 2(80) = 528$ kg/ha. Sediment washoff from Equation III-69 is:

$$Y_9 = [1 - \exp(-1.8(0.5))] \, 528$$
$$= 313 \text{ kg/ha}.$$

On the following day:

$$X_{10} = X_9 - Y_9 + 80$$
$$= 528 - 313 + 80$$
$$= 295 \text{ kg/ha}.$$

On June 15, $X_{15} = 295 + 5(80) = 695$ kg/ha, and sediment washoff in the 1.1 cm of runoff is:

$$Y_{15} = [1 - \exp(-1.8(1.1))] \, 695$$
$$= 599 \text{ kg/ha}$$

3.6.2.3 Pollutant Concentrations

Pollutant concentrations in sediment can be obtained from sampling of sediment accumulations in street gutters or sampling of storm sewer flows. General values for conventional pollutants are given in Table III-23. Concentrations of metals and organic compounds are given in Tables III-24 and 25.

TABLE III-23

CONCENTRATIONS OF CONVENTIONAL POLLUTANTS

IN URBAN SEDIMENT (SARTOR AND BOYD, 1972,

CITED IN NOVOTNY AND CHESTERS, 1980)

	Land Use		
Pollutant	Residential (mg/kg)	Commercial (mg/kg)	Industrial (mg/kg)
BOD$_5$	9,200	8,300	7,500
COD	20,800	19,400	35,700
Kjeldahl Nitrogen	1,700	1,100	1,400
Nitrate-Nitrogen	50	500	60
Phosphate-Phosphorus	900	800	1,200

TABLE III-24

CONCENTRATIONS OF METAL IN URBAN SEDIMENT

(AMY, et al, 1974)

	Residential (mg/k)	Commercial (mg/k)	Industrial		Weighted Mean (mg/kg)
			Light	Heavy	
			(mg/kg)		
Cd	3.0	4.2	4.0	3.9	3.4
Cr	192	225	288	278	211
Cu	93	133	128	107	104
Fe	20,600	23,300	21,800	28,600	22,000
Pb	1,430	3,440	2,780	1,160	1,810
Mn	392	397	490	570	418
Ni	28	48	41	37	35
Sr	21	18	27	23	21
Zn	350	520	368	317	370

TABLE III-25

CONCENTRATIONS OF MERCURY AND ORGANIC COMPOUNDS

IN URBAN SEDIMENT (AMY, et al, 1974)

Pollutant	Concentration (mg/kg)
Hg	0.083
Endrin	0.0002
Dieldrin	0.028
PCB	0.770
Methoxychlor	0.500
DDT	0.076
Lindane	0.0029
Methyl Parathion	0.002
DDD	0.082

3.6.2.4 Loading Computations

The basic loading function for pollutants from urban runoff events (Equation III-57) is deceptively simple. Storm runoff and sediment accumulation, which are required by the loading function, depend on dynamic processes and are not easily computed. If the Curve Number Equation (Equation III-3) is used for runoff, curve numbers must be selected based on antecedent precipitation. Conversely, the runoff coefficient/depression storage runoff equation (Equation III-60) requires the daily moisture calculations indicated by Equations III-61 and 62. Sediment accumulation is determined using Equations III-66, 68, 69, and 70.

Event-based urban runoff loading computations are too complex to be routinely done by hand. Although the following example demonstrates that hand calculations are possible, loading estimates are most efficiently done by computer. Indeed, the equations described in this section are the basis of the STORM computer model of urban runoff waste loads.

———————————————— EXAMPLE III-10 ————————————————————

Lead in Urban Runoff From a Storm Event

Estimate the washoff of lead from a 200-ha urban area during a 2-cm rainstorm. The area has a population density of 25 persons/ha and is 60% residential and 40% commercial. The previous storm 20 days ago washed the area clean. Streets were cleaned 9 days ago with an efficiency of 55%. Daily evaporation rate during the 20-day period was 0.2 cm/day.

Solution:

Since this is a multi-land use area, we will use weighted loads as in Equations III-59 and 57. Equation III-60 will be used to compute runoff:

$$Q = CR(P - DS)$$

To obtain runoff and depression storage coefficients from Equations III-63 and 64, the impervious fraction I must be calculated from Equation III-65:

$$I = 0.069 \ PD^{0.48}$$
$$= 0.069(25)^{0.48} = 0.32$$

Using the typical coefficients for impervious and pervious areas given in Section 3.6.2.1:

$$CR = 0.90(0.32) + 0.15(0.68) = 0.39$$
$$DS^* = 0.15(0.32) + 0.60(0.68) = 0.46cm$$

Since maximum depression storage is 0.46cm, and daily evaporation is 0.2 cm/day, depressions will dry within three days. Therefore, on the day of the storm DS = 0.46cm, and runoff is:

$$Q = 0.39(2-0.46) = 0.60cm$$

From Equation III-57:

$$L = 10^{-6} [1 - exp(-1.8(0.60))] \ CX$$
$$= 0.66(10)^{-6} \ CX$$

Thus 66% of the accumulated lead (CX) is washed off by the storm.

Daily sediment accumulation rates can be obtained from Table III-22. Assuming that the residential area is divided equally between single-family and multi-family residences, rates are (48+66)/2 = 57 kg/km-day for the residential area (60%) and 69 kg/km-day for the commercial portion (40%). The weighted average is:

$$z = 0.60(57) + 0.40(69) = 61.8 \ kg/km-day$$

Curb length density from Equation III-67 is:

$$Cl = 0.31 - 0.27(0.93)^{25} = 0.266 \ km/ha$$

and daily loading is:

$$x = 0.266(61.8) = 16.4 \text{ kg/ha}.$$

On day 11, when streets are cleaned, $X = 11(16.4) = 180.4$ kg/ha. Cleaning removes 55%, leaving 81.2 kg/ha. On the storm day:

$$X = 81.2 + 9(16.4) = 229 \text{ kg/ha}.$$

Lead concentrations, from Table III-24, are 1430 mg/kg and 3440 mg/kg for residential and commercial areas, respectively, producing a weighted average of:

$$C = 0.60(1430) + 0.40(3440) = 2234 \text{ mg/kg}.$$

Substituting these values of X and C in the loading function produces the lead load in runoff:

$$L = 0.66(10)^{-6} \, 2234(229) = 0.34 \text{ kg/ha}$$

or, over the 200-ha area:

$$200(0.34) = 68 \text{ kg}.$$

———————————————— END OF EXAMPLE III-10 ————————————————

3.7 GROUNDWATER WASTE LOADS

3.7.1 Characteristics

Groundwater pollution is of major concern because it endangers water supplies. Organic chemicals, nuclear wastes, nitrates and other compounds may leach from such sources as waste land application sites, storage lagoons, landfills, croplands, lawns, gardens and construction sites. The general characteristics of the problem are shown in Figure III-21. The figure shows a "waste" which has been buried beneath the soil surface. This waste could be contaminants such as PCBs in a landfill, septic tank drainage, fertilizers, pesticides, or toxic compounds in abandoned waste dumps. In other situations the wastes may be on the soil surface or contained in a storage lagoon. Chemicals are leached from wastes by percolation, and this leachate moves through the unsaturated soil zone to an underlying aquifer or saturated zone.

Groundwater pollution is often much more difficult to manage than pollution of surface waters. Since the water supply is beneath the soil surface, pollution effects are seldom visible. When contamination is detected in samples from monitoring wells or water systems, it is usually too late to eliminate the pollution source. Chemical movement through the unsaturated zone is relatively slow in the absence of fractures or other irregularities which channelize flows. In many soils, pollutants may move less than a meter per year. A chemical which is detected in a well may have begun its transit from an abandoned waste dump 20 years ago. Even if the dump is subsequently excavated, a 20-year supply of the chemical remains in the groundwater

PRECIPITATION

EVAPOTRANSPIRATION

IRRIGATION

WASTE

UNSATURATED ZONE

PERCOLATION
(LEACHATE)

WATER TABLE

AQUIFER (SATURATED ZONE)
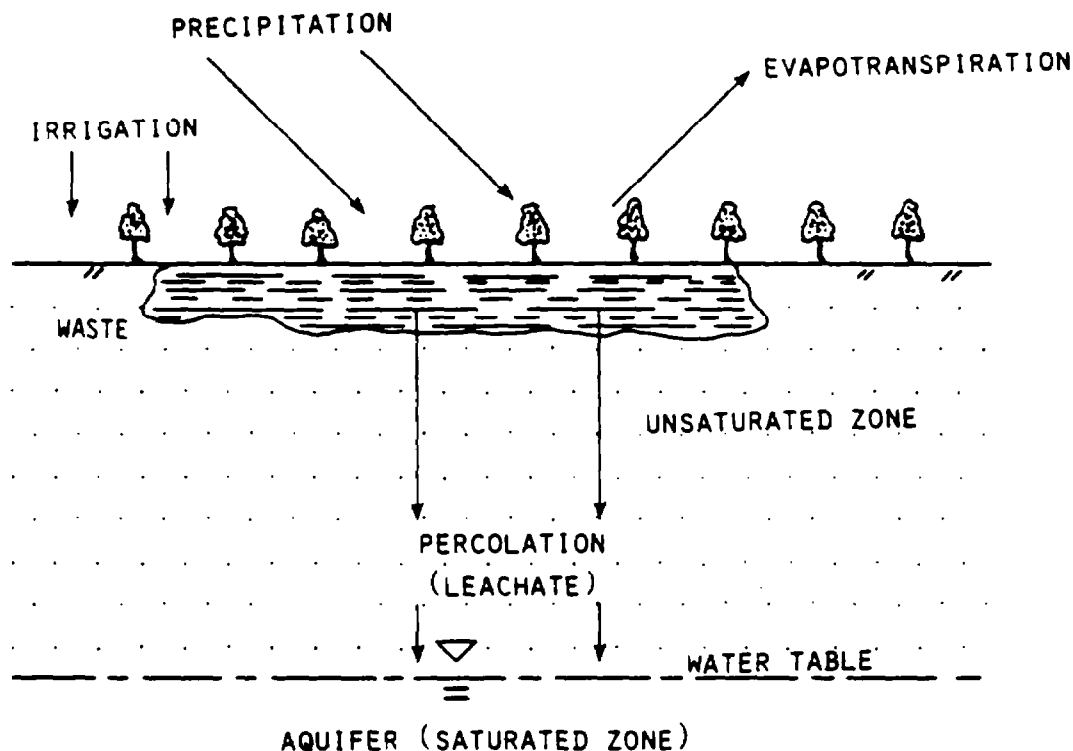
FIGURE III-21 POLLUTANT TRANSPORT TO AN AQUIFER

transport "pipeline". Compared to surface waters, the "flushing time" of aquifers is very long.

A further complication is the conservative nature of many pollutants in aquifers. Aquifers lack much of the self-purifying or assimilative capacity of surface waters. During transport through the aerated unsaturated zone, chemicals may be removed from leachate by plant uptake, volatilization, biochemical decay and adsorption. However, these removal mechanisms are often greatly reduced or eliminated once a chemical reaches the saturated zone.

Groundwater pollution problems are complex, and they are often analyzed by computer models based on the differential equations describing water and solute movement through porous media (Bachmat et al., 1980). These models are well beyond the scope of this screening manual. The discussion in this section is limited to simple procedures to estimate pollution loads to the saturated zone. Pollutant movement in the aquifer is not considered and steady-state, uniform one-dimensional flow is assumed. Since the time scale of groundwater pollution is measured in years, the loading estimates are annual values.

Succeeding subsections discuss water balances, nitrate loads from land application sites and leaching of organic chemicals.

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3.7.2 Water Balance

Little downward movement of a chemical is possible in the absence of percolation. Although some movement due to diffusion is possible, convection and dispersion associated with a water flux are the major transport mechanisms in the unsaturated zone. Based on the processes shown in Figure III-21, percolation is given by:

$$Q = P + I - E \qquad (III-71)$$

where

Q = annual percolation (cm)

I = annual irrigation (cm)

P = annual precipitation (cm)

E = annual evapotranspiration (cm).

Equation III-71 applies to a waste source in or on the soil surface which is not contained within an impermeable layer or storage lagoon. In the latter cases, percolation is equal to seepage or leakage through the layer or lagoon bottom.

Mean annual potential evapotranspiration minus precipitation is shown in Figure III-22. For a vigorous plant cover, ET is approximately equal to potential ET and the values in Figure III-22, converted to centimeters, can be used in Equation III-71 to provide a simple screening device for groundwater pollution. In the absence of irrigation, negative values of E-P (i.e. P > E and hence Q > 0) identify areas of potential groundwater pollution. Conversely, nonirrigated areas with positive E-P, and hence neglible percolation, are less likely to have contaminated groundwater.

These conclusions apply only when a vigorous plant cover is maintained on the waste site to maximize ET. A denuded or fallow site will produce little ET and maximize opportunities for percolation.

3.7.3 Nitrate Loads to Groundwater From Waste Application Sites

Municipal sewage and sewage sludges are often applied to land. Land application may thus eliminate a major surface-water pollution source, but it may also create a groundwater pollution problem. A major concern is the leaching of inorganic nitrogen, in the form of nitrate, from the wastes and subsequent transport to the saturated zone. Nitrate is extremely mobile in soils, and since it is toxic to infants and livestock, it is often considered the most critical pollutant from land application systems.

This subsection presents a simple nitrate loading calculation procedure adapted from Haith (1983). The procedure estimates nitrate concentrations as nitrogen in percolation from the root zone of a land application site.
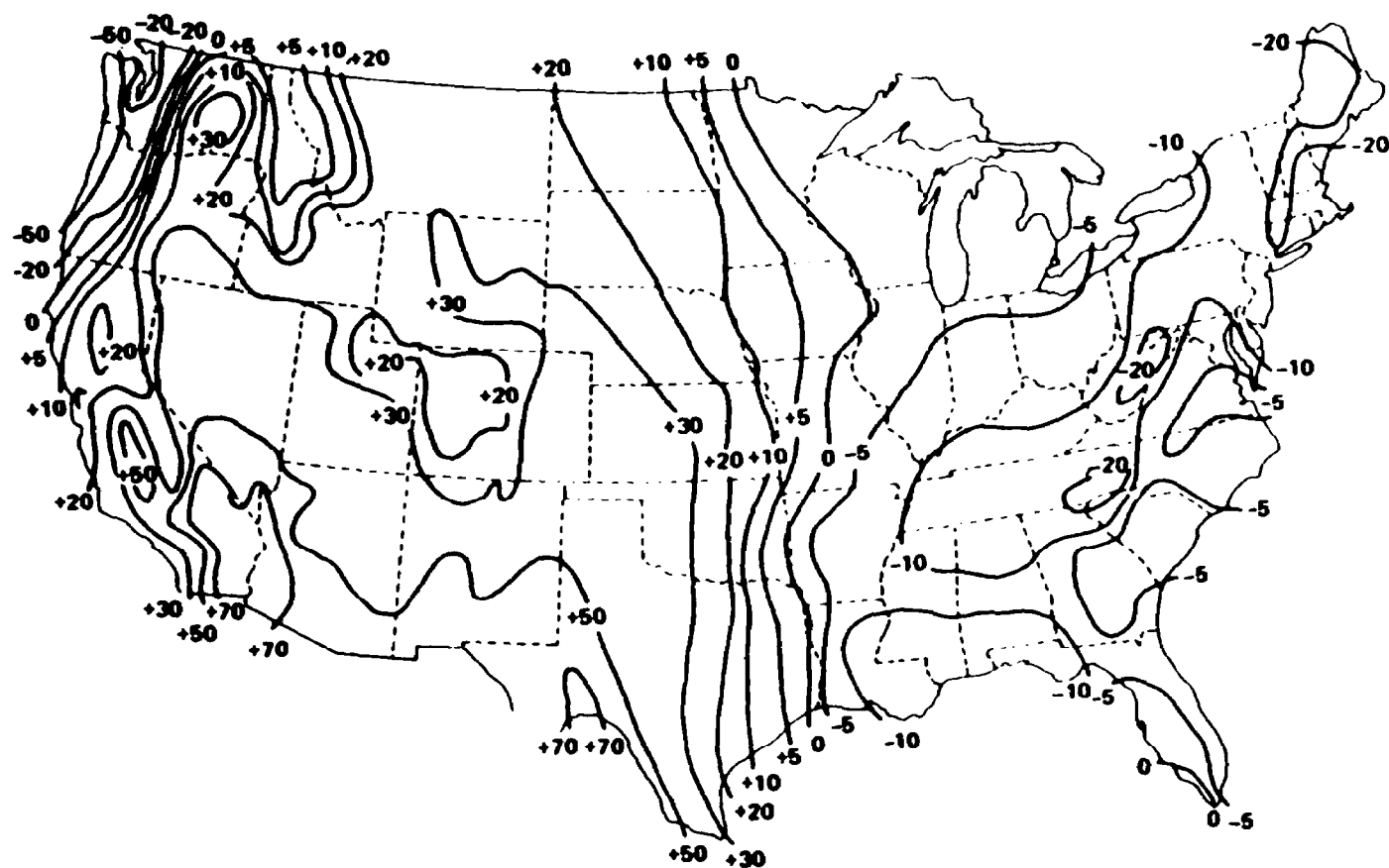
FIGURE III-22 MEAN ANNUAL POTENTIAL EVAPOTRANSPIRATION MINUS PRECIPITATION IN INCHES
(1IN = 2.54CM) (POUND ET AL, 1976)

3.7.3.1 Model Description

Components of the model are shown in Figure III-23. An annual application of nitrogen in waste is divided into organic and inorganic forms. Inorganic nitrogen is subject to volatilization losses, and the remainder is considered available for plant or crop uptake and leaching. Waste organic nitrogen consists of two components, a labile or readily mineralizable fraction which is available for plants and leaching during the first year following application, and a stabilized fraction which mineralizes at rates comparable to other forms of soil organic nitrogen. The available nitrogen supply thus consists of sludge inorganic nitrogen, rapidly mineralized sludge organic nitrogen and slowly mineralized so·' and sludge organic nitrogen. Since inorganic nitrogen in the soil is rapidly oxidized to nitrate, it is assumed that all available nitrogen is nitrate.

Annual mass balances for soil organic nitrogen and available nitrogen are:

$$O_{t+1} = O_t(1-m) + (1-a)1000 \ NFX_t \tag{III-72}$$

$$A_t = mO_t + (1-v)1000 \ N(1-F)X_t + a1000 \ NFX_t$$

$$= mO_t + 1000 \ N \ [(1-v)(1-F) + aF] \ X_t \tag{III-73}$$

where

O_t = soil organic nitrogen (including stabilized waste organic nitrogen) at beginning of year t (kg/ha)

X_t = waste application of dry solids in year t (t/ha)

m = annual mineralization rate for soil nitrogen

a = fraction of waste organic nitrogen mineralized during year of application

N = nitrogen fraction of solids

F = organic fraction of waste solids

A_t = available nitrogen (nitrate-nitrogen) in year t (kg/ha)

v = fraction of waste inorganic nitrogen which is volatilized.

Nitrogen loss by leaching is the difference between available nitrogen and crop uptake:

$$L_t = A_t - Cn_t \tag{III-74}$$

where

L_t = nitrate-nitrogen leachate in year t (kg/ha)

Cn_t = crop nitrogen uptake in year t (kg/ha).

Since there are no additional removal mechanisms for nitrate once it passes
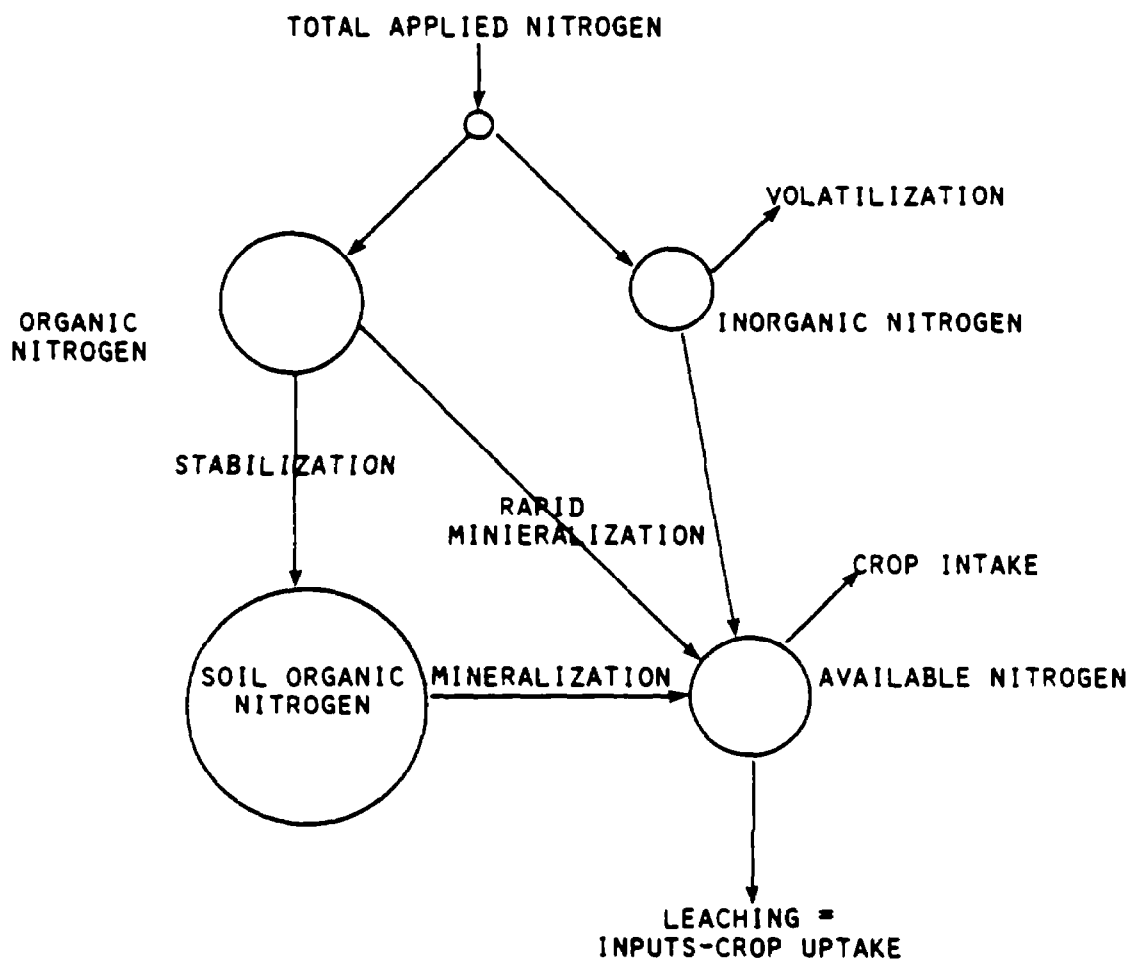
FIGURE III-23 NITROGEN DYNAMICS AT A LAND APPLICATION SITE

below the root zone, L_t is also the nitrate-nitrogen waste load to the saturated zone, although if the water table is well below the soil surface, the load may not reach the aquifer for several years.

3.7.3.2 Steady-State Loading Function

The loading calculation given by Equation III-74 is complicated somewhat by the need for sequential computations for soil organic nitrogen by Equation III-72. However, after many years of waste application at an average rate X (t/ha):

$$O_t = O_0(1-m)^t + BX [1 + (1-m) + (1-m)^2 + ...]$$

$$\approx O_0(1-m)^t + BX/m \qquad (III-75)$$

-236-

where

B = (1-a)1000 N F, and O_o is the initial soil organic nitrogen level.
The steady-state organic nitrogen level $\bar{O}$ is BX/m or:

$$\bar{O} = (1-a)1000 \ N \ F \ X/m \qquad\qquad (III-76)$$

Substituting $\bar{O}$ into Equations III-73 and 74 produces the steady-state
loading function:

$$L = 1000NX \ [1 - v(1-F)]-Cn \qquad\qquad (III-77)$$

where

L = annual steady-state nitrate-nitrogen load to groundwater (kg/ha)

X = average annual solids application rate (t/ha)

N = nitrogen fraction of solids

F = organic fraction of waste nitrogen

v = fraction of waste inorganic nitrogen which is volatilized

Cn = average crop nitrogen uptake.

3.7.3.3 Loading Function Data

Typical values for crop nitrogen uptake are given in Table III-26. Volatiliza-
tion rates (v) are based on the ammonium content of the waste and the method of
application. If the waste is sprayed or spread on the soil surface, all ammonia can
be assumed to volatilize. For example, if 70% of the inorganic nitrogen in the waste
is in the ammonium form, then v = 0.70. Conversely, when wastes are injected or
otherwise directly incorporated in the soil, there is little opportunity for
volatilization and v = 0.

Waste properties (X, N, F) will depend on the specific waste and the operation
of the disposal site.

```
r-------------------------------EXAMPLE III-11 ----------------------------------
|                                                                               |
|             Nitrate-Nitrogen Load from a Sludge Land Application Site          |
|                                                                               |
|   Determine the steady-state loading of nitrate-nitrogen from a land applica- |
| tion site for sewage sludge in central Florida. The sludge is spread on fescue at |
| an annual rate of 10t/ha. The sludge solids are 5% nitrogen and 70% of the    |
| nitrogen is organic. The inorganic nitrogen is 90% ammonia nitrogen. Also     |
| estimate the average nitrate-nitrogen concentration in percolation entering the |
| saturated zone.                                                               |
```

TABLE III-26

TYPICAL VALUES OF CROP NITROGEN

UPTAKE (POWELL, 1976)

Crop	Annual Nitrogen Uptake (kg/ha)
Forage Crops	
Coastal Bermuda Grass	540-670
Reed Canary Grass	250-400
Fescue	300
Alfalfa	160-250
Sweet Clover	180
Red Clover	90-140
Lespedeza Hay	150
Field Crops	
Corn	170
Soybeans	100-110
Potatoes	220
Cotton	70-110
Wheat	60-90
Sugar Beets	80
Barley	70
Oats	60
Forest	
Young Deciduous ($\leq$ 5 yrs)	110
Young Evergreen ($\leq$ 5 yrs)	70
Medium and Mature Deciduous	30-60
Medium and Mature Evergreen	20-30

Solution:

Equation III-76 is used to determine steady-state loading:

$$L = 1000NX [1 - v(1-F)]-Cn$$

where $X = 10$, $N = 0.05$, $F = 0.7$. Also, since the inorganic nitrogen is 90% ammonia and the sludge is spread on the soil surface, $v = 0.9$. Crop uptake Cn is 300 kg/ha from Table III-26.

$$L = 1000(0.05)10 [1-0.9(0.3)] -300$$
$$= 65 \text{ kg/ha}$$

To determine the nitrate-nitrogen concentration, percolation Q must be estimated. From Figure III-22, E-P = -5in = -12.7cm for central Florida. Neglecting water in the sludge, Equation III-71 indicates percolation

$$Q = P-E = 12.7cm$$

Since 1cm over 1 ha is 100 m^3, total percolation is 1270 m^3, and the nitrate-nitrogen concentration is

$$65/1270 = 0.051 \text{ kg/m}^3 = 51 \text{ mg/l}$$

which greatly exceeds the drinking water standard of 10 mg/l.

————————— END OF EXAMPLE III-11 —————————

3.7.4 Leaching of Organic Chemicals

The potential for groundwater pollution from an organic chemical is determined by adsorption and degradation processes. Organic chemicals are partially adsorbed by soil particles, and movement of a chemical is retarded or slowed compared to the movement of the percolation water. Degradation of organic compounds by biochemical processes and volatilization in the unsaturated zone will reduce the quantity of the chemical so that only a fraction of the original compound will remain to enter an aquifer. If the chemical is strongly adsorbed and rapidly degraded, and the water table is well below the soil surface, there is minimal chance of groundwater contamination. Conversely, pollution is favored by any of the following conditions: weak adsorption, slow degradation, or high water table.

3.7.4.1 Adsorption

Simple procedures for modeling movement of adsorbed chemicals are based on the concept of a retardation factor, R (Freeze and Cherry, 1979) which is defined as:

$$R = u/u_s \tag{III-78}$$

where

u = mean water velocity (cm/yr)

u_s = mean chemical (solute) velocity (cm/yr).

Hartley and Graham-Bryce (1980) have shown that R is equivalent to the ratio of total to dissolved chemical. Consider a soil element with volume one cm^3 containing an organic chemical which is both dissolved in soil water and adsorbed to soil particles. Total chemical in the element is:

$$C = fd + ba \qquad \text{(III-79)}$$

where

C = total chemical ($\mu g/cm^3$)

d = concentration of chemical in the soil water ($\mu g/cm^3$)

f = soil water content (cm^3/cm^3)

a = concentration of chemical on soil particles ($\mu g/g$)

b = soil bulk density (g/cm^3).

If we assume a linear equilibrium adsorption relationship:

$$a = K_D d \qquad \text{(III-80)}$$

where

K_D = adsorption partition or distribution coefficient (cm^3/g)

then the ratio of total to dissolved chemical is $(fd + bK_D d) / fd$, or:

$$R = 1 + (bK_D/f) \qquad \text{(III-81)}$$

The retardation factor is thus a function of a chemical property (K_D) and two soil properties (b and f). For flow in the unsaturated zone, the moisture content f is generally assumed to be field capacity. Typical field capacities and bulk densities are given in Table III-27. The partition coefficient K_D may be estimated from the octanol-water partition coefficient K_{ow} using Equations III-38 and III-36 as explained in Section 3.4.4.3.3.1. Values of K_{ow} for many organic compounds are given in Chapter 2 of this manual.

The retardation factor provides a general indication of a chemical's mobility in the soil. For nonadsorbed ions such as chloride and nitrate, R approaches unity and the chemical moves at approximately the same velocity as the percolation. For strongly adsorbed chemicals, R is much larger than one and movement through the soil is slow compared to the percolation velocity ($u_s << u$).

The retardation factor also is used to estimate the distance which a chemical moves in t years. Thus, $Z/X = ut/u_s t = R$, or:

$$X = Z/R \qquad \text{(III-82)}$$

where

> Z = water displacement during time t (cm)

> X = chemical displacement during time t (cm).

Assuming plug flow, annual water displacement (cm/yr) due to percolation is:

$$Z = Q/w \qquad (III-83)$$

where

> Q = annual percolation (cm)

> w = available water capacity (cm).

Available water capacity is used in Equation III-83 rather than field capacity or porosity since unsaturated soils drain to field capacity during percolation, and soil water held below wilting point does not participate in the flow process. Mean values of w are given in Table III-13 or may be computed from Table III-27 as w = field capacity - wilting point.

Equations III-83, 82 and 81 can be combined to estimate the mean annual downward movement of an organic chemical:

$$X = \frac{Q/w}{1 + bK_D/f} \qquad (III-84)$$

TABLE III-27

MEAN SOIL PROPERTIES (BAES AND SHARP, 1983)

Soil Type	Bulk Density (g/cm^3)	Field Capacity cm^3/cm^3	Wilting Point cm^3/cm^3	Porosity cm^3/cm^3
Silt loam	1.33	0.35	0.13	0.49
Clay and clay loam	1.30	0.36	0.22	0.51
Sandy loam	1.50	0.22	0.08	0.43
Loam	1.42	0.32	0.13	0.46

Due to dispersion, portions of the chemical will be displaced greater or lesser distances than X. If a chemical is initially at the soil surface, the location of its center mass after percolation Q is given by X (see Figure III-24).

The time required for the chemical center of mass to reach the aquifer, and hence the mean travel time of the chemical through the unsaturated zone is:

$$T = 100H/X \qquad \text{(III-85)}$$

where

T = mean time for a chemical to reach the water table (yr)

H = depth to the water table (m).

3.7.4.2 Degradation

In the absence of chemical decomposition, even strongly adsorbed chemicals will eventually reach aquifers. The degree of groundwater pollution by an organic chemical is very much influenced by degradation or decay rates. Degradation of organic compounds is discussed in detail in Chapter 2 of this manual. A first order process is generally assumed such that:

$$C(t) = C(0) \exp(-k_s t) \qquad \text{(III-86)}$$

where

$C(t)$ = chemical in the soil at time t (g/ha)

k_s = decay rate (yr^{-1}).

Equation III-86 may be used to estimate the chemical mass entering the saturated zone. From Equation III-85, the average travel time to the water table is T and hence the chemical entering the saturated zone is:

$$C(T) = C(0) \exp(-k_s T) \qquad \text{(III-87)}$$

where

$C(T)$ = chemical mass entering the water table T years after leaching begins (g/ha)

$C(0)$ = initial chemical mass at the soil surface (g/ha).

Equation III-87 is only approximate because due to dispersion, portions of the chemical will require more or less time than T to reach the aquifer. Moreover, decay rates (k_s) are uncertain for most chemicals. Although representative values are
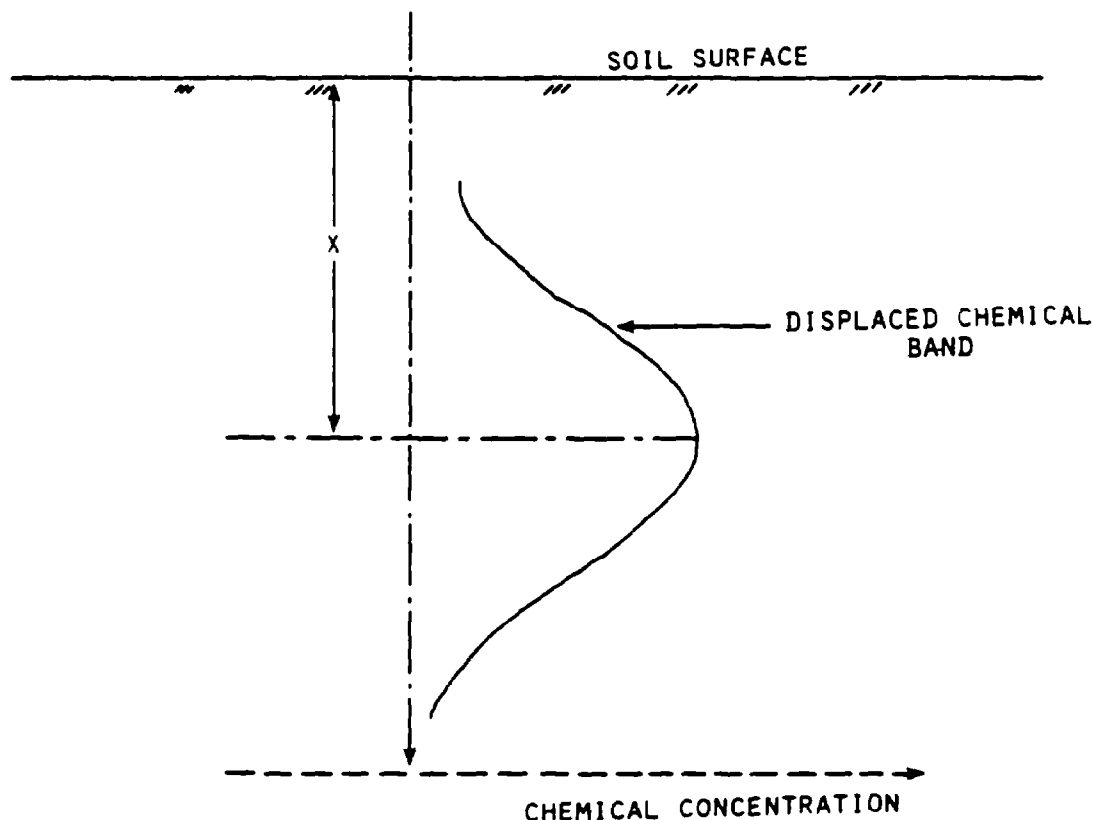
FIGURE III-24 DOWNWARD MOVEMENT OF A CHEMICAL IN SOIL

given in Chapter 2, most reported rates were measured in waste treatment systems and surface waters. Few data are available for estimation of decay rates in the subsoil.

3.7.4.3 Groundwater Loads of Organic Chemicals

Equations III-84, 85 and 87 may be used to estimate organic chemical loads to aquifers. Due to the limitations of the equations (linear adsorption, first order decay, dispersion, uncertain rates, homogeneous porous media), the calculated loads should only be considered "order-of-magnitude" estimates.

EXAMPLE III-12

Napthalene Leaching from a Waste Storage Site

50,000 g/ha of napthalene is leaching from an abandoned waste disposal site. The site is on a sandy loam with 1% organic matter. Water table depth is 1.5m. Mean annual percolation is 40cm. Based on the information in Chapter 2, napthalene has an octanol-water partition coefficient of $K_{ow} = 2300$ and a

half-life of 1700 days.

How much napthalene will reach the aquifer and what will be the resulting napthalene concentration at the water table surface?

Solution:

Equations III-36, 37 and 38 must be used to estimate the partition coefficient K_D:

$$K_D = K_{oc} \ (\%OC/100) \qquad\qquad (III-36)$$

$$\%OC = 0.59 \ (\%OM) \qquad\qquad (III-37)$$

$$K_{oc} = 0.66 \ K_{ow}^{1.029} \qquad\qquad (III-38)$$

The organic carbon partition coefficient is:

$K_{oc} = 0.66(2,300)^{1.029} = 1900$

$\%OC = 0.59(1) = 0.59$

$K_D = 1900(0.59/100) = 11.2$

Bulk density (b), field capacity (f) and available water capacity (w) may be estimated from the data in Table III-27 for sandy loams:

$b = 1.5 \ g/cm^3$

$f = 0.22 \ cm^3/cm^3$

$w = 0.22-0.08 = 0.14 cm^3/cm^3$.

Annual napthalene movement is given by Equation III-84:

$$X = \frac{40/0.14}{1 + 1.5(11.2)/0.22} = 3.7 \ cm/yr \qquad\qquad (III-84)$$

Average time to reach the water table is:

$$T = 100 \ H/X \qquad\qquad (III-85)$$

or

$T = 100(1.5)/3.7 = 40.5 \ yr.$

To use Equation III-87 to calculate the napthalene remaining after 40.5 years, we must first determine the decay rate k_s. From Equation III-86, when t = half-life = 1700/365 = 4.66 yr, $C(t) = 0.5C(0)$. Hence:

$0.5 = exp(-4.66k_s)$

or

$$k_s = -\ln(0.5)/4.66 = 0.149$$

Using Equation III-87:

$$C(T) = 50,000 \exp [-0.149(40.5)]$$
$$= 120 \text{ g/ha}$$

Thus approximately 120 g/ha of the original 50,000 g/ha will eventually leach into the aquifer. The center of mass of the napthalene will reach the aquifer in a little over 40 years.

To determine the napthalene concentration in water at the aquifer surface, we must first divide the 120 g/ha into dissolved and adsorbed components. The retardation factor R is the ratio of total to dissolved chemical. Equation III-81 gives:

$$R = 1 + bK_D/f$$
$$= 1 + 1.5(11.2)/0.22 = 77$$

The dissolved napthalene mass is 120/R:

$$120/77 = 1.56 \text{ g/ha}$$

Assuming this mass is dissolved in one year's percolation flow, 40cm = 4000m^3/ha, the concentration is 1.56/4000 = 0.00039 g/m^3 = 0.39 μg/l.

─────────────── END OF EXAMPLE III-12 ───────────────

3.8 ATMOSPHERIC WASTE LOADS

Atmospheric waste loads are direct mass inputs of pollutants from the atmosphere to surface wate . These loads occur as a result of both dry deposition and scavenging by precipitation. For the purposes of water quality screening studies, atmospheric loads are often considered constant, and are best determined by monitoring. The sum of atmospheric and background waste load (see Section 3.3), generally constitutes the minimum pollution input to a surface water body.

Regional data are available for a limited number of pollutants. Figure III-25 and Table III-28 indicate atmospheric nutrient loads for regions in the U.S.

3.8.1 Dry Deposition

Pollutants occur in the atmosphere as 1) particulates; 2) gases; or 3) dissolved in water vapor. Cautreels and Van Cauwenberghe (1978) give distribution coefficients between the gas and particulate phases for 55 aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, phthalic acid esters, fatty acid esters, aromatic acids and basic compounds.

Both particulates and gases may settle out onto receptor surfaces. For particles

TABLE III-28

ATMOSPHERIC CONTRIBUTIONS OF NITROGEN AND PHOSPHORUS IN PRECIPITATION

	N Contribution in Kg/ha/yr				P Contribution in Kg/ha/yr			
	NO_3-N+NH_4-N		Total N		Inorganic P		Total P	
	Low	High	Low	High	Low	High	Low	High
Northeastern U.S.	5.7	12.1	5.7	12.1	-	-	-	-
Southeastern U.S.	1.5	12.3	-	-	-	-	-	-
Midwestern U.S.	0.2	20.9	1.7	20.9	-	-	-	-
West/Southwestern U.S.	1.7	5.7	9.0	14.6	-	-	-	-
United States	-	-	-	-	0.18	0.18	0.08	0.80

Source: Weiner, et al. (1976)
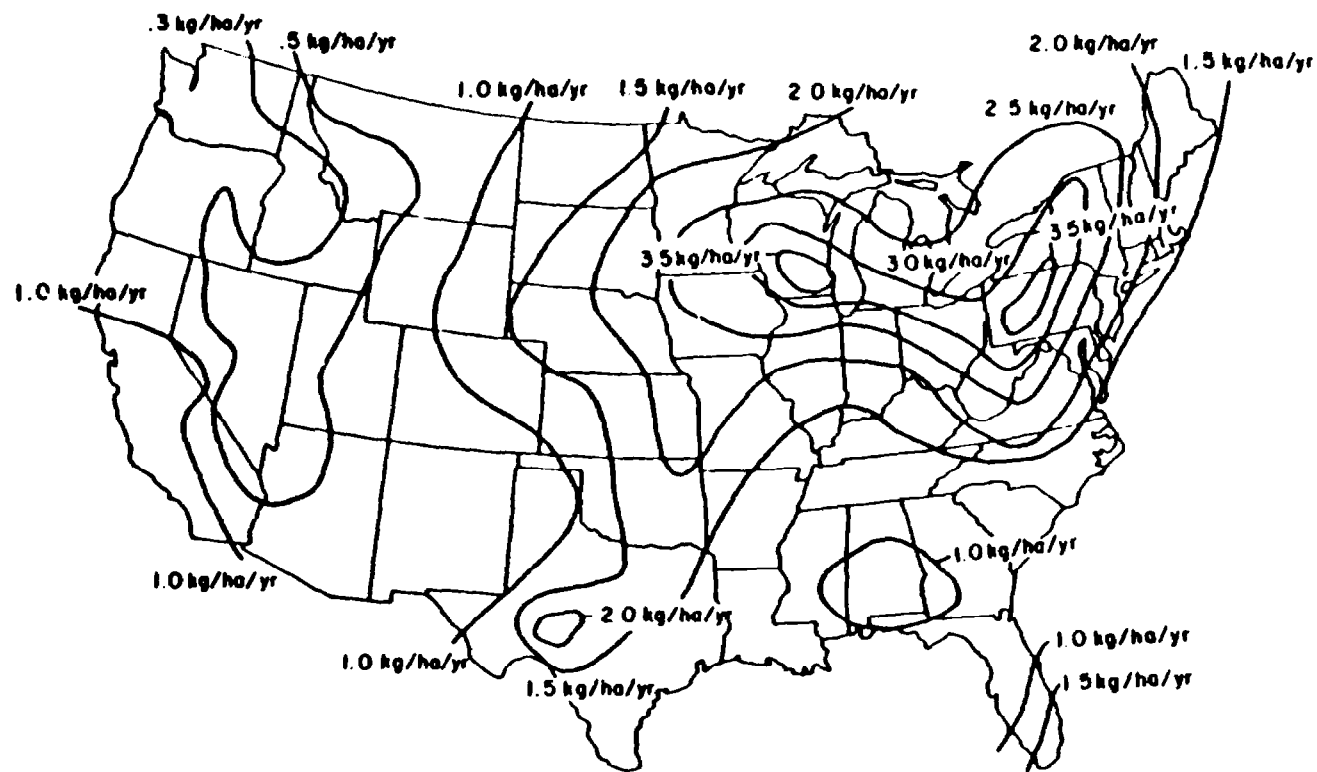
FIGURE III-25 NITROGEN (NH_4-N AND NO_3-N) IN PRECIPITATION, (PERSONAL COMMUNICATION WITH MRI, J.H. CRAVENS, REGIONAL FORESTER, U.S.D.A-FS EASTERN REGION, 1974)

< 0.3 μm in diameter, the major process is Brownian diffusion. For diameters 0.5 to 5 μm inertial impaction-interception governs and for diameters > 5 μm, gravitational settling is dominant. For gravitational settling. Stokes' Law may be used to predict the settling velocity. Since Stokes' Law is applicable only to quiescent media, it should give an upper bound for V_d (the deposition velocity). It is stated as:

$$V_d = \frac{g \, (ad)^2 \, (\rho - \rho_a)}{18\mu} \tag{III-88}$$

where

V_d = settling velocity (cm/sec)

a = conversion factor (10^{-4})

g = acceleration of gravity, 981.46 (cm/sec^2)

μ = viscosity of air, 0.000177 (g/cm-sec) at 10°C

ρ = particle density, ~ 2 (g/cm^3)

ρ_a = density of air, 0.01243 (g/cm^3) at 10°C

d = particle diameter (microns).

For particles < 5 μm in diameter Stokes Law is not applicable and experimental values for the deposition velocity should be used. Eisenreich et al. (1981) suggest values of V_d = 0.1 to 0.5 cm/sec for trace organics. Some experimental values are shown in Table III-29.

Once the settling velocity is known, the following procedure can be used to predict the dry deposition loadings:

$$L = V_d \, C_p \, A \, f \tag{III-89}$$

where

L = load of the pollutant delivered to the receptor surface as dry deposition (mass/sec)

V_d = particle settling velocity (m/sec)

C_p = concentration of atmospheric particulates (mass/m^3)

A = projected receptor area (m^2)

f = fraction (by mass) of the pollutant in the particulates.

Normally, smaller size particles are more chemically and physically reactive than larger particulates, and therefore pollutants will be associated with these smaller particles. Obviously the particle size to which pollutants are adsorbed affects their atmospheric residence time and, hence, loadings. According to Neff (1979), most polycyclic aromatic hydrocarbons are associated with particulates in the 1 to 2 micron range. Cautree:s and Cauwenberghe (1978) have shown that aerosol

TABLE III-29

FIELD-MEASURED DRY DEPOSITION VELOCITIES

Compound	V_d (cm/s)	Collection Surface
PCB (Aroclor 1242, 1254)	0.5	---
PCB	0.3-3	Mineral-oil-coated plates
PCB, DDT (gas phase)	0.19	Estimated
PCB, DDT	1.0	Estimated
PCB (total)	0.14	Glycerol-coated plates
PCB (Aroclor 1016)	0.04	Glycerin-water, Al pans
PCB	0.43	---

Source: Eisenreich et al., 1981

polycyclic aromatic hydrocarbons are associated with particles of median diameter
from 0.7 to 1.4μm. In addition, they give the concentrations of 50 trace organic
compounds associated with different size particles. Higher weight polycyclic aromatic
hydrocarbons, alkanes, and carboxylic acids had significant mass fractions associated
with >1 μm diameter particles.

— EXAMPLE III-13 —

Dry Atmospheric Deposition of Pollutants
Adsorbed to Particulates

Estimate the maximum daily loading of pyrene to a watershed having an area of
$10^6 m^2$ overlain by an air mass having a mean daily particulate concentration
of 50 μg/m^3. The average pyrene content of the particulates is 1.0×10^{-4}
μg-pyrene/μg. Assume a deposition velocity of 0.1 cm/sec.

Solution:

Compute the daily dry deposited load of pyrene, using Equation III-89:

$$L = V_d \, C_p \, A \, F$$

$$= 0.001 \, \frac{m}{sec} \quad \frac{50 \, \mu g}{m^3} \quad 10^6 m^2 \quad 1.0 \times 10^{-4} \, \frac{\mu g \; pyrene}{\mu g} \quad \frac{86400 \; sec}{day}$$

$$= 4.32 \times 10^5 \; \mu g/day$$

— END OF EXAMPLE III-13 —

Gas phase pollutants may also be deposited directly to the watershed surface.
In this case the loading equation is:

$$L = V_d \, C \, A \tag{III-90}$$

where

L	=	dry deposited load (mass/sec)
V_d	=	gas deposition velocity (m/sec)
A	=	receptor area (m^2)
C	=	ambient concentration of the gas phase pollutant (mass/m^3).

——————————————— EXAMPLE III-14 ———————————

Dry Atmospheric Deposition of Gaseous Pollutants

Estimate the annual deposition of toxaphene to a 1 ha area at Stoneville, MS during 1974. The mean monthly atmospheric concentrations are shown in Table III-30. Assume an average deposition velocity of 0.2 cm/sec for the entire year.

Solution:

$$L = \sum_{n=1}^{12} V_d \, C_n \, A \, t_n$$

Month n	V_d (m/sec)	C_n (ng/m^3)	A (m^2)	t_n (sec)	L (ng)
1	.002	10.9	10^4	31 x 86400	5.84×10^8
2	.002	9.7	10^4	28 x 86400	4.69×10^8
3	.002	19.1	10^4	31 x 86400	1.02×10^9
4	.002	27.7	10^4	30 x 86400	1.43×10^9
5	.002	44.3	10^4	31 x 86400	2.37×10^9
6	.002	38.6	10^4	30 x 86400	2.00×10^9
7	.002	175.0	10^4	31 x 86400	9.37×10^9
8	.002	903.6	10^4	31 x 86400	4.84×10^{10}
9	.002	524.6	10^4	30 x 86400	2.72×10^{10}
10	.002	114.8	10^4	31 x 86400	6.15×10^9
11	.002	32.9	10^4	30 x 86400	1.71×10^9
12	.002	12.6	10^4	31 x 86400	6.75×10^8

$$1.01 \times 10^{11} \text{ ng/year}$$

or __101.4 g/year__

TABLE III-30

AVERAGE MONTHLY ATMOSPHERIC LEVELS OF

FOUR PESTICIDES AT STONEVILLE, MISSISSIPPI

	Endrin (ngm^{-1})			Toxaphene (ngm^{-1})		
	1972	1973	1974	1972	1973	1974
January	1.	0.1	0.2	0.0	0.0	10.9
February	1.1	0.1	9.2	13.0	0.0	9.7
March	2.1	0.7	0.6	68.0	16.9	19.1
April	3.1	0.7	0.5	67.4	10.8	27.7
May	1.0	1.2	0.7	32.4	46.8	44.3
June	0.9	3.8	0.7	44.2	109.9	38.5
July	5.2	0.7	9.3	400.7	41.1	175.0
August	10.1	5.0	27.2	1540.0	268.8	903.6
September	8.5	8.4	18.8	827.9	322.6	524.6
October	4.0	5.0	4.3	97.9	161.1	114.9
November	0.5	1.1	1.0	9.3	0.0	32.9
December	0.0	0.2	0.5	0.0	9.9	12.5
Average	3.2	2.3	5.3	258.4	82.3	159.5

	Methyl Parathion (ngm^{-1})			Total DDT (ngm^{-1})		
January	0.0	0.0	1.0	10.8	3.9	3.0
February	0.0	0.0	0.3	12.6	4.8	3.6
March	0.0	0.0	0.3	32.6	11.1	7.6
April	0.0	0.0	0.6	34.1	11.4	7.7
May	0.0	0.0	0.6	17.2	18.6	15.6
June	1.6	22.8	0.9	16.2	49.5	12.8
July	61.4	4.5	40.9	117.3	9.6	24.3
August	216.9	129.3	341.1	515.3	25.6	37.9
September	111.7	791.1	167.9	378.8	24.6	19.4
October	1.4	17.1	2.0	37.6	18.9	5.1
November	0.0	0.0	0.0	14.5	11.9	3.3
December	0.0	0.1	0.0	6.3	2.4	2.1
Average	32.8	80.4	46.3	99.5	16.0	11.9

Source   Arthur et al (1976)

--- END OF EXAMPLE III-14 ---

3.8.2 Wet Deposition (Precipitation Scavenging)

Precipitation falling through the atmosphere tends to scavenge particulates and absorb gases so that it contains a variety of substances. Because of the volume of precipitation which generally occurs, it may constitute a significant pollutant loading. Load calculation for wet deposition is given by:

$$L = 10 \, C \, P \, A \tag{III-91}$$

where

    L = load of the pollutant delivered to the receptor as wet deposition (mass/sec)

    C = concentration of the pollutant in precipitation (mass/liter)

    P = precipitation rate (cm/sec)

    A = projected receptor area (m^2).

3.9 POINT SOURCE WASTE LOADS

The purpose of this section is to help users estimate waste loadings of toxic and conventional pollutants from municipal and industrial point sources. Removal efficiencies and discharge concentrations are both provided.

When possible site-specific data should be used in lieu of the guidance presented here. Since permitted dischargers are required to routinely monitor their discharges, often the point source data required are available.

When only a few measurements of effluent quality are available, those data may not be representative of long-term averages. Long-term averages are typically required for most of the steady-state analyses contained in this document. Figure III-26, for example, shows influent cadmium loading to the Kokomo, Indiana, wastewater treatment plant (Yost et al., 1981). Cadmium loading appears to exhibit a weekly cycle, with loadings the lowest on Sundays. For this case, seven-day averages would be appropriate for preliminary analyses.

When using the data presented in the following sections, users should keep in mind the variability of removal efficiencies and influent and effluent pollutant concentrations between point sources. The following factors all contribute to effluent quality variability:

    ● Geographic location

    ● Climate

    ● Mixture of influent sources (industrial/domestic)

    ● Size of community

    ● Design flow rate versus actual flow rate.
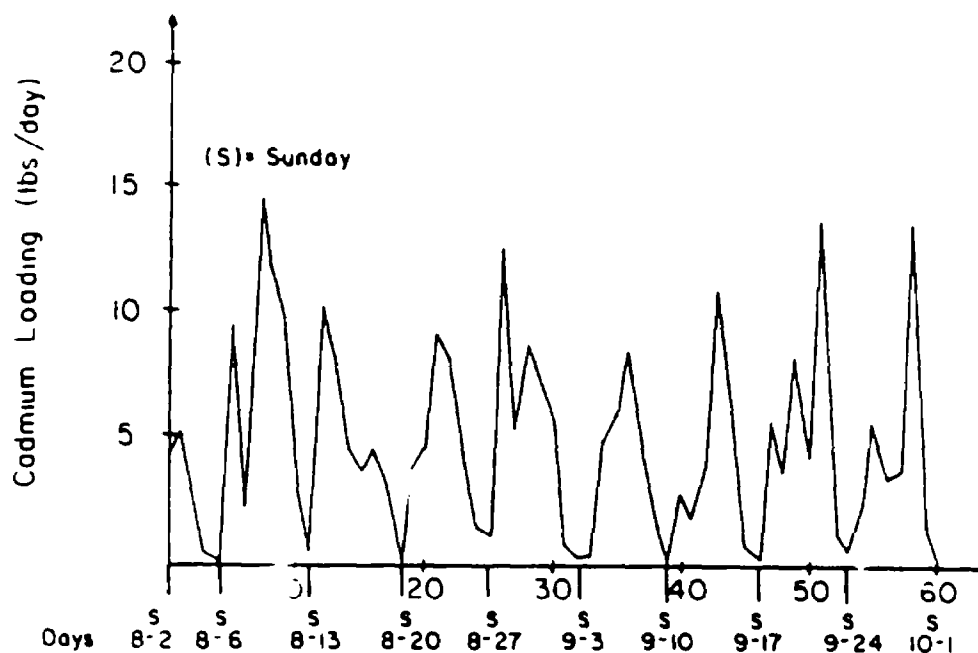
FIGURE III-26 INFLUENT CADMIUM LOADING TO PLANT DURING STUDY
(FROM YOST ET AL, 1981)

3.9.1 Municipal Waste Loads

Table III-31 summarizes typical influent concentrations of conventional pollutants for wastewater treatment plants. Concentration ranges are shown for strong, medium, and weak wastewater. Table III-32 summarizes typical removal efficiencies of common conventional pollutants from a variety of wastewater treatment plant types. Scheme number 0 in the table denotes the raw wastewater characteristics. The table shows both percent removal and effluent concentrations based on the characteristics of the raw wastewater chosen. The removal efficiencies can be used for the range of concentrations shown previously in Table III-31, assuming the plant is operating within design conditions.

Table III-33 summarizes effluent phosphorus and nitrogen concentrations for 662 primary treatment plants, trickling filters, activated sludge plants, and stabilization ponds. The data were collected as part of the National Eutrophication Survey initiated by the U.S. Environmental Protection Agency in 1972 (Gakstatler et al., 1978). The user can cross-compare effluent nutrient levels predicted based on joint use of Tables III-31 and III-32 against the values in Table III-33 to help get a typical range of values. Table III-33 also shows per capita flow rates, per capita total phosphorus loads, and per capita total nitrogen loads for each treatment type. These

TABLE III-31

TYPICAL INFLUENT MUNICIPAL WASTE CONCENTRATIONS

Constituent	Concentration mg/l		
	Strong	Medium**	Weak
Solids, total	1,200	720	350
Dissolved, total	850	500	250
Fixed	525	300	145
Volatile	325	200	105
Suspended, total	350	220	100
Fixed	75	55	20
Volatile	275	165	80
Settlable solids, (ml/liter)	20	10	5
Biochemical oxygen demand, 5-day, 20° (BOD_5-20°)	400	220	110
Total organic carbon (TOC)	290	160	80
Chemical oxygen demand (COD)	1,000	500	250
Nitrogen, (total as N)	85	40	20
Organic	35	15	8
Free ammonia	50	25	12
Nitrites	0	0	0
Nitrates	0	0	0
Phosphorus (total as P)	15	8	4
Organic	5	3	1
Inorganic	10	5	3
Chlorides*	100	50	30
Alkalinity (as $CaCO_3$)*	200	100	50
Grease	150	100	50

*Values should be increased by amount in carriage water.
**In the absence of other data use medium strength data for planning purposes.

Source: Metcalf and Eddy, 1979

TABLE III-32

MUNICIPAL WASTEWATER TREATMENT SYSTEM PERFORMANCE

Influent: see Scheme Number 0 for assumed characteristics.

| Scheme Number** | Effluent Concentrations (mg/l), (% Total Removal Efficiencies*) | | | | |
	BOD_5	COD	SS	P_T, (mgP/l)	N_T, (mgN/l)
0 Raw waste water	200(0%)	500(0%)	200(0%)	10(0%)	40(0%)
1	130(35%)	375(25%)	100(25%)	9(10%)	32(20%)
2	40(80%)	125(75%)	30(85%)	7.5(25%)	26(35%)
3	25(88%)	100(80%)	12(94%)	7(30%)	24(40%)
4	18(91%)	70(86%)	7(96%)	1(90%)	22(45%)
5	18(91%)	70(86%)	7(96%)	1(90%)	4(90%)
6	13(94%)	60(88%)	1(99.5%)	1(90%)	3(92%)
7	2(99%)	15(97%)	1(99.5%)	1(90%)	2(95%)

*Efficiencies for wastewater treatment are for the approximate concentration range, as measured by BOD_5, of $100 \leq BOD_5 \leq 400$, (mg/l).

**Scheme No.	Process
0	No treatment
1	Primary
2	Primary, plus Activated Sludge (Secondary Treatment)
3	Primary, Activated Sludge, plus Polishing Filter (High Efficiency or Super Secondary)
4	Primary, Activated Sludge, Polishing Filter, plus Phosphorus Removal and Recarbonation
5	Primary, Activated Sludge, Polishing Filter, Phosphorus Removal, plus Nitrogen Stripping and Recarbonation
6	Primary, Activated Sludge, Polishing Filter, Phosphorus Removal, Nitrogen Stripping Recarbonation, plus Pressure Filtration
7	Primary, Activated Sludge, Polishing Filter, Phosphorus Removal, Nitrogen Stripping Recarbonation, Pressure Filtration, plus Activated Carbon Adsorption

Source: Meta Systems, 1973

TABLE III-33

MEDIAN AND MEAN PHOSPHORUS AND NITROGEN CONCENTRATIONS AND MEDIAN LOADS IN WASTEWATER EFFLUENTS FOLLOWING FOUR CONVENTIONAL TREATMENT PROCESSES (Gakstatter et al., 1978)

		Treatment Type			
		Primary	Trickling Filter	Activated Sludge	Stabilization Pond
Number of Sampled Plants		55	244	244	119
Total Population Served		1,086,784	3,459,893	4,357,138	270,287
Ortho-P Conc. (mg/l)	Median	3.5 ± 0.29*	5.1 ± 0.21	4.6 ± 0.24	3.9 ± 0.34
	Mean	4.0 ± 0.62	5.4 ± 0.38	5.3 ± 0.40	4.8 ± 0.62
Total-P Conc. (mg/l)	Median	6.6 ± 0.66	6.9 ± 0.28	5.8 ± 0.29	5.2 ± 0.45
	Mean	7.7 ± 1.19	7.2 ± 0.50	6.8 ± 0.51	6.6 ± 0.81
Total-P Load (kg/cap·y)	Median	1.1 ± 0.10	1.2 ± 0.05	1.0 ± 0.06	0.9 ± 0.10
Total-N Load (kg/cap·y)	Median	3.7	2.9	2.4	2.0
Inorganic-N Conc. (mg/l)	Median	6.4 ± 1.00	7.1 ± 0.38	6.5 ± 0.45	1.3 ± 0.29
	Mean	8.3 ± 1.40	8.2 ± 0.60	8.4 ± 0.69	5.5 ± 1.95
Total-N Conc. (mg/l)	Median	22.4 ± 1.30	16.4 ± 0.54	13.6 ± 0.62	11.5 ± 0.84
	Mean	23.8 ± 3.48	17.9 ± 1.23	15.8 ± 1.16	17.1 ± 3.59
Total-N Load	Median	4.2 ± 0.40	2.9 ± 0.17	2.2 ± 0.15	2.0 ± 0.26
TN:TP Ratio	Median	3.4	2.4	2.4	2.2
Per Capita Flow (1/cap·d)	Median	473 ± 72	439 ± 19	394 ± 26	378 ± 38

*Value ± 1 standard error.

can be used to generate loadings based on population served. The typical per capita flow ranges between 378 and 473 ℓ/(cap-d).

Table III-34 summarizes phosphorus removal from plants that use chemical addition for phosphorus removal. The phosphorus removal efficiencies vary from 71 percent to 98 percent, and average 85 percent. This is only 5 percent lower than the percent phosphorus removals shown earlier in Table III-32 for process types 4 through 7 (which included phosphorus removal processes).

Barth and Stensel (1981) also summarize nitrogen removal performance of single-stage and two-stage activated sludge nitrification plants, but do not report removal efficiencies for the nitrification augmented processes.

Removal of metals and toxic organics from municipal wastewater treatment plants has been monitored over a considerably shorter historical time span than for the conventional pollutants. Table III-35 summarizes influent metal concentrations, effluent metal concentrations, and removal efficiencies for treatment plants at selected cities (Yost et al., 1981). From the table, it is clearly seen that there is a wide variability in influent metal concentrations, effluent concentrations, and removal efficiencies (even for the same type of treatment process). The variability of influent concentrations is not unexpected due to the variety of sources that contribute to municipal wastewater. Minear et al. (1981) have shown that the correlation between influent metal concentrations and percent industrial flow is very poor. Figure III-27 illustrates for copper. However, for a single treatment plant with fixed industrial sources, the correlation should be better.

E. C. Jordan Co. (1982) documents a 30-day study of priority pollutants at the Moccasin Bend wastewater treatment plant in Chattanooga, Tennessee. The plant is a 42 MGD conventional-activated sludge treatment plant that treats an average dry weather flow of 42 MGD. Approximately 50 percent of the flow originates from industry. Table III-36 summarizes the variability of influent priority pollutants, BOD, and TSS. Table III-37 summarizes the removal efficiencies for the primary and secondary units. Note the generally poor removal efficiencies associated with primary treatment. A number of the pollutants do not appear to be removed at all.

Table III-38 summarizes effluent concentrations in five Southern California wastewater treatment plants. Note that these are generally very large dischargers (four are over 100 MGD), and may not be typical of smaller plants. The effluent trace metal concentrations are, in many cases, higher than the influent concentrations at the Moccasin Bend plant.

The most comprehensive study to date on priority pollutants in publicly owned treatment plants was completed by Burns and Roe (1982). They collected data from 40 POTWs. Table III-39 summarizes the occurrence of priority pollutants in the influents and effluents of the 40 plants for pollutants detected in at least 10 percent of the samples. Note the high occurrence of metals in both influent and effluent samples.

TABLE III-34

YEARLY AVERAGE PHOSPHORUS REMOVAL PERFORMANCE (Barth and Stensel, 1981)

Plant	Design Capacity (mgd)	Flowsheet	Chemical & Addition Point		Performance, mg/l			Phosphorus Removal Efficiency
					BOD$_5$	TSS	Total P	
Angola, N.Y.	3.1	Extended aeration--solids contact--tertiary filter	FeCl$_3$ + polymer to solids contact	Infl. Effl.	130 2	264 2	6.8 0.9	87%
Ely, Minn.	1.0	Primary--rock trickling filter--solids contact--tertiary filter	Alum + polymer before secondary clarifier	Infl. Effl.	180 15	123 13	3.8 0.6	84%
Roanoke, Va.	35	Primary--2-stage activated sludge--nitrification--flocculation--tertiary filter	Pickle liquor to 1st stg. aeration and alum/polymer before floccula-tion basin	Infl. Effl.	220 2	340 1	11.9 0.2	98%
Rochester, N.Y.	20	Primary--activated sludge	Alum before final clarifier	Infl. Effl.	186 16	165 9	6.3 0.8	87%
Gladstone, Mich.	1.0	Primary--rotating biological contactor	Alum prior to RBC	Infl. Effl.	129 12	118 16	3.5 0.9	74%
Grand Haven, Mich.	3.2	Primary--activated sludge (domestic & tannery)	Pickle liquor be-fore primary	Infl. Efl.	389 16	432 19	5.0 0.6	88%
Blue Plains, D.C.	330	Primary--2-stage activated sludge--nitrification	FeCl$_3$ to secondary	Infl. Effl.	140 28	135 28	6.2 1.8	71%
Lima, Ohio	18.5	Primary--activated sludge--nitrification towers	FeCl$_3$ + polymer prior to primaries	Infl. Effl.	157 5	126 9	5.1 0.8	84%
Marlborough, Mass.	5.5	Primary--2-stage activated sludge--nitrification	Alum or FeSO$_4$ to 1st-stg. aeration	Infl. Effl.	159 3	306 8	6.8 0.6	91%

TABLE III-35

METAL CONCENTRATIONS AND REMOVAL EFFICIENCIES

IN TREATMENT PLANTS AT SELECTED CITIES

City	Treatment Received		Cd	Cr	Cu	Ni	Zn	Fe	Pb
Anderson, Indiana	Secondary Treatment	Influent, µg/l	9.5	1180	2820	2790	1500	-	160
		Effluent, µg/l	3.9	142	395	885	375	-	40
		Removal Efficiencies, %	59	88	86	41	75	-	75
Buffalo, New York	Secondary Treatment	Influent, µg/l	18	208	137	50	337	-	99
		Effluent, µg/l	11.2	78.6	53.4	44.5	704	-	25.9
		Removal Efficiencies, %	37.7	62.2	61.0	11.0	41.3	-	73.8
Dayton, Ohio	Trickling Filters	Influent, µg/l	27	-	-	-	-	-	-
		Effluent, µg/l	16	-	-	-	-	-	-
		Removal Efficiencies, %	40.7	-	-	-	-	-	-
Grand Rapids, Michigan	Secondary Treatment	Influent, µg/l	-	400	500	500	1200	-	-
		Effluent, µg/l	-	136-325	215-435	295-410	588-780	-	-
		Removal Efficiencies, %	-	19-66	13-57	18-41	35-51	-	-
Muddy Creek, Ohio	Conventional Activated Sludge	Influent, µg/l	8	-	-	-	-	-	-
		Effluent, µg/l	62.5	-	-	-	-	-	-
		Removal Efficiencies, %	3	-	-	-	-	-	-
Muncie, Indiana	Secondary Treatment	Influent, µg/l	-	240	260	140	1150	-	930
		Effluent, µg/l	-	53	83	140	345	-	167
		Removal Efficiencies, %	-	78	68	0	70	-	82

TABLE III-35

(Continued)

City	Treatment Received		Cd	Cr	Cu	Ni	Zn	Fe	Pb
Pittsburgh,	Secondary	Influent, µg/l	21	95	127	78	648	-	119
Pennsylvania	Treatment	Effluent, µg/l	7	31	56	70	227	-	23
		Removal Efficiencies, %	67	67	56	10	65	-	81
Wahiawa,	Step	Influent, µg/l	5-65	12-18	62-90	60-70	200-320	1000-1180	40-70
Hawaii	Aeration	Effluent, µg/l	2-27	8-12	16-23	35-41	53-93	150-177	11-19
		Removal Efficiencies, %	59	32	74	42	71	85	73
Winnipeg,	Pure	Influent, µg/l	-	166	210	32	329	-	117
Man.	Oxygen	Effluent, µg/l	-	53	48	32	66	-	60
		Removal Efficiencies, %	-	68	77	0	80	-	49
Burlington,	Conventional	Influent, µg/l	6	290	310	330	2400	1540	230
Ontario	Activated	Effluent, µg/l	1	61	84	277	552	416	16
	Sludge	Removal Efficiencies, %	80	79	73	16	77	73	93
Average of 6 Cities	-	Influent, µg/l	20.2	220	146	-	733	-	210
near Kansas City		Effluent, µg/l	-	-	-	-	-	-	-
		Removal Efficiencies, %	16	37	49	-	47	-	49
Survey of 20 Plants	-	Influent, µg/l	20	970	300	110	1120	6580	170
in Ontario		Effluent, µg/l	-	-	-	-	-	-	-
		Removal Efficiencies, %	19	62	54	42	56	69	51
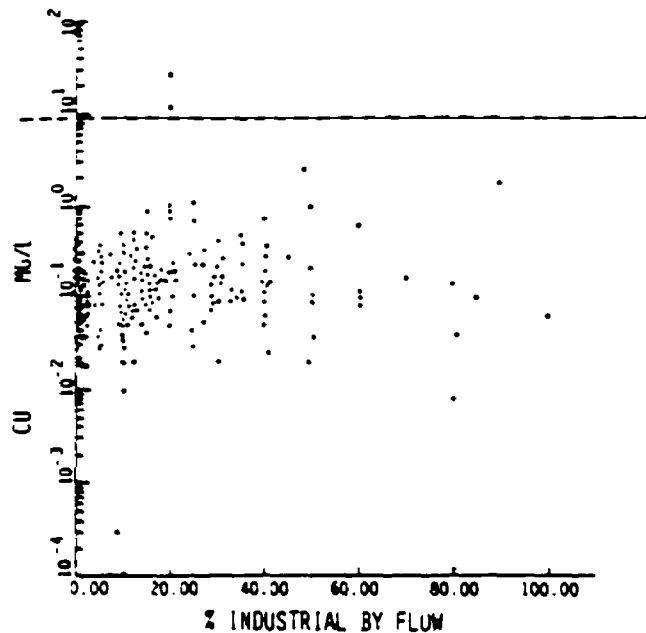
FIGURE III-27 INFLUENT COPPER CONCENTRATIONS TO WASTEWATER TREATMENT
PLANTS AS A FUNCTION OF PERCENT INDUSTRIAL FLOW

Table III-40 summarizes removal efficiencies of a number of the pollutants as a function of different types of treatment. There is a significant increase in percentage removal between primary treatment plants and secondary activated sludge treatment plants for each of the pollutants in the table.

3.9.2 Industrial Waste Loads

Compared to municipal discharges, effluent levels from industrial sources are less easily predictable because of the variety of categories and treatment processes used. Table III-41 shows 35 major industrial categories and frequently detected priority pollutants associated with the categories. Keith and Telliard (1979) have estimated the frequency of occurrence of the priority pollutants in industrial wastewater. Their results were shown previously in Table II-3. If industrial wastes are thought to contribute a significant percentage of pollutants to the water body being analyzed, the user should try to obtain more specific data on the industries present. Local agencies can provide effluent data for the industries in question. However, the industries may not be required to monitor for the specific pollutant(s) of concern. The Effluent Guidelines Division of the U.S. EPA can also provide guidelines for specific categories of pollutants. They have developed extensive documentation for each major industrial category. The "treatability manual" (USEPA, 1982 . b, c, d) is one such source that contains data related to approximately 200 pollutants associated with industrial processes. The manual contains the following information:

TABLE III-36

INFLUENT VARIABILITY ANALYSIS AT MOCCASIN BEND WASTEWATER TREATMENT PLANT

Parameter [1]	30-Day Study		Six-Day Study	
	Mean (µg/l)	Standard Deviation (µg/l)	Mean (µg/l)	Standard Deviation (µg/l)
Volatiles				
Benzene	18	10	14	8
1,1,1-Trichloroethane	30	49	43	49
Chloroform	73	36	77	59
1,2-Trans-Dichloro-ethylene	1	1	2	1
Ethylbenzene(2)	23	18	20	17
Methylene Chloride(2)	88	86	40	30
Toluene(2)	321	325	378	236
Trichloroethylene	26	51	10	12
Tetrachloroethylene	52	87	81	52
Acids				
Phenol	201	155	448	209
2,4-Dichlorophenol	5	7	2	2
Base Neutrals				
1,2,4-Trichlorobenzene	17	22	100	45
1,3-Dichlorobenzene	2	6	1	1
1,4-Dichlorobenzene	5	8	4	3
Naphthalene	11	11	55	45
Bis(2-Ethylhexyl) Phthalate	12	15	14	7
Di-N-Butyl Phthalate	5	14	4	2
Diethyl Phthalate	4	8	6	3
Phenanthrene	1	2	3	1
Metals				
Chromium	225	527	226	160
Copper	77	25	123	24
Cyanide	83	84	4747	1664
Mercury ng.l)	303	270	333	816
Nickel	73	76	98	37
Silver	5	2	21	7
Zinc	332	164	486	132
Conventional				
BOD5	303	115	435	112
TSS	232	93	327	95

1 Influent variability analysis conducted on priority toxic pollutants detected
  50 percent of the time or greater in addition to lead and cadmium for combined
  36-day period.
2 Outlier values were removed from data base.

TABLE III-37

SELECTED POLLUTANT MASS PERCENT REMOVALS AT

MOCCASIN BEND WASTEWATER TREATMENT PLANT

	Percent Removal		
Pollutant[1]	Primary Treatment	Secondary Treatment[2]	Overall Treatment
Metals			
Cadmium	25	42	56
Chromium	0	95	79
Copper	21	75	80
Cyanide	0	15	11
Lead	12	69	69
Mercury	21	100	100
Nickel	0	49	49
Silver	17	83	86
Zinc	18	70	75
Volatiles			
Benzene	7	78	80
1,1,1-Trichlorethane	13	80	82
Chloroform	1	56	56
1,2-Trans-Dichloroethylene	0	100	100
Ethylbenzene	0	89	87
Methylene Chloride	16	47	55
Tetrachlorethylene	25	88	91
Toluene	10	86	87
Trichloroethylene	42	78	87
Acids			
Phenol	0	92	91
2,4-Dichlorophenol	2	46	47
Base/Neutrals			
1,2,4-Trichlorobenzene	12	79	82
1,3-Dichlorobenzene	14	30	40
1,4-Dichlorobenzene	0	88	88
Naphthalene	0	92	91
Bis(2-Ethlyhexyl) Phthalate	0	77	57
Di-N-Butyl Phthalate	40	6	44
Diethyl Phthalate	0	36	0
Phenanthrene	0	36	0
Conventional/Non-Conventional			
BOD5	10	86	88
TSS	30	82	87

1 Priority toxic pollutants listed were detected in the influent wastewater 50 percent of the time or greater (with the exception lead and cadmium which were detected 46 percent of the time).

2 Percent removal based on mass removal in activated sludge treatment units alone.

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TABLE III-38

1981 EFFLUENT CONCENTRATIONS FROM FIVE SOUTHERN

CALIFORNIA WASTEWATER TREATMENT PLANTS

	JWPCP	Hyperion 5 mile	7 mile (Sludge)	Orange County	Point Loma	Oxnard
Flow MGD	364	369	4.72	212	130	17.7
General Constituents (mg/l)						
Suspended Solids	167	77	7,100**	119	114	56.9
Settled Solids	0.3	0.9		1.1	0.95	<0.1
BOD	202	169		151	161	114
Oil + Grease	23.3	22	353	21.1	29.3	12.2
NH3-N	39.3	16.1	-	25.7	27.7	17.0
Organic-N	14.0	7.3	266	-	-	5.09
Total-P	9.2	6.9	214	-	-	-
MBAS	5.37	4.12	-	-	4.38	-
CN	0.08	0.08	0.442	0.04	0.013	0.001
Phenols	2.85	0.06	0.37	0.09	0.073	0.10
Turbidity	79	63	-	79	53	44
Toxicity (T.U.)	4.2	0.81	-	1.0	1.3	2.1
Trace Metals (µg/l)						
Ag	8.0	25.0	739.0	13.0	13.0	3.0
As	5.0	12.0	183.0	3.0	5.0	20.0
Cd	16.0	17.0	892.0	26.0	8.0	3.0
Cr	11.0	54.0	3,340.0	82.0	43.0	0.1
Cu	154.0	200.0	9,320.0	248.0	133.0	93.0
Hg	1.8	0.7	36.0	0.4	0.8	0.05
Ni	148.0	108.0	2,400.0	69.0	7.5	6.0
Pb	0.0	50.0	2,000.0	74.0	136.0	11.0
Se	29.0	1.0	44.0	-	-	-
Zn	500.0	217.0	11,800.0	220.0	190.0	91.0
Chlorinated Hydro-carbons (µg/l)						
DDT	0.84	0.050	0.58	0.02	0.084	Not detected
PCB	0.54	0.76	3.05	1.55	0.665	<0.033
TICH	1.61	0.94	4.68	1.56	0.816	<0.033

*except as noted
**Total solids

TABLE III-39

OCCURRENCE OF PRIORITY POLLUTANTS IN POTW
INF_ENTS AND EFFLUENTS FOR POLLUTANTS DETECTED
IN AT LEAST 10 PERCENT OF THE SAMPLES (BURNS AND ROE, 1982)

Parameter	Number of Samples Analyzed	Number of Times Detected	Percent of Samples Where Detected	Units	Minimum Value Detected	Maximum Value
Zinc	282	282	100	ug/1	22	9250
Cyanide	284	283	100	ug/1	3	7580
Copper	282	281	100	ug/1	7	2300
Toluene	288	276	96	ug/1	1	13000
Chromium	282	268	95	ug/1	8	2380
Tetrachloroethylene	288	273	95	ug/1	1	5700
Methylene chloride	288	266	92	ug/1	1	49000
bis(2-Chloroethoxy)methane	287	265	92	ug/1	2	670
Chloroform	288	263	91	ug/1	1	430
Trichloroethylene	288	260	90	ug/1	1	1800
1,1,1-Trichloroethane	288	244	85	ug/1	1	30000
Ethylbenzene	288	231	80	ug/1	1	730
Nickel	282	224	79	ug/1	5	5970
Phenol	288	220	79	ug/1	1	1400
Silver	282	208	71	ug/1	2	320
Mercury	282	196	70	ng/1	200	4000
Di-n-butyl phthalate	287	185	64	ug/1	1	140
Lead	282	176	62	ug/1	16	2540
1,2-trans-Dichloroethylene	288	179	62	ug/1	1	200
Benzene	288	175	61	ug/1	1	1560
Butyl benzyl phthalate	287	165	57	ug/1	2	560
Cadmium	282	157	56	ug/1	1	1800
Diethyl phthalate	287	151	53	ug/1	1	42
Napthalene	287	142	49	ug/1	1	150
1,1-Dichloroethane	288	89	31	ug/1	1	24
Pentachlorophenol	287	84	29	ug/1	1	640

TABLE III-39

(Continued)

	INFLUENT					
Parameter	Number of Samples Analyzed	Number of Times Detected	Percent of Samples Where Detected	Units	Minimum Value Detected	Maximum Value
Y-BHC	288	75	26	ng/l	20	3900
1,1-Dichloroethylene	288	74	26	ug/l	1	243
1,2-Dichlorobenzene	287	67	23	ug/l	1	440
Phenanthrene	287	57	20	ug/l	1	93
Anthracene	287	52	18	ug/l	1	93
1,4-Dichlorobenzene	287	49	17	ug/l	2	200
Arsenic	282	43	15	ug/l	2	80
1,2-Dichloroethane	288	42	15	ug/l	1	76000
Antimony	282	39	14	ug/l	1	192
Chlorobenzene	288	36	13	ug/l	1	1500
Dimethyl phthalate	287	33	11	ug/l	1	110
Methyl chloride	288	33	11	ug/l	1	1900
1,2,4-Trichlorobenzene	287	28	10	ug/l	3	4300
2,4-Dimethylphenol	288	28	10	ug/l	1	55

	EFFLUENT					
Parameter	Number of Samples Analyzed	Number of Times Detected	Percent of Samples Where Detected	Units	Minimum Value Detected	Maximum Value
Cyanide	276	268	97	ug/l	2	2140
Zinc	289	272	94	ug/l	18	3150
Copper	289	263	91	ug/l	3	255
Methylene chloride	302	260	86	ug/l	1	62000
Chromium	289	247	85	ug/l	2	759
bis(2-Ethylhexyl) phthalate	302	254	84	ug/l	1	370

TABLE III-39

(Continued)

Parameter	EFFLUENT					
	Number of Samples Analyzed	Number of Times Detected	Percent of Samples Where Detected	Units	Minimum Value Detected	Maximum Value
Chloroform	302	247	82	ug/l	1	87
Tetrachloroethylene	302	239	79	ug/l	1	1200
Nickel	289	216	75	ug/l	7	679
Toluene	302	160	53	ug/l	1	1100
Di-n-butyl phthalate	302	158	52	ug/l	1	97
1,1,1-Trichloroethane	302	157	52	ug/l	1	3500
Trichloroethylene	302	137	45	ug/l	1	230
Y-BHC	303	99	33	ng/l	10	1400
Mercury	288	86	31	ng/l	200	1200
Phenol	302	87	29	ug/l	1	89
Cadmium	289	81	28	ug/l	2	82
Silver	289	73	25	ug/l	1	30
Ethylbenzene	302	73	24	ug/l	1	49
Benzene	302	69	23	ug/l	1	72
Lead	289	61	21	ug/l	20	217
Pentachlorophenoi	301	63	21	ug/l	1	440
Dichlorobromomethane	302	47	16	ug/l	1	6
Diethyl phthalate	301	39	13	ug/l	1	7
1,2-trans-Dichloroethylene	302	39	13	ug/l	1	17
Antimony	289	37	13	ug/l	1	69
Arsenic	289	35	12	ug/l	1	72
Butyl benzyl phthalate	302	34	11	ug/l	1	34
Selenium	289	29	10	ug/l	1	150
1,1-Dichloroethylene	302	29	10	ug/l	1	11

TABLE III-40

MEDIAN PERCENT REMOVALS OF SELECTED POLLUTANTS
THROUGH POTW TREATMENT PROCESSES (BURNS AND ROE, 1982)

Parameter	Primary		Secondary Activated Sludge *		Secondary Trickling Filter		Secondary O₂ Activated Sludge		Secondary Rotating Biological Contactors		Secondary Aerated Lagoon		Parallel Activated Sludge/Trickling Filter Plants — Activated Sludge Side		Parallel — Trickling Filter Side		Tertiary	
BOD	(12)	19	(22)	90	(5)	77	(3)	91	(1)	92	(1)	80	(4)	92	(4)	82	(8)	93
Total suspended solids	(12)	45	(22)	90	(5)	78	(3)	84	(1)	58	(1)	77	(4)	94	(4)	91	(8)	94
Cadmium	(6)	15	(6)	85	(1)	11	(2)	83	(0)	-	(1)	44	(2)	91	(2)	84	(3)	78
Chromium	(12)	27	(22)	84	(3)	48	(3)	76	(0)	-	(1)	49	(4)	75	(4)	63	(8)	89
Copper	(12)	22	(22)	84	(5)	49	(3)	92	(1)	97	(1)	21	(4)	89	(4)	75	(8)	90
Cyanide	(12)	27	(22)	62	(5)	57	(3)	80	(1)	96	(1)	7	(4)	66	(4)	68	(3)	57
Lead	(1)	57	(2)	82	(1)	20	(1)	97	(0)	-	(1)	0	(0)	-	(0)	-	(1)	81
Mercury	(8)	10	(8)	76	(2)	56	(3)	83	(0)	-	(1)	0	(2)	91	(2)	49	(5)	78
Nickel	(9)	14	(15)	34	(2)	47	(2)	18	(0)	-	(1)	14	(4)	34	(4)	0	(5)	39
Silver	(4)	20	(5)	83	(2)	55	(2)	80	(0)	-	(1)	0	(2)	79	(2)	83	(1)	75
Zinc	(12)	27	(22)	81	(5)	43	(3)	81	(1)	81	(1)	51	(4)	82	(4)	73	(8)	84
Benzene	(8)	25	(10)	77	(3)	80	(2)	87	(0)	-	(0)	-	(1)	92	(1)	92	(1)	99
bis(2-Ethylhexyl)phthalate	(12)	0	(8)	62	(5)	24	(3)	64	(1)	86	(1)	23	(4)	87	(4)	72	(8)	65
Butyl benzyl phthalate	(4)	62	(2)	94	(1)	70	(3)	84	(0)	-	(1)	93	(1)	80	(1)	93	(3)	86
Chloroform	(11)	14	(20)	62	(5)	75	(3)	50	(0)	-	(0)	-	(3)	75	(4)	69	(7)	41
Di-n-butyl phthalate	(3)	36	(6)	68	(5)	50	(1)	98	(0)	-	(1)	50	(1)	97	(3)	50	(0)	-
Diethyl phthalate	(1)	56	(2)	91	(0)	-	(0)	-	(0)	-	(0)	-	(0)	-	(0)	-	(0)	-
Ethylbenzene	(12)	13	(10)	90	(5)	90	(3)	86	(0)	-	(1)	83	(3)	97	(4)	89	(7)	86

TABLE III-40

(Continued)

Parameter	Primary		Secondary Activated Sludge*		Secondary Trickling Filter		Secondary O2 Activated Sludge		Secondary Rotating Biological Contactors		Secondary Aerated Lagoon		Parallel Activated Sludge/Trickling Filter Plants				Tertiary	
													Activated Sludge Side		Trickling Filter Side			
Methylene chloride	(12)	0	(14)	48	(5)	76	(3)	34	(0)	-	(1)	96	(4)	52	(4)	32	(8)	78
Napthalene	(4)	44	(6)	92	(0)	-	(0)	-	(0)	-	(0)	-	(0)	-	(0)	-	(4)	84
Phenol	(11)	8	(15)	89	(0)	-	(3)	99+	(1)	99+	(1)	50	(3)	89	(3)	94	(6)	95
Tetrachloroethylene	(12)	4	(20)	82	(5)	82	(3)	75	(1)	50	(1)	91	(4)	76	(4)	62	(8)	94
Toluene	(12)	0	(21)	93	(5)	88	(3)	99+	(1)	99+	(1)	89	(4)	97+	(4)	93	(8)	98
Trichloroethylene	(12)	20	(20)	90	(5)	96	(2)	67	(1)	67	(1)	97	(4)	97	(4)	95	(7)	97
1,1,1-Trichloroethane	(10)	40	(17)	88	(5)	92	(3)	80	(0)	-	(1)	91	(3)	99+	(3)	91	(7)	96
1,2-trans-Dichloroethylene	(9)	36	(19)	80	(4)	97	(2)	85	(0)	-	(1)	88	(0)	-	(0)		(3)	88

*POTW 8, predominantly (96 percent) activated sludge, was included in the activated sludge plants.

Note: Number in ( ) is number of plants with calculated removals.

Only plants with average influent concentrations greater than three times the most frequent detection limit of each pollutant are included in removal calculations.

TABLE III-41

INDUSTRIAL CATEGORIES AND FREQUENTLY DETECTED

PRIORITY POLLUTANTS BY CATEGORY

	Soaps & Detergents	Adhesives & Sealants	Leather	Textiles	Gum & Wood	Pulp & Paper	Timber	Printing & Publishing	Paint & Ink	Pesticides	Pharmaceuticals	Organics & Plastics	Rubber	Coal Mining	Ore Mining	Paving & Roofing	Steam & Electric	Petroleum Refining	Iron & Steel	Foundries	Electroplating	Nonferrous Metals	Batteries	Coil Coating	Photographic	Inorganic Chemicals	Electrical	Auto & Other Laundries	Phosphate	Plastics Processing	Porcelain/Enameling	Landfill	Mech Products	Oil & Gas
Benzene						●			●			●		●					●															
Carbon tetrachloride												●																						
Chlorobenzene												●																						
1,2 dichloroethane												●																						
1,1,1 trichloroethane												●																						●
Chloroform								●	●	●		●		●					●			●												
1,1 dichloroethylene												●																						
1,2 trans-dichloroethylene												●																						
2,4 dimethylphenol												●																						
Ethylbenzene												●																						
Methylene chloride						●	●	●		●	●		●								●						●							●
Dichlorobromomethane												●																						
Trichlorofluoromethane												●																						
Naphthalene												●							●															
Pentachlorophenol					●	●																												
Phenol		●			●	●						●							●														●	●
Bis(2-ethylhexyl) phthalate		●										●		●					●	●	●													
Butyl benzyl phthalate												●							●															
Di-n-butyl phthalate												●							●															
Di-n-octyl phthalate												●							●															
Dimethylphthalate												●																						
Chrysene																			●															
Anthracene												●							●															
Fluorene																			●															
Phenanthrene												●							●															
Pyrene																			●															
Tetrachloroethylene												●																						●
Toluene		●			●	●						●		●					●														●	●
Trichloroethylene												●																						
Antimony		●										●							●		●													
Arsenic												●									●													
Beryllium																			●															
Cadmium						●	●		●										●	●														
Chromium		●	●			●	●				●					●			●					●										
Copper	●	●				●	●		●			●		●				●	●															
Cyanide		●				●			●									●																
Lead	●	●				●			●					●																				
Mercury												●																						
Nickel		●																																
Silver		●			●																													
Thallium												●																						
Zinc		●	●											●								●				●								

Volume I

- Summary of fate of approximately 200 pollutants in different industries
- Number of times each pollutant detected
- Minimum, maximum, and mean concentration of each pollutant
- Percent removal for different treatment processes
- Effluent concentration ranges

Volume II

- Description of each industrial category
- Pollutants associated with various categories

Volume III

- Technology for control/removal of pollutants (physical-chemical, biological, disposal)
- Removal data

Volume IV

- Cost estimation for treatment.

The treatability manual is typically available at regional EPA headquarters.

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CHAPTER 4

RIVERS AND STREAMS

4.1 INTRODUCTION

The purpose of this chapter is to present simplified tools which can be used to predict responses of rivers and streams to the impact of pollutants. The introductory sections to the chapter should be read prior to solving any problems in order to become familiar with the topics that will be covered and the limitations of the formulations presented.

Rivers throughout this country are subject to a wide spectrum of geological, biological, climatological, and anthropogenic impacts which produce a variety of water quality problems. Approaches which provide guidance to the solution of these problems, especially ones restricted to hand calculations, must be limited in scope. The following guidelines have been used in selecting topics to be considered in this chapter: 1. widely occurring problems, 2. those amenable to hand calculations, and 3. those for which planners can obtain sufficient data.

4.1.1 Scope

The major problem areas to be considered are:

- Carbonaceous (CBOD) and nitrogenous (NBOD) biochemical oxygen demand
- Dissolved oxygen
- Temperature (with a discussion of low flow)
- Nutrients and eutrophication potential
- Coliform organisms
- Conservative constituents
- Sedimentation and suspended solids
- Toxic substances.

Beginning in 1974, the U.S. Environmental Protection Agency has for several years published the National Water Quality Inventory which is a compilation of current water quality conditions and recent trends in the nation's rivers and lakes. Several of the tables in that report series are relevant to this document and are included here. Table IV-1 illustrates reference water quality levels used to define acceptable pollutant limits in U.S. waterways. Table IV-2 shows water quality conditions in eight major waterways in the United States, while Table IV-3 summarizes the most widely observed water quality problems in the U.S. These tables will be cited throughout this chapter.

Local water quality standards, when they exist, are preferable to the general guidelines provided in Table IV-1. Table IV-4 shows example standards for dissolved oxygen and water temperature for the states of Virginia and Maryland. Parts of the

TABLE IV-1

REFERENCE LEVEL VALUES OF SELECTED WATER QUALITY INDICATORS FOR U.S. WATERWAYS (U.S. EPA, 1976)

Parameter	Reference Level
Ammonia	≤ 0.02 mg/l as unionized ammonia (for freshwater aquatic life)
Color	≤ 75 platinum-cobalt units (for water supply)
Dissolved Oxygen	≥ 5.0 mg/l (to maintain fish populations)
Dissolved Solids	≤ 250 mg/l (for water supply)
Fecal Coliforms	log mean ≤ 200 per ml over 30 days and 90 percent ≤ 400 per ml (for bathing waters)
Nitrate-N	≤ 10 mg/l (water supply)
pH	between 6.5 and 9.0 (for freshwater aquatic life)
Phenols	≤ 1 µg/l (for water supply)
Suspended Solids and Turbidity	shall not reduce the depth of the compensation point by more than 10 percent (aquatic life)
Total Dissolved Gases	≤ 110 percent saturation (aquatic life)

standards are significantly different from the reference levels in Table IV-1. For example the daily average dissolved oxygen standard for natural trout water for the state of Virginia is 7.0 mg/l, while 5.0 mg/l is recommended for the protection of aquatic life (Table IV-1). Thus, when local standards exist, they should be used in lieu of general reference levels.

4.1.2 Significance of Problem Areas

Oxygen depletion is often the result of excessive CBOD and NBOD loadings particularly in combination with high temperature and low flow conditions. Increased nutrient loadings to streams which produce elevated ambient concentrations can pose substantial potential for eutrophication. The nutrient problem is currently one of the most widespread areas of concern regarding river water quality. The health

TABLE IV-2

CONDITION OF EIGHT MAJOR WATERWAYS (EPA,1974)

River	Harmful Substances	Physical Modification	Eutrophication Potential
Mississippi		High* turbidity and solids below Missouri River	High*, increasing nutrients but no algae
Missouri	Trace metals present in middle river	High* suspended solids, turbidity in middle and lower river	High*, increasing nutrients but no algae
Ohio	High*, increasing iron and manganese	High* suspended solids in lower river, some improvements	High* nutrients but no algae
Tennessee			Small increase in nutrients but no algae
Detroit area rivers	Cyanide present but diminshing	Suspended solids improving, local temperature effects from discharges	Nutrients discharged to Lake Erie decreasing
Columbia	Severe gas super saturation; some radio-activity in lower river	Occasional high* temperatures	High* nutrients but no algae, except for slime growths in lower river
Snake	Severe gas super-saturation, signif-cant pesticides	Turbidity from natural erosion, agricultural practices, reservoir flushing	Nuisance algal blooms each summer
Willamette	Significant sulfite waste liquor from pulp and paper wastes	High* turbidity at high flow, high temperature in summer	High* level of nutrients but not excessive algae

TABLE IV-2 (continued)

River	Salinity, Acidity, and Alkalinity	Oxygen Depletion	Health Hazards and Aesthetic Degradation
Mississippi	High* salinity, acidity below major tributaries	Oxygen-demanding loads from large cities evident	Commercial fishing eliminated in lower river by phenols, bacteria near cities
Missouri	High* dissolved salts in middle and lower river	High* organic loads from feedlots, improved near cities	High* bacteria and viruses present in wet and dry periods
Ohio	Low* alkalinity especially in upper river	Occasional low* dissolved oxygen near Cincinnati and Pittsburgh	High* bacteria especially in high population areas
Tennessee		Low* BOD and decreasing COD in reservoirs	High* bacteria in small areas near cities, low radionuclides
Detroit area rivers	Acids and chloride low,* improving despite large discharges	Low* dissolved oxygen only at mouths of area tributaries	Phenols decreasing, bacteria unchanged-to-higher
Columbia	Approaches ideal for fresh waters	Dissolved oxygen close to saturation	Very low* bacteria
Snake	High* dissolved solids from irrigation in middle river	Dissolved oxygen close to saturation	High* bacteria below population centers
Willamette	Low* dissolved mineral salts, improved pH	Improved dissolved oxygen, no standards violations	High* bacteria, but improving

*High (or low) relative to other rivers, or relative to other sections of river, or to national reference levels. Does not necessarily imply standards violations or dangerous condition.

TABLE IV-3

WATER QUALITY PROBLEM AREAS REPORTED BY STATES*
NUMBER REPORTING PROBLEMS/TOTAL (EPA,1975)

	Middle Atlantic, Northeast	South	Great Lakes	Central	Southwest	West	Islands	Total
Oxygen depletion	11/13	9/9	6/6	6/8	4/4	6/6	4/6	46/52
Eutrophi- cation potential	11/13	6/9	6/6	8/8	2/4	6/6	-/6	43/52
Health hazards	11/13	8/9	5/6	8/8	3/4	5/6	5/6	45/52
Salinity, acidity, alkalinity	3/13	6/9	2/6	6/8	4/4	4/6	2/6	27/52
Physical modification	7/13	3/9	3/6	8/8	3/4	6/6	5/6	35/52
Harmful substances	6/13	6/9	5/6	4/8	4/4	2/6	3/6	30/52

* Localized or statewide problems discussed by the States in their reports.

hazards category in Table IV-3 lists elevated coliform levels as a problem of particular concern in northeastern and Great Lakes States. Salinity has been identified as a major problem in the central and southwestern states.

Because of their importance, each of the problem areas described will be addressed in this chapter. As shown in Table IV-5, many states routinely measure the parameters associated with these problems. The total number of states responding to the survey was 47. Because of the routine surveys conducted, data are commonly available for performing hand calculations. NBOD, though not directly measured, can be found from measurements of organic and ammonia nitrogen. Chloride concentration measurements can be directly converted to salinity.

4.1.3 Applicability to Other Problems

The tools which are presented in this chapter are designed to address specific water quality problems. However, a number of the tools, which are based on the law of mass conservation, can be directly applied to other problems with little or no modification. In the case of temperature prediction, an energy balance is used (which is analogous to a mass balance).

TABLE IV-4

EXAMPLE RIVER WATER QUALITY STANDARDS

| Class | Description | Dissolved Oxygen | | Temperature, °F | |
		Minimum	Average	T_N	T_{MAX}
Virginia					
III	Coastal and Piedmont	4.0	5.0	5	90
IV	Mountainous	4.0	5.0	5	87
V	Put and Take Trout Waters	5.0	6.0	5	70
VI	Natural Trout Waters	6.0	7.0	5	68
Maryland					
I	Water Contact, Recreation	4.0*	5.0*		90**
III	Natural Trout Waters	5.0*	6.0*		68**
IV	Recreational Trout Waters	5.0*	5.0*		75**

*These values apply except where lower values occur naturally.
**These apply outside the mixing zone. If natural temperature of receiving water is greater than the standard, then that becomes the standard.

The degree of commonality of source and sinks of a particular pollutant (e.g., a nutrient) or water quality indicator (e.g., dissolved oxygen) is responsible for the similarities and differences among the specific equations. For example, CBOD and NBOD produce a similar general effect (oxygen depletion), generally have similar sources and sinks, and for purposes of this study are assumed to follow first order decay kinetics. Coliforms, also assumed to decay by first order kinetics, are handled by the mass-balance approach. Conservative substances are different from BOD and coliforms in that they do not decay. Finally, there are some instances where a more subjective analysis is indicated and neither a mass nor energy balance is presented.

Once the similarities among water quality parameters are understood, handling two seemingly different problems can often be accomplished in a straightforward and similar fashion. For example, the distribution of toxic substances that are either conservative or follow a first order decay may be evaluated using techniques described for conservative substances and coliforms, respectively.

4.1.4 Sources of Pollutants

Pollutant loadings originate from three general sources: point, nonpoint, and natural. Each of these can constitute a major hurdle in meeting the 1983 goals of

TABLE IV-5

WATER QUALITY PARAMETERS
COMMONLY MONITORED BY STATES* (EPA,1975)

Parameter	Number of States
Flow	47
Dissolved oxygen	47
Coliform bacteria	45
Nitrogen (any form)	39
Phosphorus (any form)	35
pH	35
BOD/COD/TOC	27
Water temperature	29
Turbidity	26
Solids (any type)	27
Metals (any type)	17
Chlorides	19
Alkalinity	15
Conductivity	16
Color	11
Sulfate	14

*Only parameters listed by at least 10 States and specified as being part of each State's monitoring program are included.

fishable and swimmable waters. Specifically, point sources (30 states), nonpoint sources (37 states), and natural conditions (21 states) are all major contributors to water quality problems (EPA, 1975).

It is imperative that the capacity to assess impacts of nonpoint sources be a part of the hand calculation methodology for rivers. Table IV-6 illustrates the importance of nonpoint source nutrient loading for selected rivers in Iowa. Up to 96 percent of the annual phosphorus load and up to 99 percent of the total nitrogen load are from nonpoint sources. Admittedly, quantification of nonpoint source loads is often difficult. Nevertheless, simplified nonpoint source terms will be included in some of the mass-balance formulations. The methodology supplied in Chapter III can be used to estimate the nonpoint source loading rates.

4.1.5 Assumptions

In deriving the mass-balance equations, a number of assumptions were made. Users should be aware of each assumption so that the tools are not misapplied. The

TABLE IV-6

ANNUAL PHOSPHORUS AND NITROGEN LOAD FOR SELECTED IOWA RIVER BASINS (EPA,1975)

River	Total (lbs/year)	Point Sources (lbs/year)	Nonpoint Sources (lbs/year)	Percent of Total from Nonpoint Sources
PHOSPHORUS				
Floyd	720,207	29,807	690,400	95.9
Little Sioux	1,851,632	129,088	1,722,544	93.0
Chariton	879,916	48,203	831,713	94.5
Des Moines	5,621,007	586,015	5,034,992	89.6
Iowa	1,723,975*	103,445*	1,620,530*	94.0
Cedar	5,099,507	1,526,775	3,572,732	70.1
NITROGEN				
Floyd	1,705,984	65,171	1,640,813	96.2
Little Sioux	9,609,556	85,308	9,522,248	99.1
Chariton	1,585,427	24,795	1,560,632	98.4
Des Moines	41,334,897	695,235	40,639,662	98.3
Iowa	2,075,830	91,287	1,984,543	95.6
Cedar	6,804,881	1,552,334	5,252,547	77.2

*Orthophosphate

most important assumptions are:

- The system is at steady-state.
- Dispersion is small compared to advection (i.e., plug flow is assumed).
- The river system is vertically and laterally mixed.
- When pollutants decay, the rates are first order.

The steady-state assumption means that conditions are not changing with time, but only as a function of distance along the river. The time scale or steady-state generally should be on the order of a week or longer. For example, the summer low flow period generally represents a steady-state situation. However, storm events, and the dynamic responses of a river to them, must be considered a transient phenomenon.

Dispersion effects can usually be neglected when pollutant input into a river is continuous. Under these conditions the plug flow assumption is reasonable because the net dispersive transport is small. However, when a slug of pollutant is discharged instantaneously, dispersive transport is important since high concentration gradients exist around the centroid of the discharged pollutant.

The fully-mixed assumption presupposes that concentration gradients exist only in the direction of flow (longitudinal direction) and not in either the vertical or

lateral direction. The final major assumption is that all decay rates can be approximated by first order kinetics. This means that the decay rate of a substance is proportional to the amount present. First order decay is traditionally used in CBOD computations, and occasionally in nitrogen oxidation. The oxidation of inorganic nitrogen actually proceeds in stages from ammonia-N to nitrite-N to nitrate-N. However, for purposes of this report, the first order decay rate is acceptable for NBOD and coliforms, as well as CBOD. Before applying first order decay to other substances, however, care should be taken to determine the validity of the assumption.

For a few of the analyses which follow, several of the aforementioned assumptions are relaxed. In the discussion of mixing zones, Section 4.1.9, partial mixing is discussed for wide rivers. In the discussion on toxicants, Section 4.9, the spill analysis requires that an unsteady-state situation be analyzed where the effects of dispersion are included.

4.1.6 Data Requirements

Required in the analysis of most water quality problems are one or more types of data. For example, stream velocity (U), volumetric flow rate (Q), and stream temperatures (T) are commonly needed. Decay rates, specific to the particular problem at hand, are also required.

The U.S. Environmental Protection Agency has published two documents (Bowie et al., 1985 and Zison et al., 1978) intended to provide water quality modelers with a comprehensive source of information on rate constants and coefficients. The document provides extensive information on both biological and water quality parameters commonly used in surface water modeling. The contents of the document will be useful to the users of this document who are often faced with limited information on process rates for the water bodies being analyzed.

Stream velocity is the most basic hydraulic parameter needed for the analyses presented in this chapter. Ideally, the appropriate stream velocity is the travel time of neutrally buoyant particles over the reach being investigated divided by the distance traveled. Note that this concept of velocity is different from the velocity determined by:

$$U = \frac{Q}{A} \qquad \text{(IV-1)}$$

As defined by Equation IV-1, this concept of velocity exists only at the point in the river where the cross-sectional area is A. If the point of measurement is not typical of the reach being investigated, then neither will the velocity be typical. Consequently, should the user predict stream velocity based on cross-sectional area, a location typical of the river reach being investigated should be chosen.

An alternate method of predicting stream velocity, which does not depend on either flowrate Q or cross-sectional area A is Manning's Equation. A complete description of the use of this approach is given in many texts on surface water hydraulics, one of the best being Chow (1959).

According to Manning's Equation stream velocity under uniform flow conditions is expressible as:

$$U = \frac{1.49}{n} S^{1/2} R_H^{2/3} \qquad (IV-2)$$

where

n = Manning's n

S = slope, ft/ft

R_H = hydraulic radius, ft.

Manning's n is the roughness of the stream bed, and can be predicted as outlined in Chow (1959). Barnes (1967) provides roughness data for 90 streams in the United States, and includes cross-sectional areas and photographs of the streams investigated. The slope can be estimated using topographic maps to predict elevation changes between two locations and then overlying a string over the stream path to predict distance. The hydraulic radius (which is the ratio of the cross-sectional area to wetted perimeter) can be estimated in terms of depth when the stream width is much greater than the depth. Specifically:

$$R_H = \begin{cases} \text{depth, if channel cross-section is rectangular} \\ \\ 2/3 \text{ maximum depth, if channel cross-section is parabolic} \end{cases}$$

4.1.7 Selection of Season

It is reasonable to expect that a particular water quality problem may be more severe at one time of the year than another. Table IV-7 shows that pollutant levels can depend on season (summer or winter) and flow rate (high flow or low flow). Dissolved oxygen problems, for example, are clearly associated with summer, low flow conditions. Consequently, for any particular pollution problem, users should strive to perform the analysis under critical conditions. Where planning is performed with consideration of the aggravated situation and where proper abatement action is taken, it is likely that pollution concentrations will be below problem levels during other times of the year. If a problem in fact exists, then it is under these conditions that it will be most pronounced.

In the following sections, hand calculation methods for each problem area are described with illustrative examples. Table IV-8 provides a summary of the material presented.

TABLE IV-7

MAJOR WATERWAYS: SEASONAL AND FLOW ANALYSIS, 1968-72 (EPA, 1974)

Parameters	Winter, High Flow	Summer, Low Flow	Winter, Low Flow	Summer, High Flow	Dominant Effect
		(number of reaches exceeding reference levels)**			
Suspended solids	9	5	0	4	High flow
Turbidity	13	4	1	7	High flow
Color	11	6	3	4	High flow
Ammonia	14	3	7	1	Cold weather
Nitrite	3	7	5	1	Low flow
Nitrate(as N)	12	4	8	1	Cold weather
Nitrate(as NO₃)	8	3	6	1	Cold weather
Nitrite plus nitrate	2	3	2	1	Inconclusive
Organic nitrogen	3	6	0	3	Warm weather
Total Kjeldahl nitrogen	3	5	0	3	Warm weather
Total phosphorus	10	3	5	2	Cold weather
Total phosphate	8	3	5	1	Cold weather
Dissolved phosphate	6	3	4	0	Cold weather
Dissolved solids(105°C)	4	7	6	3	Low flow
Dissolved solids(180°C)	3	8	6	2	Low flow
Chlorides	4	15	10	0	Low flow
Sulfates	5	13	5	5	Warm weather,low flow
Alkalinity	6	12	10	0	Low flow
ph	15	4	6	4	Cold weather,high flow
Dissolved oxygen	0	19	0	9	Warm weather
BOD₅	11	6	8	1	Cold weather
COD (.025N)	6	5	3	2	Cold weather
Total coliforms(MFD)*	4	10	2	5	Warm weather
Total coliforms(MFI)*	8	6	2	4	High flow,warm weather
Total coliforms(MPN)*	4	2	3	3	Inconclusive
Fecal coliforms(MF)*	6	6	3	4	Inconclusive
Fecal coliforms(MPN)*	4	0	1	0	Cold weather
Phenols	5	0	1	0	Inconclusive
Odor	4	0	0	0	Inconclusive

*Membrane filter delayed, membrane filter immediate, most probable number, membrane filter

**Reference levels are available in Table IV-1. Thirty reaches were analyzed during each season.

TABLE IV-8

WATER QUALITY ANALYSES FOR RIVER SCREENING METHODOLOGY

Water Quality Constituent	Computational Procedures	Supporting Information Included
Water temperature	- equilibrium temperature - mixing temperature - temperature profile for point sources	- shortwave solar radiation - longwave solar radiation - vapor pressure
Carbonaceous and nitrogenous biochemical oxygen demand	- BOD profiles for point sources - BOD profiles with benthic sources added - BOD profiles with both benthic and nonpoint sources added	- graphs, tables, and equations for decay rates
Dissolved oxygen	- CBOD-NBOD-DO profile for point sources - DO profiles with photosynthetic oxygen production and benthic uptake added - critical dissolved oxygen conditions - waste assimilative capacity	- reaeration rates for shallow and deep streams - saturation dissolved oxygen levels corrected for temperature, altitude, salinity - photosynthetic oxygen production and benthic uptake data - tabulated solutions for critical dissolved oxygen levels
Nutrients	- growth limiting nutrient - nutrient profiles for point sources - nutrient profiles for nonpoint sources	- nitrogen/phosphorus ratios for growth limitation - nonpoint source loading rates by land use type
Coliform organisms	- coliform profiles for point sources - coliform profiles for nonpoint sources	- decay rates
Sediment	- bed load - suspended load - total load	- median bed particle sizes for numerous rivers - critical shear stress - sediment transport propensity factor - approximate bed load/suspended load relationship
Toxicants	- toxicant profiles for point and nonpoint sources - mass flux volatilized, advected, and transformed - spill analysis of low and high density toxicants - time required to desorb toxicant from bedded sediments	- vapor pressure, solubility, octanol-water portion coefficient for priority pollutants - Henry's Law Constant:

4.1.8 River Segmentation

Although the tools presented in this chapter are of a simplified nature they can be used to analyze complex river systems (i.e., those which have a number of different point and nonpoint sources of pollution, tributaries and withdrawals). Analysis of these systems is accomplished by dividing the river into segments. The basic tenet which must be followed is simply this: Segments are created so that one of the analytical tools presented in this chapter can be used to predict the pollutant

concentration profile within the segment.

Analyses of river systems normally begin at a segment where the boundary conditions are known, and proceed sequentially downstream. Thus the results found for one segment are used as the upstream boundary condition for the next segment. Based on the tools in this chapter, the following rules should be followed when segmenting:

1. Point sources of pollutants enter the river just above the upstream boundary of a segment. Tributaries are treated as point sources.

2. Nonpoint sources enter a river throughout the length of a segment.

3. Pollutant concentrations at the upstream end of segments are obtained by mixing the pollutant concentration in the river with the contribution of the point source at that location (if one exists). The location where mixing occurs is called a mixing zone.

4. Generally constant hydraulic variables (e.g., depth and velocity) are used throughout a segment. If there is a gradual change in the hydraulic variables over distance, an average value can be used. If there is an abrupt change in the variable, such as a velocity change caused by a significant deepening of the channel, then a new segment can be created at this boundary.

5. Decay rates, reaeration rates, and other rate coefficients remain constant within a segment. If rate coefficients are known to change significantly from one location to another in a river, then different segments should be created. This rule is consistent with rule (4), since rate coefficients are often functions of hydraulic variables.

— EXAMPLE IV-1 —

Figure IV-1a shows a stretch of the James River, located in Virginia. On the stretch of the river shown, there is a tributary (Falling Creek), a sewage treatment plant (STP), and a nonpoint source of runoff (agricultural). Segment the river between locations A and B in order to determine the profile of a pollutant which is discharged from each of the three sources.

First, it should be noted that often there is more than one way to segment the river to successfully solve the problem. The most obvious method will be illustrated here. Figure IV-1b shows the proposed solution. There are two mixing zones - the first around the treatment plant and the second around the tributary which is treated as a point source. The first segment is located from below the first mixing zone to above the second mixing zone, and has a nonpoint source discharging throughout the length of the segment, consistent with rule (2). The second segment is located below the second mixing zone and continues downstream to
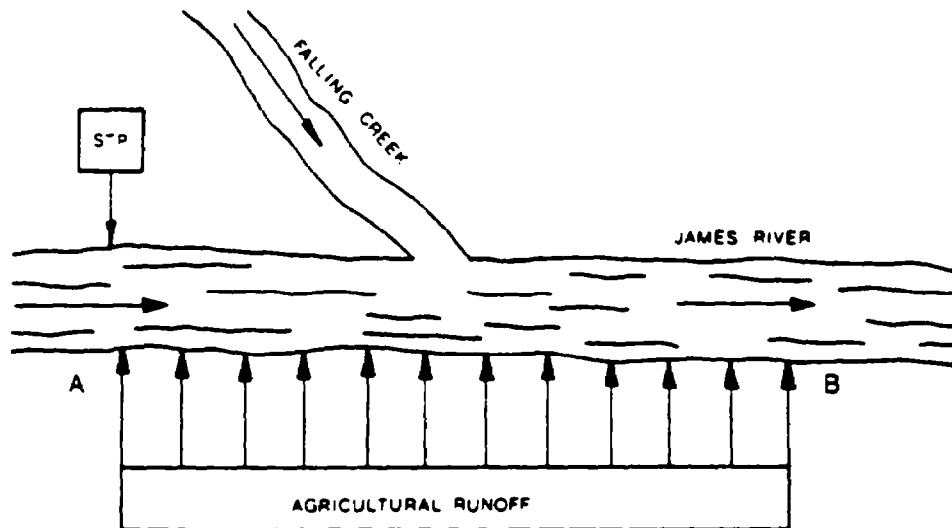
(a) River Segment Being Analyzed
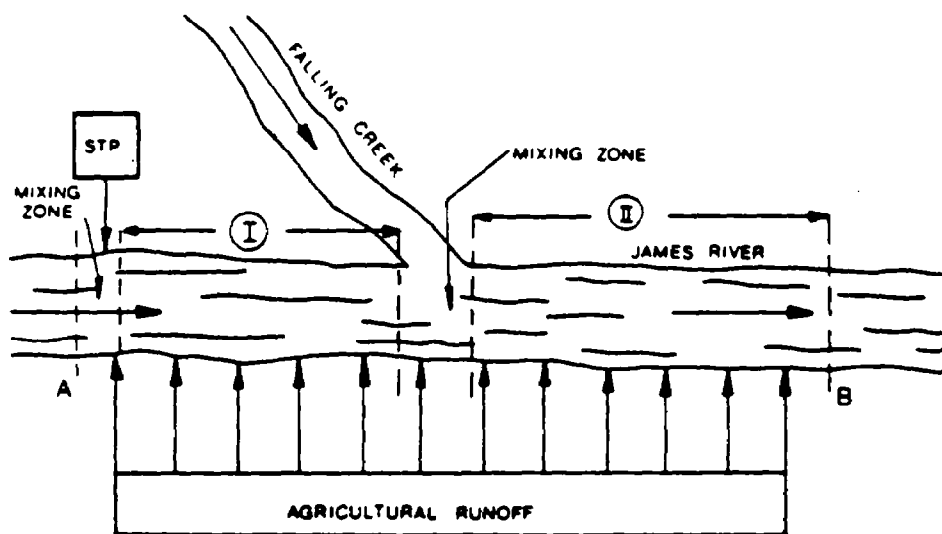
(b) Proposed Segmentation Scheme

FIGURE IV-1   ILLUSTRATION OF RIVER SEGMENTATION
PROCEDURE ON THE JAMES RIVER.

location B, which is the end of the nonpoint source. If Falling Creek had not
been present, a single segment and a single mixing zone would have been sufficient
to analyze the problem.

— — — — — — — — — — — — — END OF EXAMPLE IV-1 — — — — — — — — — — — — — —

A second, more comprehensive example will illustrate a number of points about segmentation not covered in the previous example. One of these points is that the segmentation scheme used can vary depending on the pollutant being analyzed.

r — — — — — — — — — — — — — · EXAMPLE IV-2 — · — · — · — · — · — · — · — · — ·

Segment the river shown in Figure IV-2 beginning at location A and continuing to location B in order to determine the instream BOD distribution. How would the segmentation differ when predicting the dissolved oxygen profile?

Both point and nonpoint sources discharge to the river in Figure IV-2. Several flows are diverted, and the river width changes over parts of the reach being investigated. Each of the rules stated earlier will be utilized to segment the river system. Figure IV-3 shows one solution to the problem. Depending on the distances between the various sources of pollutants, which are not given in the
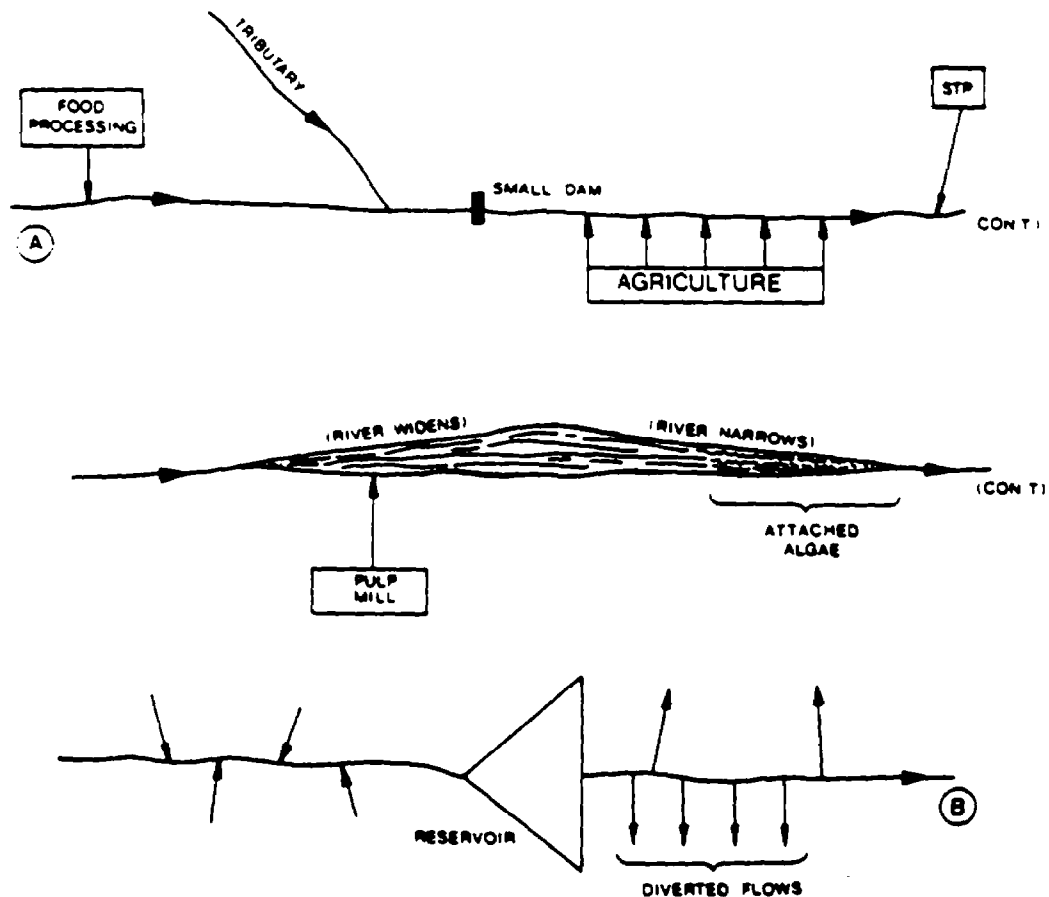
FIGURE IV-2   HYPOTHETICAL RIVER HAVING A VARIETY OF POLLUTANT SOURCES AND SINKS.

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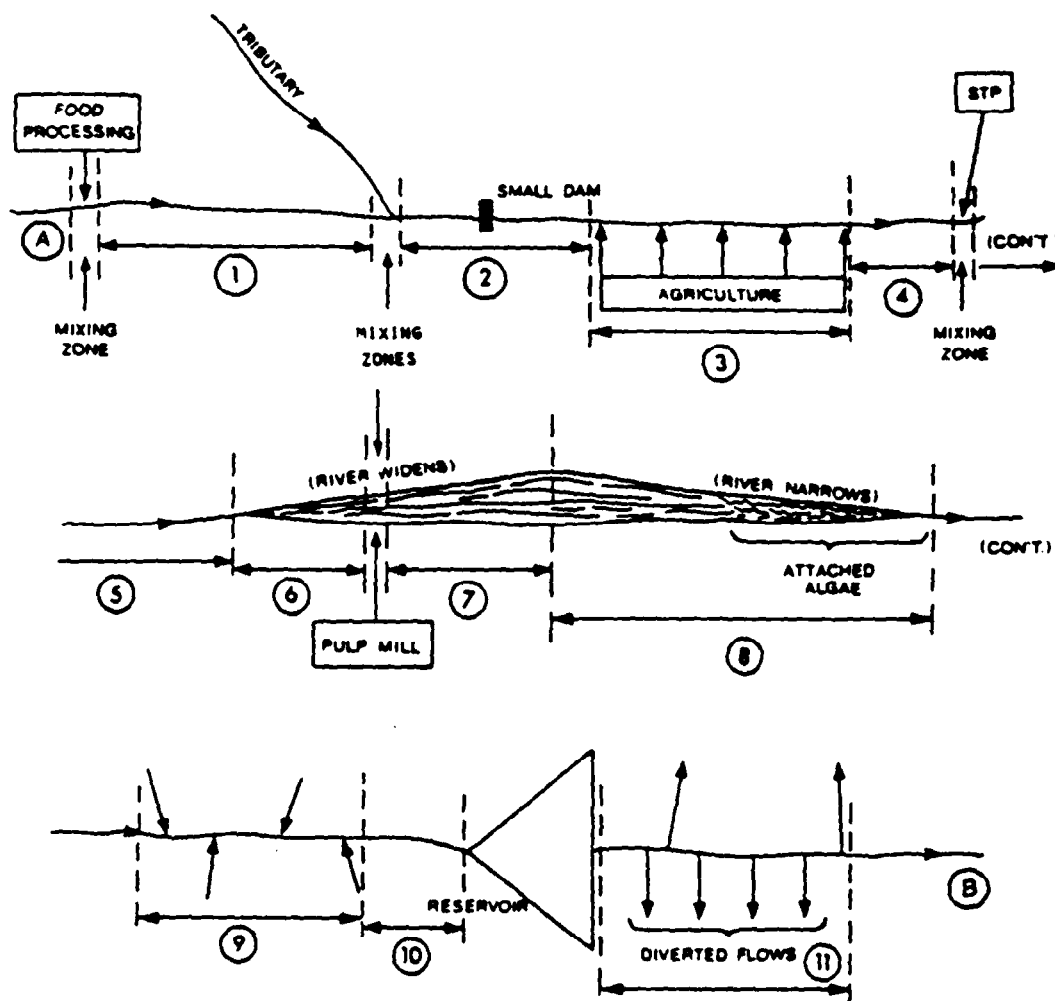
FIGURE IV-3   RIVER SEGMENTATION FOR BOD DISTRIBUTION.

problem, it might be possible to combine some of the segments. The reservoir is assumed to be analyzed using the methods in Chapter 5, and so is not segmented.

Mixing zones are included around the four point sources: the food processing plant, the tributary, the sewage treatment plant, and the pulp mill. In segments 9 and 11 there appear to be a number of point sources and diversions. Strictly speaking, segments 9 and 11 do not follow the rules presented earlier, which require mixing zones around each point source. However, the point sources and sinks within segments 9 and 11 are assumed to represent equivalent nonpoint sources, which act over the length of each segment. This approach can obviously simplify the analysis of complex river systems by decreasing the number of segments analyzed. However, the analysis is more approximate because the nonpoint source is assumed to be uniformly distributed throughout the segment. Example IV-5 presented later shows a specific application of the concept of an equivalent nonpoint source.

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In segment 2 the presence of the small dam is assumed not to influence
the BOD profile, so that its presence does not require a mixing zone. However if
dissolved oxygen profile were being calculated, segment 2 would be divided
two segments, with a mixing zone around the dam. This division is required
because the dissolved oxygen concentration can rapidly change (almost instantane-
ously) as the water flows over the dam. The dissolved oxygen concentration just
below the dam should be used as the upstream boundary conditions for the next
segment. The specific information required to accomplish this is discussed later
in Section 4.3.

A second difference in segmenting for dissolved oxygen occurs in Segment 8.
The presence of the attached algae is assumed not to influence the BOD profile,
but the algae are internal sources of oxygen. Thus segment 8 would be subdivided
at the upstream location of the attached algal growth.

—·—·—·—·—·—·—·—·—·— END OF EXAMPLE IV-2 —·—·—·—·—·—·—·—·—·—·—·—·—

4.1.9 Mixing Zones

A mixing zone, as used in this document, is nothing more than a short reach of
a river where a point source and river water mix. It is often assumed, for both
simple and more complex approaches (e.g., QUAL-II computer model), that mixing is
instantaneous and complete across the entire width of the channel. With several
exceptions, such an approach is used in this document.

Assuming complete mixing, the concentration of a pollutant in a river after
mixing is:

$$C = \frac{C_u Q_u + C_w Q_w}{Q_w + Q_u} \qquad (IV-3a)$$

$$= \frac{C_u Q_u + W/5.38}{Q_w + Q_u} \qquad (IV-3b)$$

where

C = concentration of pollutant in river following mixing, mg/l

C_w = concentration in point source, mg/l

C_u = concentration in river above point source, mg/l

Q_w = discharge rate of point source, ft^3/sec

Q_u = flow rate of river above point of discharge, ft^3/sec

W = pollutant mass emission rate, lbs/day.

The concentration C is the pollutant level in the mixing zones shown in the earlier
Figures IV-1 and IV-3. These concentrations become the upstream boundary conditions
for the adjacent downstream segment.
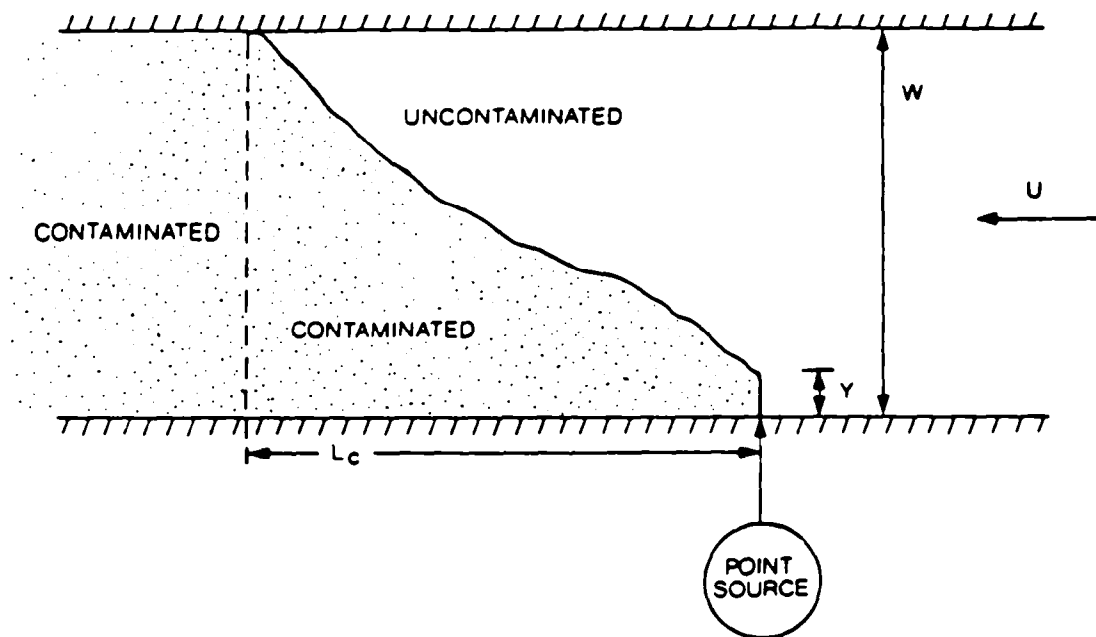
FIGURE IV-4   POLLUTANT DISCHARGE WHERE INITIAL MIXING
OCCURS A FRACTIONAL DISTANCE ACROSS THE RIVER.

Although it is convenient to assume that complete mixing occurs, this assumption may be inaccurate for wide rivers, depending on the characteristics of the point source outfall and diffuser. Figure IV-4 illustrates such a case. The river is wide enough so that the wastewater is initially mixed with only a fraction of the total river flow. As the pollutant-riverwater mixture is transported downstream mixing continues until the pollutant is completely mixed across the channel.

The initial pollutant concentration at the point of discharge is:

$$C = \frac{\frac{Y}{W} Q_u C_u + Q_w C_w}{Q_w + \frac{Y}{W} Q_u}$$ (IV-4)

where

$\frac{Y}{W}$ = fractional distance across river where initial mixing occurs.

All other variables have been previously defined.

The significance of incomplete initial mixing is that pollutant concentrations can be initially much higher than if complete mixing occurs. For example, if the upstream contribution of the pollutant is negligible ($C_u = 0$) and if the fraction of river flow which initially mixes is far greater than the wastewater flow ($\frac{Y}{W} Q_u >> Q_w$), then:

$$C = \frac{W}{Y} C_{cm}$$ (IV-5)

where

C = concentration of pollutant if there is incomplete initial mixing

C_{cm} = concentration of pollutant if there is complete initial mixing.

If $Y/W = 0.1$, then the pollutant concentration following incomplete mixing is 10 times higher than if complete mixing were to occur.

The distance L_c to complete mixing (see Figure IV-4) can be estimated (as an upper limit) by the following expression:

$$L_c = \frac{0.4\ W^2\ U}{\varepsilon_t} \qquad \text{(IV-6)}$$

where

L_c = distance below point source where complete mixing occurs

W = width of river

U = river velocity

ε_t = lateral diffusion coefficient.

Values of the lateral diffusion coefficient can be estimated from the data given in Table IV-9. Also, the following predictive formula can be used:

$$\frac{\varepsilon_t}{Du^*} = \begin{cases} 0.1\text{-}0.2, & \text{for a straight rectangular flume} \\ 0.25, & \text{for irrigation channels} \\ 0.4\text{-}0.8, & \text{many natural channels} \end{cases} \qquad \text{(IV-7)}$$

where

D = mean depth of flow

u^* = friction velocity = $\sqrt{gDS}$

S = slope of channel.

The actual distance L_c is probably less than that calculated from Equation IV-6 because of secondary mixing, river curvature, and initial momentum of the discharge. It is also sensitive to river width.

4.1.10 Water and Pollutant Balances

Many river systems are hydrologically complex. Flow patterns are influenced by tributaries, nonpoint sources of runoff, flow withdrawals, as well as point sources of pollution. If the planner intends to perform water quality analyses on a basin-wide scale, it is probably prudent that a water budget be first completed. A water budget is a statement that:

$$\frac{dS}{dt} = \sum \text{Inflows} - \sum \text{Outflows} = 0, \text{ for steady-state} \qquad \text{(IV-8)}$$

TABLE IV-9

EXPERIMENTAL MEASUREMENTS OF TRANSVERSE MIXING IN OPEN CHANNELS WITH CURVES AND IRREGULAR SIDES

Channel	Channel geometry	Channel width, w (m)	Mean depth of flow, d (m)	Mean velocity, $\bar{u}$ (m/s)	Shear velocity, u^* (m/s)	Transverse mixing coefficient, (m²/sec)	ε_z
Missouri River near Blair, Nebraska	Meandering river	200	-	1.75	0.074	0.12	0.6
Laboratory	Smooth sides and bottom; 0.15 m long groins on both sides	2.2	0.097	0.11	-	-	0.16-0.49
	Smooth sides and bottom, 0.5 m long groins on both sides	2.2	0.097	0.11	-	-	0.3-0.4
Laboratory model of the IJssel River	Groins on sides and gentle curvature	1.22	0.9	0.13	0.0078	-	0.45-0.77
IJssel River	Groins on sides and gentle curvature	69.5	4.0	0.96	0.075	-	0.5
Mackenzie River from Fort Simpson to Norman Wells	Generally straight alignment or slight curvature, numerous island and sand bars	1240	6.7	1.77	0.152	0.67	3.4
Missouri River downstream of Cooper Nuclear station, Nebraska	Reach includes one 90° and one 180° bend	210-270	4	5.4	0.08	1.1	3.4
Potomac River, 29 km reach below the Dickerson Power Plant	Gently meandering river with up to 60° bends	350	0.73-1.74	0.29-0.58	0.033-0.051	-	0.52-0.65

from: Fischer, H.B., E.J. List, R.C.Y. Koh, J. Imberger, and N.H. Brooks, 1979. Mixing in Inland and Coastal Waters. Academic Press, New York.

where

S = storage in the river channel.

For the steady-state situations, which are examined here, the water budget simply states that inflows to the system equal outflows from the system. A water budget thus provides a method of determining whether the major flow contributions have been accurately assessed or not. If a large imbalance in the water budget exists, accurate evaluation of the major sources of pollutant might be difficult to achieve. An accurate water balance helps to minimize the possibility of inaccurate assessment of pollutant concentration. It does not eliminate the possibility.

Once a water balance has been completed, then a pollutant balance of a conservative pollutant can be developed based on the following relationship:

$$\sum_{in} Flux = \sum_{out} Flux \quad \text{,at steady-state} \tag{IV-9}$$

where the fluxes are the rates of entry and loss of the pollutant into and out of the system, respectively. One of the following two expressions can be used to predict the mass loading rates:

$$M = 5.38 \, C \, Q \qquad \text{(IV-10)}$$

where

  M = mass loading rate, lbs/day
  C = concentration, mg/l
  Q = flow rate, ft^3/sec

and

$$M = 86.4 \, C \, Q \qquad \text{(IV-11)}$$

where

  M = mass loading rate, kgs/day
  Q = flow rate, m^3/sec.

When nutrient and water balances are developed, the following considerations should be kept in mind:

- In most instances it is probably not possible to develop water or nutrient balances where inflows and outflows balance to within less than 10 percent of each other.
- The system's upstream boundary must be included in the balance as a source and the downstream boundary as a loss.
- All sources and losses should be mutually exclusive of each other.
- Choose system boundaries to coincide with locations of gaging stations when possible.
- Try to use comparable periods of record of data. This will help to minimize the impacts of trends which could be present in one record but not in another.
- It is typically easier to develop water and mass balances on an annual basis, although balances can be developed for each season of the year. However, if the system is not at steady state, inflows and outflows should not balance.

Table IV-10 shows a suggested method of tabulating the results of water and pollutant balances. Total nitrogen (TN) and total phosphorus (TP) are the pollutants. All flow rates and loading rates are tabulated individually. Once total loading rates have been tabulated, the percent contribution from each source can be determined. Percent contributions help to determine the relative importances of each source as a contributor to pollution, and can provide a method to prioritize pollution abatement efforts.

TABLE IV-10

SUGGESTED CONFIGURATION FOR WATER AND NUTRIENT BALANCE TABLE

SOURCES	FLOW RATE	LOADING RATE			
		TN	%	TP	%
- UPSTREAM					
- TRIBUTARIES					
- IRRIGATION RETURNS					
- MUNICIPAL					
- INDUSTRIAL					
⋮					
TOTAL					
LOSSES					
- DOWNSTREAM					
- DIVERSIONS					
⋮					
TOTAL					
$\dfrac{\text{SOURCES}-\text{LOSSES}}{\text{LOSSES}} \times 100$					

EXAMPLE IV-3

Figure IV-5 shows a hypothetical river which has three tributaries, a nonpoint source of runoff, and two diversions. Develop a water balance for this system. The known flow rates are:

Identification Number	Flow rate (cfs)
1	2000
2	4000
3	1200
4	200
5	800
6	1000
7	2000
8	6000
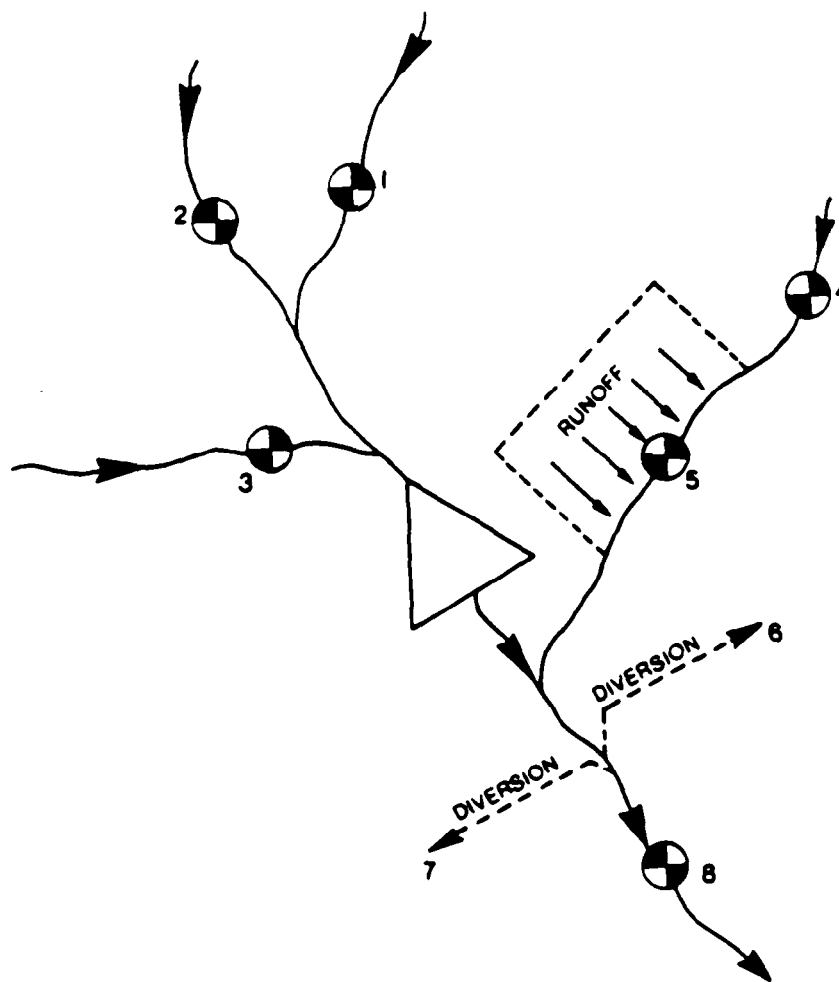
FIGURE IV-5   ILLUSTRATION OF WATER BALANCE

The flowrates at locations 1,2,3, and 5 are assumed to comprise the inflow rates to the system. The total inflows are:

Identification Number	Inflows
1	2000 cfs
2	4000 cfs
3	1200 cfs
5	800 cfs
Total	8000 cfs

The inflow from gage 4 is not needed because gage 5 is located further downstream on the same tributary. The outflows consist of diversions 6 and 7 and the downstream outflow past gage 8:

Identification Number	Outflows
6	1000 cfs
7	2000 cfs
8	6000 cfs
	9000 cfs

The inflows and outflows differ by 1000 cfs. There are several reasons for the imbalance. One, the flow rate past each gage is not measured perfectly, but differs by some degree from the actual flow rate. Two, the gage at location 5 does not catch all of the nonpoint source runoff, so there is an additional inflow to the system which has not be quantified. Three, depending on the size of the reservoir, direct precipitation and evaporation might be significant.

————————— END OF EXAMPLE IV-3 —————————————

The following example illustrates both a water and nutrient balance, and is based on work performed by Tetra Tech on the Snake River in Idaho (Mills 1979).

——————————— EXAMPLE IV-4 ————————————————

Develop annual water and phosphorus balances for water year 1976 for the Snake River from Heise, Idaho, to below American Falls Reservoir, a distance of 150 miles. A sketch is shown in Figure IV-6. Estimate the phosphorus retention coefficient for American Falls Reservoir. The retention coefficient is defined as:

$$R_p = \frac{\text{Flux Input} - \text{Flux Output}}{\text{Flux Input}}$$
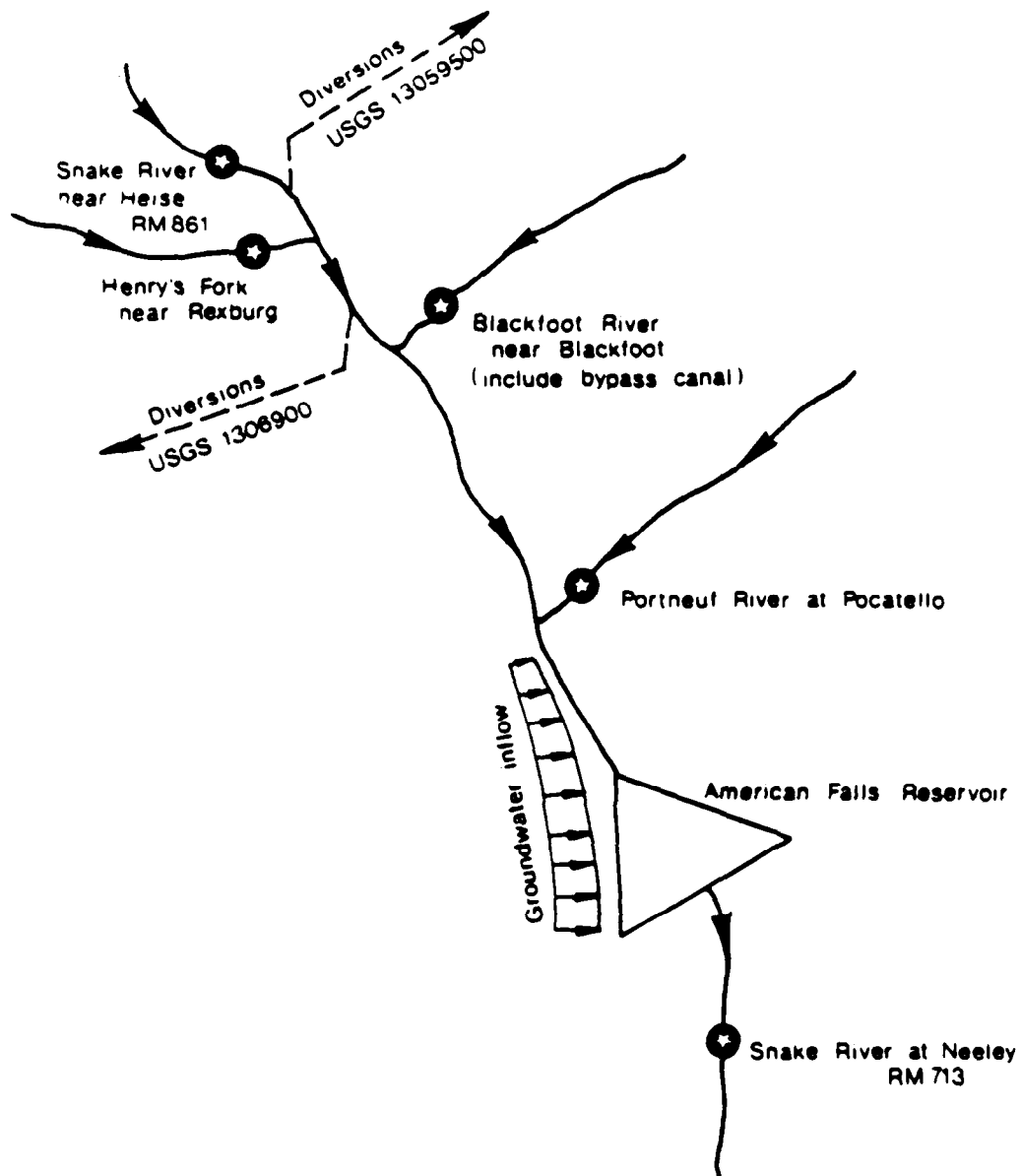
FIGURE IV-6   SKETCH OF SNAKE RIVER FROM HEISE TO NEELEY, IDAHO.

The required data are shown below:

        Surface area of American Falls Reservoir = 56,600 acres

        Evaporation rate in this part of United States = 33 inches/year

        Precipitation = 11 inches/year

        Ground water inflow into Snake River: 500 cfs

        Ground water inflow into American Falls Reservoir: 2,100 cfs.

The total phosphorus concentrations were generated during the study of Mills

(1979) and are provided here:

Source	mg/l
In rainwater	0.03
Snake River near Heise	0.05
Henrys For..	0.11
Blackfoot River	0.26
Portneuf River	0.68
Groundwater inflow	0.23
Snake River near Neeley	0.08

The surface inflow rates are gaged by the U.S. Geological Survey and are reported in the U.S. Geological Survey Water Data Report for Idaho (1976). An example of how the information is tabulated in these reports is shown in Figure IV-7. From an entry in the Table, the mean flow rate for water year 1976 is 8549 cfs at USGS 30307500, near Heise. Rather than showing the remaining tabulations from the USGS report the flow rates from water year 1976 will simply be tabulated, as contained in the report.

Source	Flow rate
Blackfoot River	453 cfs
Henrys Fork	3,235 cfs
Portneuf River	412 cfs
USGS 13059500 (diversion)	2,333,700 ac-ft/yr
USGS 13069000 (diversion)	800,900 ac-ft/yr

Based on this information the water and total phosphorus balances are calculated and shown in Table IV-11. The flow rates are all converted to units of cfs. This requires converting the precipitation, evaporation, and diversions to these units. A precipitation rate of 11 inches per year is equivalent to 71 cfs:

11 ÷ 12 x 56600 x 43560 ÷ 366 ÷ 24 ÷ 3600 = 71 cfs

The diverted flow in ac-ft/yr is converted to cfs as shown:

USGS 13059500: 2333700 x 43560 ÷ 366 ÷ 24 ÷ 3600 = 3214

The percent difference between inflow rates and outflow rates is 4 percent.

Based on these flow rates, and the concentrations of total phosphorus presented earlier, the sources and losses of total phosphorus can be tabulated. For example, the mass flux of total phosphorus flowing past Heise can be calculated using Equation IV-10:

M = 5.38 x 8549 x 0.05 = 2300 lbs/day

Continuing in this manner, the sources and losses are as tabulated in Table IV-11. The large imbalance is caused by retention at American Falls Reservoir. The phosphorus loading to the reservoir is:

9589 - 865 - 415 = 8309 lbs/day

Discharge, in Cubic Feet per Second, water year October 1975 to September 1976
Mean values

Day	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
1	7770	3930	3550	3720	4130	4000	10900	18400	19000	9780	13200	5650
2	6920	3910	3580	3730	4140	4800	11100	18400	19100	10000	12600	5960
3	6770	3930	3560	3750	4130	5990	9360	18600	18000	10900	12000	6480
4	6270	3930	3560	3800	4130	6150	9430	18900	14800	10500	10200	6940
6	6200	3930	3730	3800	4540	6300	10400	18200	10800	10200	9880	7140
7	5970	3930	3760	3790	4770	6320	11700	18300	10700	10200	9390	7140
8	5790	3910	3760	3780	4640	6070	12800	18200	10700	10500	8640	7150
9	5430	3830	3760	3440	4710	6120	14000	18100	11000	11500	8410	6990
10	5100	3790	3780	3590	4440	6050	15400	18200	12200	12100	8260	6900
11	4710	3810	3780	3900	4280	7890	16000	19800	12300	11900	8060	6920
12	4440	3810	3780	3910	4270	8800	16100	18400	12100	11700	7670	7000
13	4440	3650	3730	3920	4230	8800	16100	18200	12000	12100	7460	6960
14	4470	3480	3720	3900	3940	8890	16000	18900	11900	12700	7420	6350
15	4240	3320	3710	3900	3740	8550	18000	19500	11800	13500	7450	5800
16	4100	3240	3720	4060	3750	8920	16000	19400	11900	13700	7440	5700
17	4100	3300	3690	4080	3740	9440	16200	19300	11900	13600	7390	5720
18	4100	3290	3680	4090	3670	9780	16300	20400	12000	13700	7450	5500
19	4100	3250	3680	4080	3950	9720	16100	22400	11900	13600	7140	5290
20	4100	3310	3670	4040	3950	9680	16600	23800	11900	13600	6950	5310
21	4090	3100	3680	4040	3960	9820	17200	23800	11900	13600	6750	5290
22	3950	3520	3680	4040	4000	9820	17300	23800	11300	13500	6680	5170
23	3960	3370	3700	4040	4010	9930	17400	23800	10700	13500	6810	4930
24	3930	3370	3700	4060	4010	10100	17400	24200	10100	13500	6250	4840
25	3910	3350	3700	4090	3980	10100	17400	24000	9880	13500	5950	4840
26	3930	3330	3690	4090	3990	10100	17200	24000	9400	13500	5810	4830
27	3960	3390	3700	4090	3980	10000	17100	23900	9370	13500	5710	4820
28	3960	3390	3670	4100	4000	9990	17700	24000	9340	13500	5690	4680
29	3910	3450	3670	4090	4010	10400	18100	22200	9310	13500	5680	4580
30	3950	3520	3700	4100	--	10600	18200	20400	9310	13500	5690	4570
31	3930	--	3700	4100	--	10500	--	19700	--	13500	5640	--
Total	141790	107360	114370	122630	119480	259810	450820	637000	363410	383690	244770	176110
Mean	4574	3573	3689	3955	4120	8380	15027	20548	12113	12438	7895	5870
Max	7770	3930	3780	4100	4770	10600	18200	24200	19100	13700	13200	7150
Min	3910	3120	3550	3720	3740	4000	9330	18100	9310	9780	5640	4570
Ac-Ft	293000	212900	226900	243200	237000	515300	894200	1293000	720800	764800	485500	349300
Mean	3320	3840	3708	3270	3081	3054	6005	25280	25000	13610	6490	4677
Ac-Ft	265500	228500	228000	201100	177200	187200	357300	1591400	1487300	837100	399100	278300

Cal Yr 1975 Total 2695880 Mean 7933 Max 21700 Min 2940 Ac-Ft 5744000 Mean† 8015 Ac-Ft 5802600
Wtr Yr 1976 Total 3129230 Mean 8549 Max 24200 Min 3120 Ac-Ft 6207000 Mean 8595 Ac-Ft 6239600

† Adjusted for storage in Jackson Lake and Palisades Reservoir; no account taken for time of travel between reservoirs and Heise gaging station.

FIGURE IV-7 EXAMPLE OF FLOW RATE INFORMATION TABULATED IN
U.S. GEOLOGICAL SURVEY'S WATER DATA REPORT

TABLE IV-11

SOLUTION TO SNAKE RIVER WATER AND PHOSPHORUS BALANCE PROBLEM

	Flow Rate (cfs)	TP Loading (lbs/day)
Sources		
Snake River at Heise	8,549	2,300.
Blackfoot River	453	1,915.
Henrys Fork	3,235	634.
Portneuf River	412	1,510.
Ground water inflow into Snake River	500	619.
Ground water inflow into American Falls Reservoir	2,100	2,600.
Precipitation on American Falls Reservoir	71	11.
$\sum$ Sources	15,320	9,589.

Losses	Flow Rate (cfs)	TP Loading (lbs/day)
USGS 13059500	3,214.	865
USGS 13069000	1,103	415
Snake River at Neeley	11,360.	4,890
Evaporation	215.	-
$\sum$ Losses	15,892.	6,170

For flow, $\left(\dfrac{\text{Losses-Sources}}{\text{Losses}}\right) 100 = 4\%$

Since the phosphorus leaving the reservoir is 4890 lbs/day, the retention coefficient is:

$$R_p = \frac{8309 - 4890}{8309} = .41$$

American Falls Reservoir retains a significant quantity of the phosphorus which enters the reservoir and consequently tends to keep phosphorus levels in the Snake River below the dam depressed compared with what they would otherwise be.

— END OF EXAMPLE IV-4 —

4.1.11 Hand Held Calculator Programs

It has become apparent that, after applying the river screening techniques contained in the original manual (Zison et al., 1977) to real systems, a substantial savings of both time and effort could be realized by programming the major computational sequences. To this end, these algorithms have been programmed on the Texas Instrument TI-59 calculator and are available upon request in a document prepared by Tetra Tech (Mills et al., 1979)*. To date the algorithms contained in Mills et al. (1979) predict:

- Equilibrium temperature
- Longitudinal instream temperature distribution
- Mixing temperatures
- BOD profiles for point and nonpoint sources
- Reaeration rates
- Dissolved oxygen profiles
- Waste assimilative capacity and critical dissolved oxygen levels
- Coliform profiles for point and nonpoint sources
- Bed material sediment transport.

For each program contained in the document the following information is provided for the user:

- A detailed set of user instructions
- A program listing
- A sample input/output sequence.

An example set of user instructions is shown in Figure IV-8. The first 6 steps are for data entry and the seventh is for calculation of the required information.

4.2 CARBONACEOUS AND NITROGENOUS OXYGEN DEMAND

4.2.1 Introduction

Many wastes discharged into waterways contain biologically oxidizable materials that exert an oxygen demand on waterway resources. This biochemical oxygen demand (BOD) can be subdivided into carbonaceous (CBOD) and nitrogenous (NBOD) components. Table IV-12 illustrates typical concentrations of NBOD and CBOD in untreated municipal waste.

CBOD represents the amount of oxygen required by bacteria to stabilize organic matter under aerobic conditions. The reaction can be approximated by:

$$C_nH_aO_bN_c + \left(n + \frac{a}{4} - \frac{b}{2} - \frac{3}{4}c\right)O_2 \rightarrow nCO_2 + \left(\frac{a}{2} - \frac{3}{2}c\right)H_2O + cNH_3 \qquad (IV-12)$$

---
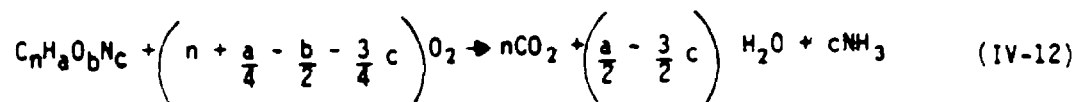
* Attention: W.B. Mills, Tetra Tech, Inc.
  3746 Mt. Diablo Blvd., Suite 300 Lafayette, California 94549

PROGRAM DESCRIPTION

Program: Critical Dissolved Oxygen Calculations

This program calculates the critical dissolved oxygen deficit downstream from a point source of pollution. It also calculates the travel time to the critical deficit.

Note that if the travel time turns out to be negative, then the critical deficit occurs at the point where pollution enters the stream.

USER INSTRUCTIONS				
STEP	PROCEDURE	ENTER	PRESS	DISPLAY
1	Enter program - see listing following these instructions	program	0	0
2	Enter reaeration rate at 20°C, k_{a20} (1/day)	k_{a20}	R/S	0
3	Enter deoxygenation rate at 20°C, k_{d20} (1/day)	k_{d20}	R/S	0
4	Enter BOD concentration in stream just below source of pollution, L_o (mg/l)	L_o	R/S	0
5	Enter dissolved oxygen deficit in stream just below source of pollution, D_o (mg/l)	D_o	R/S	0
6	Enter stream temperature, T (°C)	T	R/S	0
	Calculate and display:			
	- reaeration rate at stream temperature, k_a (1/day)		R/S	k_a
	- deoxygenation rate at stream temperature, k_d (1/day)		R/S	k_d
	- travel time to critical deficit, t_c (days)		R/S	t_c
	- critical deficit, D_c (mg/l)		R/S	D_c

FIGURE IV-8   EXAMPLE SET OF USER'S INSTRUCTIONS
FOR HAND HELD CALCULATOR PROGRAMS

This reaction assumes that the available organic matter is completely oxidized. Bacteria, however, might not be able to completely oxidize all of the available organic matter. Equation IV-13 does illustrate that oxidation of the nitrogen is not included as part of CBOD. The reduced nitrogen is oxidized to nitrate in a two step process as follows:

TABLE IV-12

MUNICIPAL WASTE CHARACTERISTICS
BEFORE TREATMENT (THOMANN, 1972)

Variable	Unit	Approx Average	Normal Range
Average Daily Flow	gal/cap/day	125	100-200
Solids			
Total	mg/l	800	450-1200
Total Volatile	mg/l	400	250-800
Total Dissolved	mg/l	500	300-800
Total Suspended	mg/l	300	100-400
Volatile Suspended	mg/l	130	80-200
Settleable	mg/l	150	-
BOD			
Carbonaceous (5 day)	mg/l	180	100-450
Carboraceous (ultimate)	mg/l	220	120-580
Nitrogenous*	mg/l	220	-
Nitrogen			
Total	mg/l N	50	15-100
Organic	mg/l N	20	5-35
Ammonia	mg/l N	28	10-60
Nitrite + Nitrate	mg/l N	2	0-6
Phosphate			
Total	mg/l PO_4	20	10-50
Ortho	mg/l PO_4	10	5-25
Poly	mg/l PO_4	10	5-25
Coliforms			
Total	million org./100 ml	30	2-50
Fecal	million org./100 ml	4	0.3-17

*Ultimate, Nitrogenous oxygen demand, exclusive of CBOD.

$$2NH_3 + 3O_2 \xrightarrow[\text{bacteria}]{\text{nitrite-forming}} 2NO_2^- + 2H^+ + 2H_2O \qquad \text{(IV-13)}$$

$$2NO_2^- + O_2 + 2H^+ \xrightarrow[\text{bacteria}]{\text{nitrate-forming}} 2NO_3^- + 2H^+ \qquad \text{(IV-14)}$$
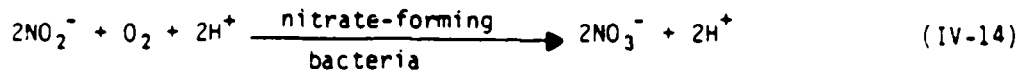
Based on Equations IV-13 and IV-14 the NBOD is:

$$NBOD = 4.57 \left(\left[Org\text{-}N \right] + \left[NH_4^+ - N \right] \right) + 1.14 \left[NO_2^- - N \right] \qquad \text{(IV-15)}$$

Typically the nitrite concentration is negligible so that:

$$NBOD = 4.57 \text{ (TON)} \qquad \text{(IV-16)}$$

where TON represents total oxidizable nitrogen, the sum of organic and ammonia nitrogen. A typical value of TON from Table IV-12 is 20 + 28 = 48 mg-N/l, which corresponds to an NBOD of 220 mg/l.

Typically in the bottle determination of CBOD and NBOD, the carbonaceous demand precedes the nitrogenous demand by 5 to 10 days, as shown in Figure IV-9. This had led workers to believe that nitrification can be ignored in river environments below a source of pollution up to a distance corresponding to a travel time of five to ten days. Such an assumption might be invalid for several reasons. Given that there are numerous sources of pollution along many rivers a viable population of nitrifying bacteria may already be present within the water column. Second, nitrifers can grow attached to the bottom substrate. Consequently, significant numbers can exist just below the discharge location and nitrification can proceed immediately. Nitrification by attached bacteria is more likely to be of significance in relatively shallow, wide rivers, which have stable bottom substrate (Mills, 1976).

CBOD is a commonly measured characteristic of waste water. The CBOD used in the formulations presented below is the ultimate CBOD. Often CBOD is expressed as $CBOD_5$, the oxygen utilized in a 5 day test. The relationship between ultimate ($CBOD_L$) and 5-day CBOD can be approximated by:

$$CBOD_L = \frac{CBOD_5}{0.68}$$

This relationship assumes a decay rate of 0.23/day, and may be different for effluents from advanced wastewater treatment plants.

The mass balance equation used in the CBOD analysis is exactly analogous to the NBOD equation. The first order decay rate assumption for NBOD stabilization is necessary to maintain this analogy, and is sufficient for hand calculations.
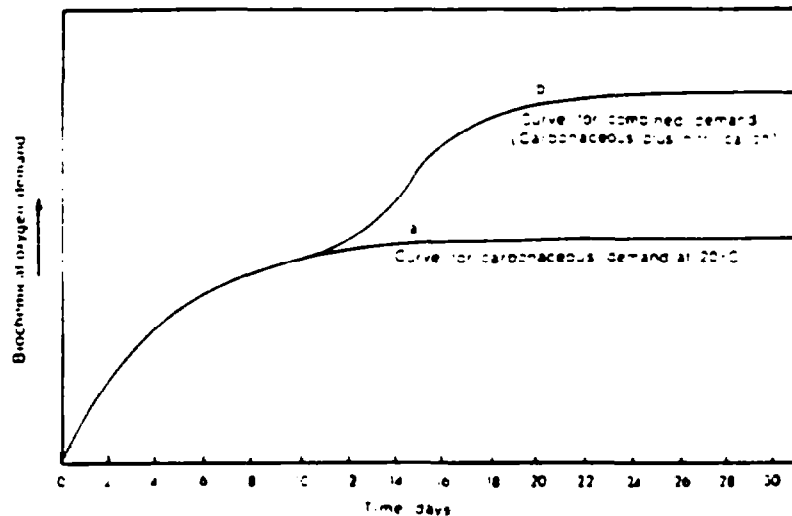
FIGURE IV-9   THE BOD CURVE. (A) CURVE FOR OXIDATION OF
CARBONACEOUS MATTER. (B) CURVE SHOWING
INFLUENCE OF NITRIFICATION.

Nitrification (the process by which ammonia is oxidized to nitrite, and nitrite to nitrate) is pH dependent with an optimum range of 8.0 to 8.5 (Wild, 1971). If the pH of the river is below 7.0, nitrification is not likely to be important.

4.2.2 BOD Decay Rate

The decay rate for CBOD will be denoted by k_L and for NBOD by k_N. Typical values of both k_L and k_N lie between 0.1 and 0.6/day, with 0.3/day being typical. k_L values can, however, exceed the range given here. Values of 1 to 3/day have been computed for shallow streams (Thomann, 1972). A figure to be presented shortly will show how k_L depends on depth. The following discussion will be directed toward k_L, but in general will also apply to k_N.

The disappearance of BOD from a river is a reflection of both settling and biochemical oxidation, as shown in Figure IV-10. Biochemical oxidation can consist of instream oxidation (k_1L) as well as absorption by attached organisms (k_4L). The total oxidation rate then, is k_d, where:

$$k_d = k_1 + k_4$$

The total loss rate k_L is:

$$k_L = k_d + k_3$$

where k_3 reflects settling losses.

-310-
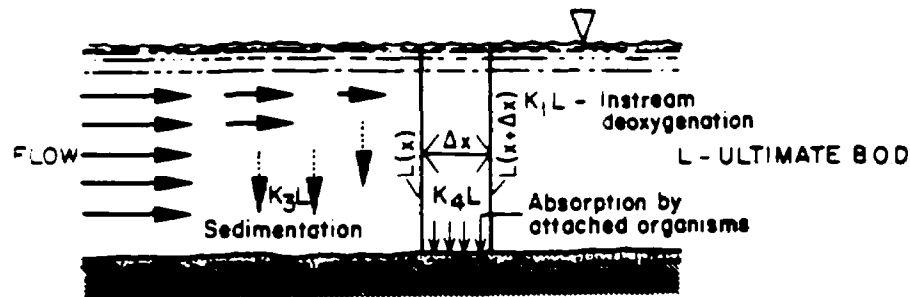
FIGURE IV-10   MECHANISMS OF BOD REMOVAL
FROM RIVERS

Settling of BOD is generally more prevalent just below a sewage discharge where the discharged material may contain a large suspended fraction. As this material is transported downstream the settling component becomes less important and the reaction rate k_L approaches the oxidation rate k_d. In this chapter, the settling component will not be explicitly considered. Neglecting settling will tend to cause estimated instream BOD levels to be somewhat higher than they actually might be along certain portions of a river. It should be noted that if instream BOD data are used to determine k_L (one such method will be explained in Figure IV-12) then the effect of settling is automatically included in k_L .

Figure IV-11 illustrates the dependence of k_L on river depth. The highest deoxygenation rates occur in shallow streams with stable, rocky beds, reflecting the significance of attached biological organisms. Bowie et al. (1985) contains observed and predicted values of k_L for various natural streams.

The decay coefficients k_L and k_N are both temperature dependent and this dependence can be estimated by:

$$k_T = k_{20} \ 1.047^{(T-20)} \qquad \qquad (IV-17)$$

where

k_{20} = k_L or k_N at $20^{\circ}C$
k_T = k_L or k_N at $T^{\circ}C$
T = water temperature, $^{\circ}C$.

Numerous methods for computing k_L from observed data are available (Nemerow, 1974). One method entails the use of a semi-log plot. The stretch of river containing the data to be plotted must have a constant stream area and flow rate, and the BOD loading must be from a point source located at a position that will be called $x = 0$. Plotting the log of BOD concentration versus distance generally produces a
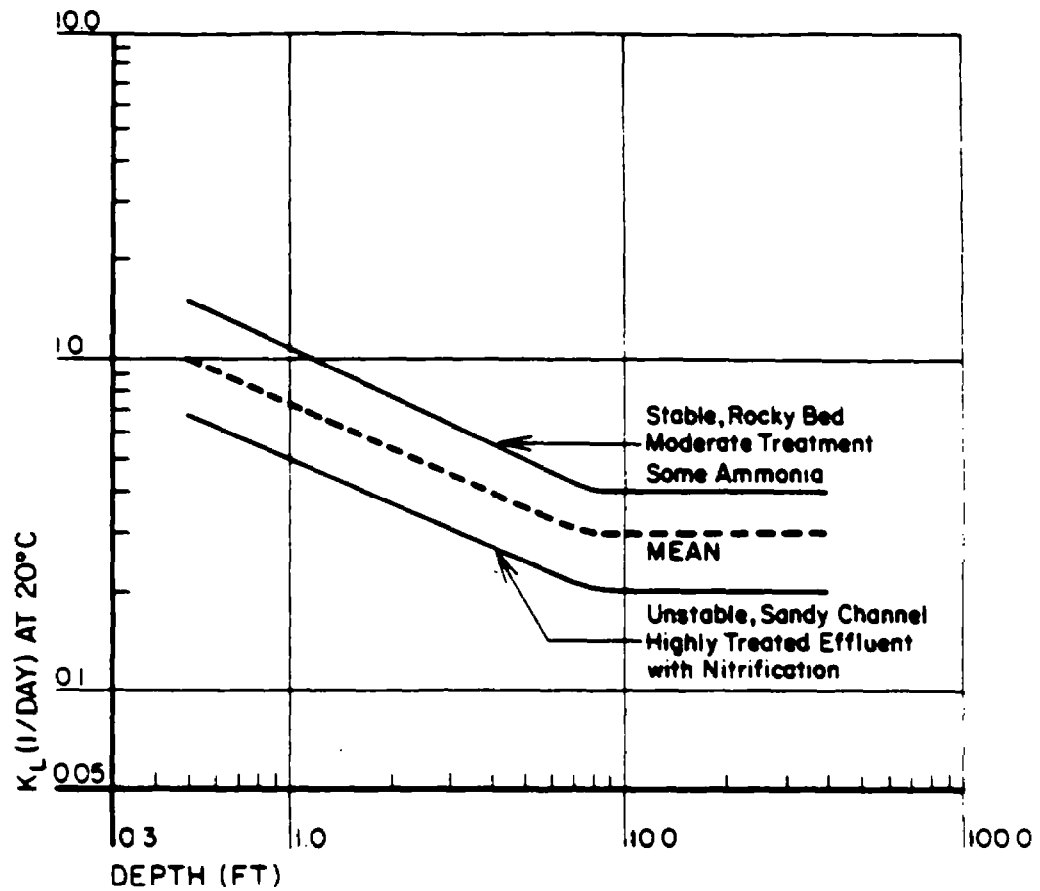
FIGURE IV-11   DEOXYGENATION COEFFICIENT AS A FUNCTION OF
DEPTH, (AFTER HYDROSCIENCE, 1971)

straight line with slope of $-k_L/U$. An example is shown in Figure IV-12. Either $CBOD_5$ or $CBOD_L$ can be plotted as the ordinate. The slope should be converted from base 10 logarithms as given in the semi-log plot to base e logarithms as needed in the formulations used in this chapter. The conversion is made by multiplying the value for log base 10 by 2.303.

Wright and McDonnell (1979) have more recently developed an expression for instream BOD decay rate based on the flow rate of the river. The expression is:

$$
k_d \left(\frac{1}{day} \right) = \begin{cases} k_{lab} & \text{if } Q>800 \text{ cfs} & \text{(IV-18a)} \\[2mm] \dfrac{10.3}{\sqrt{Q}} & \text{if } Q<800 \text{ cfs} & \text{(IV-18b)} \end{cases}
$$

-312-

U = 4 Miles/Day

K_L = -Slope x U

= $2.3 \left(\frac{0.017}{Miles}\right) \left(\frac{4\ Miles}{Day}\right)$

K_L = 0.16/Day

Slope = $2.3 \left(-\frac{0.017}{Miles}\right)$
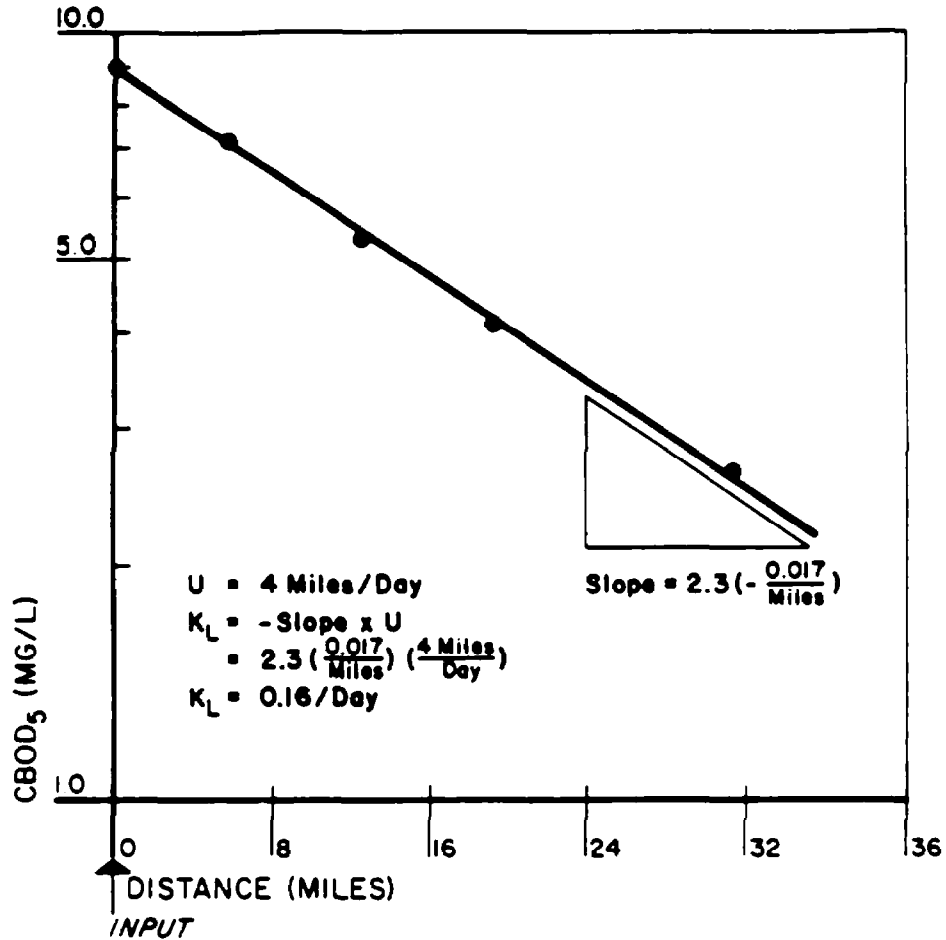
FIGURE IV-12   EXAMPLE OF COMPUTATION OF K_L FROM STREAM
DATA (FROM HYDROSCIENCE, 1971)

This expression is particularly attractive because the only hydraulic variable required is flow rate. Other predictive techniques and rate data from rivers around the country are contained in Zison et al. (1978).

4.2.3 Mass Balance of BOD

The general mass-balance equation for BOD in rivers is:

$$\frac{\partial L}{\partial t} = 0 = \frac{-1}{A} \frac{\partial}{\partial x} (QL) - k_L L + L_r \left(\frac{\partial Q}{\partial x}\right)/A + L_{rd} \qquad (IV-19)$$

where

L = CBOD (ultimate) remaining to be oxidized, mg/l

Q = volumetric flow rate, ft^3/sec

A = cross-sectional area, ft^2

L_r = concentration of CBOD entering through an incremental sideflow (distributed source), mg/l

L_{rd} = mass flux of CBOD entering, with no associated flow, mg/l/sec

x = stream distance

$\frac{\partial L}{\partial t}$ = 0 indicates that steady-state conditions are being assumed and thus no accumulation of material takes place at any point within the reach.

The NBOD equation is completely analogous in form to Equation IV-19:

$$\frac{\partial N}{\partial t} = 0 = -\frac{1}{A}\frac{\partial}{\partial x}(QN) - k_N N + N_r \left(\frac{\partial Q}{\partial x}\right)/A + N_{rd} \tag{IV-20}$$

where

N = the NBOD.

N_{rd} represents purely a mass flux of nitrogenous material, while $N_r \left(\frac{\partial Q}{\partial x}\right)/A$ is a source of NBOD entering the river reach through an incremental sideflow. Thus, in cases where a known distributed source of BOD significantly contributes to a river reach under study, and the distributed flow (flow associated with a distributed source) can be neglected, N_{rd} can be used in lieu of $N_r \left(\frac{\partial Q}{\partial x}\right)/A$. N_{rd} can be estimated by determining the mass M of BOD entering a volume of river water V in time T. N_{rd} is given by:

$$N_{rd} = \frac{M}{VT}$$

For any particular reach of a river under investigation the stream cross-sectional area can be expressed by:

$$A = A_o + \left(\frac{A_f - A_o}{x_L}\right) x = A_o + \Delta_A x \tag{IV-21}$$

where

$$\Delta_A = \frac{A_f - A_o}{x_L}$$

A_o = stream cross-sectional area at upstream end of the reach

A_f = stream cross-sectional area at downstream end of reach

x = distance downstream from beginning of reach

x_L = length of reach.

The cross-sectional area need not be measured directly, but can be computed from:

$$A = \frac{Q}{U}$$

The cross-sectional area change can reflect a change in stream velocity, perhaps due to a bed slope increase or decrease. The length of the reach under investigation, x_L, is measured in river miles along the river's centerline. If use of a constant stream area is assumed, then $\Delta_A = 0$ and $A = A_0$ throughout the reach.

4.2.4 Typical Solutions

Case 1: The only source of CBOD occurs as a point source at $x = 0$. The CBOD distribution is then expressed by:

$$L = L_0 \exp\left[\frac{-j_L}{A_0} \left(A_0 x + \Delta_A \frac{x^2}{2}\right)\right] \qquad \text{(IV-22)}$$

where

$$j_L = \frac{k_L}{U_0}$$

U_0 = stream velocity at $x = 0$

L_0 = ultimate BOD at the upstream end of the reach

L = ultimate BOD at a distance x downstream

The other terms have previously been defined.

The initial CBOD, L_0, must reflect both CBOD upstream of the reach as well as that contributed by the point source in question. It is given by:

$$L_0 = \frac{L_u Q_u + W/5.38}{Q_u + Q_W} \qquad \text{(IV-23)}$$

where

W = mass rate of discharge of CBOD, lb/day

Q_u = upstream river flow, cfs

Q_W = waste flow rate, cfs

L_u = upstream CBOD concentration, mg/l.

Case 2: For a point source of CBOD at $x = 0$ and a distributed mass influx of CBOD (with no associated flow) entering the river throughout the reach, the solution is:

$$L = \frac{L_{rd}}{k_L} + \left(L_0 - \frac{L_{rd}}{k_L}\right) \exp\left[\frac{-j_L}{A_0} \left(A_0 x + \Delta_A \frac{x^2}{2}\right)\right] \qquad \text{(IV-24)}$$

where

L_{rd} = mass rate of CBOD entering the reach per unit volume of river water, mg/l/day.

Case 3: A distributed flow enters the river carrying CBOD and a point source of CBOD exists at $x = 0$. The flow rate Q at a distance x is:

$$Q = Q_o + \frac{Q_f - Q_o}{x_L} x = Q_o + \Delta_Q x$$

where

$$\Delta_Q = \frac{Q_f - Q_o}{x_L}$$

The BOD distribution is given by (the river cross-sectional area is assumed constant throughout the reach):

$$L = \frac{L_r}{E_1} + \left(L_o - \frac{L_r}{E_1}\right)\left(\frac{Q_o}{Q}\right)^{E_1} \tag{IV-25}$$

where

$$E_1 = \frac{k_L A_o + \Delta_Q}{\Delta_Q}$$

L_r = concentration of CBOD entering the river in the distributed flow, mg/l.

Case 3 can also be used to establish the effect a purely diluting inflow (i.e. $L_r = 0$) would have on the CBOD distribution.

Case 4: For a point source at $x = 0$, a distributed source with associated inflow, and a mass flux with no associated flow (constant river cross-sectional area), the solution is:

$$L = L_o \left(\frac{Q_o}{Q}\right)^{E_1} + \frac{L_r \Delta_Q + L_{rd} A_o}{k_L A_o + \Delta_Q}\left(1 - \left(\frac{Q_o}{Q}\right)^{E_1}\right) \tag{IV-26}$$

where

$$E_1 = \frac{k_L A_o + \Delta_Q}{\Delta_Q} \text{ , as in Case 3.}$$

4.2.5 Other Simplifying Procedures

The formulations represented by Equations IV-22 through IV-26 offer a range of options for examining BOD distribution in rivers. However, there are additional methods of estimating instream concentrations and determining whether or not significant BOD levels exist. Perhaps the simplest method is assuming that BOD does not decay. An upper limit of the instream concentration at any point can then be determined by incorporating all known sources, and using the methods presented in Section 4.7. If the computed instream concentrations are below a threshold pollution level, then there is no need to apply Equations IV-22 through IV-26 because the inclusion of a decay rate will only lower the concentrations.

It may also be feasible, as a first estimate, to combine the CBOD and NBOD equations into one, and use that equation to estimate the distribution of the total oxygen-demanding material. To do this, all source terms must include both CBOD and NBOD. One decay coefficient is used for both CBOD and NBOD decay. The larger decay coefficient of the two should be used since that will produce the larger oxygen deficit.

In deciding which of Equations IV-22 through IV-26 to use for any analysis, the purpose of the analysis as well as data availability should be considered. If the main purpose is to estimate differences in stream concentrations caused by various levels of abatement at a sewage treatment plant, the diffuse sources of BOD need not be considered. The resulting concentration difference can be expressed as:

$$\Delta L = \begin{cases} \Delta L_o \ \exp\left[\dfrac{-j_L}{A_o} \ \left(A_o x + \Delta_A \dfrac{x^2}{2}\right)\right] & \text{(IV-27a)} \\[4ex] \Delta L_o \ \left(\dfrac{Q_o}{Q}\right)^{E_1} & \text{(IV-27b)} \end{cases}$$

where

ΔL = the change in BOD concentration due to a change, ΔL_o, in the initial concentration.

Equation IV-27A should be used for a Case 1 or Case 2 situation, and Equation IV-27B for Case 3 or Case 4. If an estimate of the absolute level of BOD is desired, however, then the appropriate expression including the nonpoint sources should be utilized. It should be noted that if the diffuse sources of BOD are large then the improvement of instream BOD concentrations by point source control will be relatively minor. In that case the planner should focus on nonpoint source control.

EXAMPLE IV-5

Estimating BOD Distribution in a River

Suppose the user wants to calculate the BOD distribution in the river shown below in Figure IV-13. There are nine point sources contributing BOD
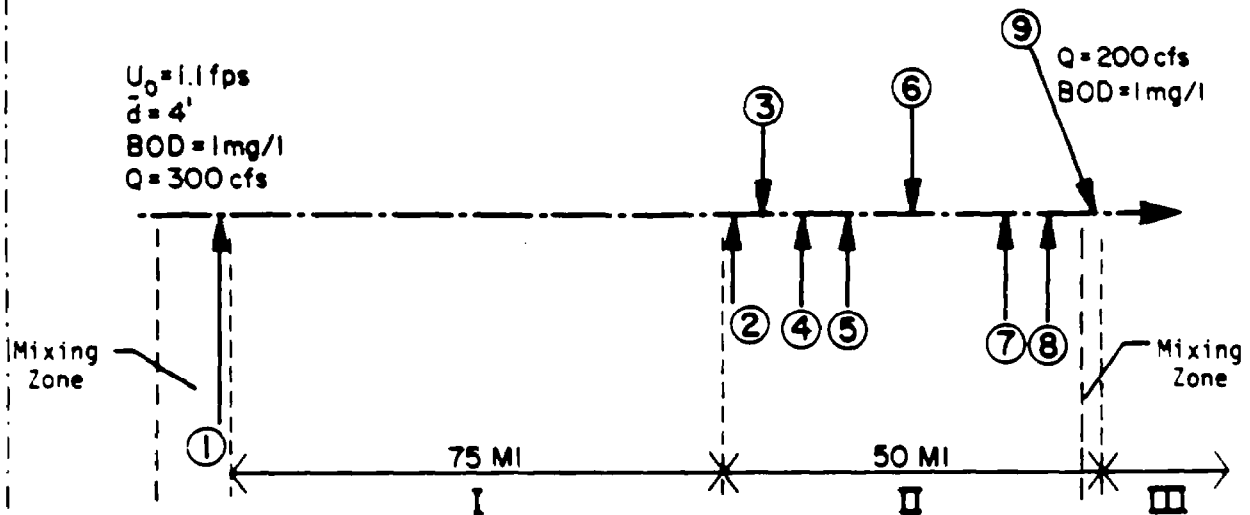
FIGURE IV-13   HYPOTHETICAL BOD WASTE LOADINGS IN A RIVER

in the stretch of river under consideration. The ninth source is assumed to be a tributary, and contributes substantially more flow than the other eight. Begin by dividing the river into reaches. The first reach (I) should include the first 75 miles in which there is one point source of BOD at the upstream end (source (1)). Equation IV-22 is applicable to that reach. Now, there are several choices available regarding the division of the river between sources (2) and (8). One choice is to divide the 50 miles into mini-reaches similar to Reach I, and reapply Equation IV-22 seven more times. A second alternative is to group adjacent point sources into fewer and larger sources, thereby requiring fewer applications of Equation IV-22. A third alternative is to assume that sources (2) through (8) comprise one continuous distributed source, the total pollutant loading of this equivalent source being equal to the sum of the individual loads. For this representation to be valid the sources should be both evenly spread spatially and be discharging comparable loads. The third alternative will be examined here, and reach II will consist of the 50 miles following Reach I. Equation IV-25 will be used to analyze Reach II. Reach III, then, will begin just downstream from the tributary (source (9)).

For Reach I, Equation IV-22 is first solved. Suppose the following charac-
teristics of waste source (1) are known:

$$Q = 20 \text{ MGD} = 1.55 \ (20) \text{ cfs}$$
$$= 31 \text{ cfs}$$
$$W = 5000 \text{ lb. BOD}_5/\text{day}$$

Recall that:

$$L_o = \frac{L_u Q_u + W/5.38}{Q_u + Q_W}$$

W must be in lb. BOD ultimate/day:

$$W = \frac{5000}{.68}$$
$$= 7353 \text{ lb. BOD}_L/\text{day}$$

then

$$L_o = \frac{(1) \ (300) + 7353/5.38}{300 + 31}$$
$$= 5.0 \text{ mg/l}$$

The decay coefficient is estimated from Figure IV-11 as 0.4/day. No correc-
tion will be made for temperature. Equation IV-22 can now be expressed as
(for constant cross-sectional area):

$$L = 5 \ \exp\left(\frac{-0.4}{(1.1)(24)(3600)} \ x\right)$$

where x is the downstream distance in feet. Note the correction needed to
convert the decay coefficient from units of 1/day to 1/sec.

The results of the above equation for selected distances downstream can
be expressed as follows:

x (miles)	L(mg/l)
0	5.0
30	2.6
60	1.3
75	0.9

For Reach II, sources (2) through (8) are assumed to contribute the following
loading:

$$BOD = 8000 \text{ lb/day}$$
$$Q = 120 \text{ MGD}$$
$$= 186 \text{ cfs}$$

The flow distribution, Q, in Reach II, is then:

$$Q = Q_o + \frac{Q_f - Q_o}{x_L} \ x$$
$$= 331 + \frac{186}{50} \ x$$

where x is in miles (from 0 to 50). L_r, the average BOD_L concentration in the incoming flow is:

$$L_r = \frac{8000 \text{ lb/day}}{120 \text{ MGD}} \times \frac{1 \text{ mg/l}}{8.34 \text{ lb/day}}$$

$$= 8.0 \text{ mg/l}$$

If the average depth in Reach II is assumed to be 5 feet, then:

$$k_L = .3/\text{day}$$

Finally, E_1 is computed:

$$E_1 = \frac{k_L A_o + \Delta_Q}{\Delta_Q} , \quad A_o = \frac{Q_o}{U_o} = \frac{331}{1.1} = 301 \text{ ft}^2$$

$$E_1 = \frac{\frac{(0.3)(301)}{(24)(3600)}}{\frac{186}{(50)(5280)}} + 1 = 2.5$$

Then, using L from the 75 mile point of Reach I as L_o:

$$L = \frac{8.0}{2.5} + \left(0.9 - \frac{8.0}{2.5}\right)\left(\frac{331}{Q}\right)^{2.5}$$

$$= 3.2 - 2.3\left(\frac{331}{Q}\right)^{2.5}$$

In tabulated form:

x (mi)	Q (cfs)	L (mg/l)
0	331	0.9
20	405	1.8
40	480	2.3
50	517	2.5

Note that the BOD concentration is increasing within this reach.

For reach III, only enough information is given to compute the initial concentration, utilizing weighted values for the BOD at the end of reach I, and that entering through the tributary (source (9)).

$$L_o = \frac{200(1) + 517(2.5)}{200 + 517} = 2.1 \text{ mg/l}$$

4.2.6 Interpretation of Results

The most frequent use of BOD data in river water quality analyses involves their relationship with the dissolved oxygen balance. This relationship will be discussed more fully in Section 4.3. At this point it is sufficient to say that t is necessary to predict the BOD distribution in a river in order to compute dissolved oxygen concentrations.

When a river receives a heavy load of organic matter, the normal processes of self purification result in a series of zones of decreasingly severe conditions succeeding one another downstream. Each zone contains characteristic animals and plants (Nemerow, 1974). A saprobicity system (saprobicity is a measure of biodegradable organic matter) has been developed that relates BOD concentrations in streams to the degree of pollution there. Correlations have been found, for example, among BOD concentrations, coliform bacteria, and dissolved oxygen in rivers (Sladecek, 1965). Sladecek (1969) has assigned 5-day BOD values of 5 mg/l to mildly polluted conditions and 10 mg/l to substantial pollution.

Sources of drinking water are subject to restraints on the maximum allowable BOD that can be contained in raw water and still quality as a drinking water source. Further, the degree of treatment of the raw water is dependent on the concentrations of certain constituents, such as BOD. One reference (HEC, 1975) has stated that water having a 5-day BOD over 4 mg/l, in combination with high levels of other constituents, represents a poor source of domestic water supply.

As discussed above, BOD in a river can come from a number of sources, both point and nonpoint. Although BOD reduction from point source might be easier to accomplish than from nonpoint sources, there is no guarantee that BOD levels will be substantially lowered.

4.3 DISSOLVED OXYGEN

4.3.1 Introduction

Historically, dissolved oxygen has been and continues to be the single most frequently used indicator of water quality in streams and rivers. Figure IV-14 shows the seasonal variability of dissolved oxygen in 22 major waterways throughout the country (EPA, 1974) from 1968 to 1972. Invariably the levels observed from June to October are lower than those observed in January to March. This is due primarily to the influence of temperature on the dissolved oxygen levels. Due to the effect of temperature, summer is the most critical season in terms of organic pollutant assimilation in rivers.

The dissolved oxygen calculations presented below range in complexity from a simple CBOD-DO relationship to a more general dissolved oxygen mass balance including CBOD, NBOD, photosynthesis, respiration, and benthic demands. It should be
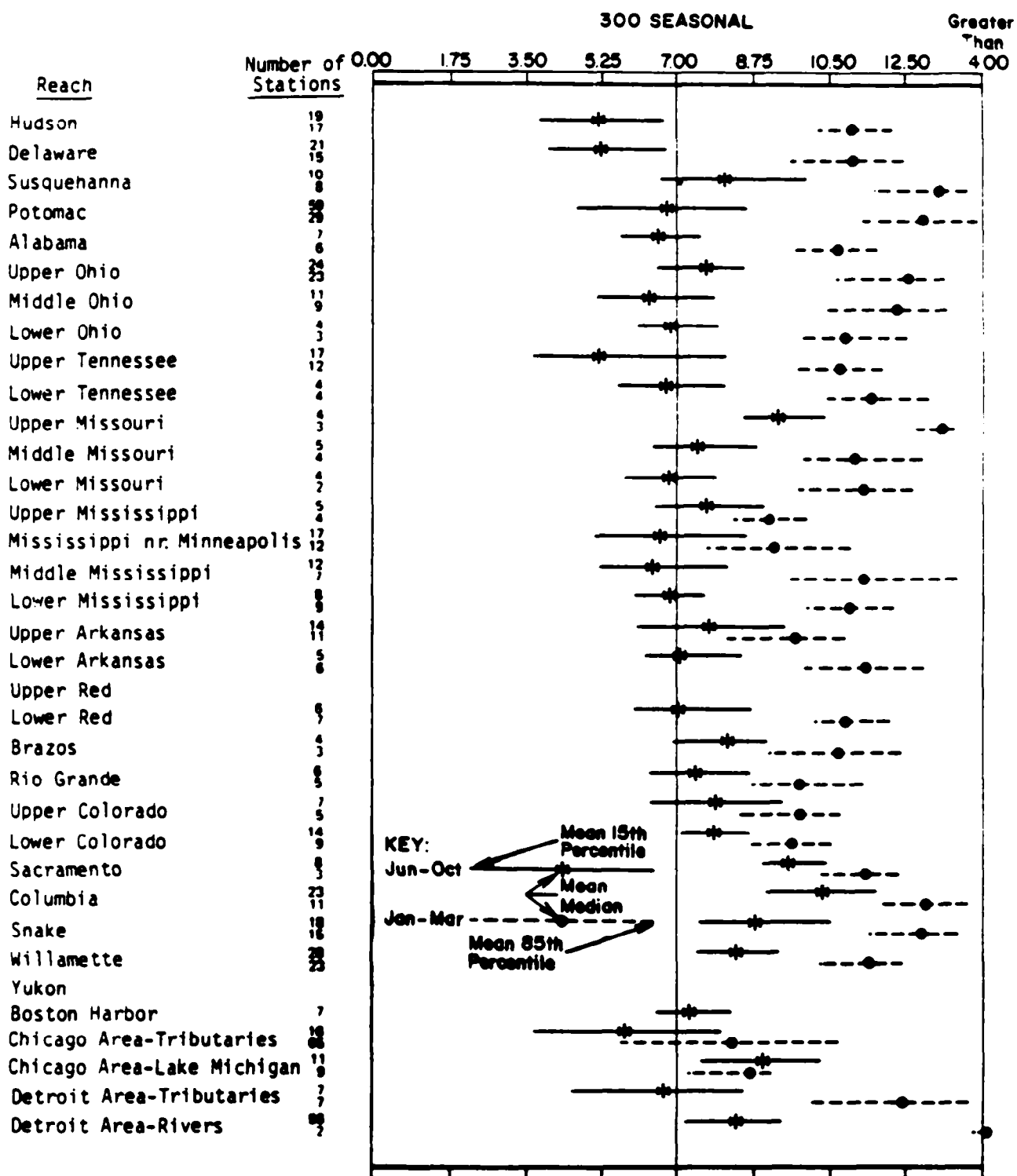
FIGURE IV-14   VARIABILITY OF DISSOLVED OXYGEN BY SEASON FOR
22 MAJOR WATERWAYS, 1968-72 (EPA, 1974)

-322-

stressed, however, that the results calculated from any of the relationships provide esimates only since each procedure incorporates various assumptions that might not be fully met. For example, waste loading inflows are assumed to remain constant in quality arc quantity over time. In reality loadings probably vary over time. Furthermore the choice of system parameters involves a certain degree of judgment. However, for any given situation, the planner can establish an envelope of possible outcomes by different realistic choices of system parameters.

4.3.2 Dissolved Oxygen Mass-Balance

The general dissolved oxygen mass-balance equation that will be utilized here is given by:

$$\frac{\partial C}{\partial t} = 0 = - \frac{1}{A}\frac{\partial (QC)}{\partial x} - k_L L - k_N N + k_a (C_s - C) - S_b + P - R \qquad (IV-28)$$

where the new symbols introduced are:

C = dissolved oxygen concentration, mg/l

k_a = reaeration coefficient, 1/day

C_s = saturation value of dissolved oxygen, mg/l

S_b = benthic oxygen demand, mg/l/day

P = rate of oxygen production due to photosynthesis, mg/l/day

R = rate of oxygen consumption due to algal respiration, mg/l/day.

Stated in words, Equation IV-24 expresses the following relationship:
At steady state, the rate of addition of dissolved oxygen to a river due to reaeration and photosynthesis equals the depletion rate caused by the net advective flow, carbonaceous oxidation, nitrogenous oxidation, benthic demands, and algal respiration.

Commonly, the dissolved oxygen mass-balance equation is expressed in terms of the deficit, D, which is the difference between the saturation and actual concentrations.

4.3.3 Reaeration Rate

The atmosphere acts as the major source for replenishing the dissolved oxygen resources of rivers. Reaeration tends to equilibrate the dissolved oxygen concentration in a river with its saturation value. Most commonly, the dissolved oxygen concentration is below saturation and there is a net influx of oxygen into the river from the atmosphere. On occasion, due to the production of dissolved oxygen by algae, rivers or streams can become supersaturated, in which case there is a net loss of oxygen to the atmosphere.

A number of expressions for the reaeration coefficient, k_a, have been

developed. Several are presented here. O'Connor's formulation (Thomann, 1972) states that:

$$k_a = \frac{(D_L \ U)^{1/2}}{H^{3/2}} \quad \text{at } 20° \text{ C} \qquad (IV-29)$$

where

D_L = oxygen diffusivity = 0.000081 ft^2/hr at 20°C
H = stream depth in ft
U = stream velocity in ft/sec.

Expressed in English units:

$$k_a = \frac{12.9 \ U^{1/2}}{H^{3/2}} \quad \text{at } 20°C \qquad (IV-30)$$

The above formula was verified on streams and rivers ranging in average depth from 1 foot to 30 feet with velocities ranging from 0.5 to 1.6 fps. Its use should be limited to streams where the reaeration coefficient is less than 12/day. Figure IV-15 illustrates how k_a changes with depth and velocity according to this relationship.

For shallow (0.4 - 2.4 feet), fast moving streams, the following expression developed by Owens (Thomann, 1972) is preferable, as the experimental work to develop this expression was done almost exclusively on shallow streams:

$$k_a = 21.6 \ \frac{U^{0.67}}{H^{1.85}} \quad \text{at } 20°C \qquad (IV-31)$$

where U is in ft/sec and H is in feet. A graphical representation of Equation IV-31 is shown in Figure IV-16.

Covar (1976) showed that there were certain combinations of river depths and velocities where a formula developed by Churchill (Churchill et al., 1962) is more accurate than either the O'Connor or Owens formulations. The Churchill expression is:

$$k_a = 11.6 U^{0.969} \ H^{-1.673} \text{ per day at } 20°C \qquad (IV-32)$$

The regions of validity, and the predicted values, for the three formulations are shown in Figure IV-17.

Recent studies have suggested that the Owens expression overestimates the reaeration rate for particularly shallow streams (e.g., less than a foot in depth). Under these circumstances the Tsivoglou-Wallace method (Tsivoglou and Wallace, 1978)
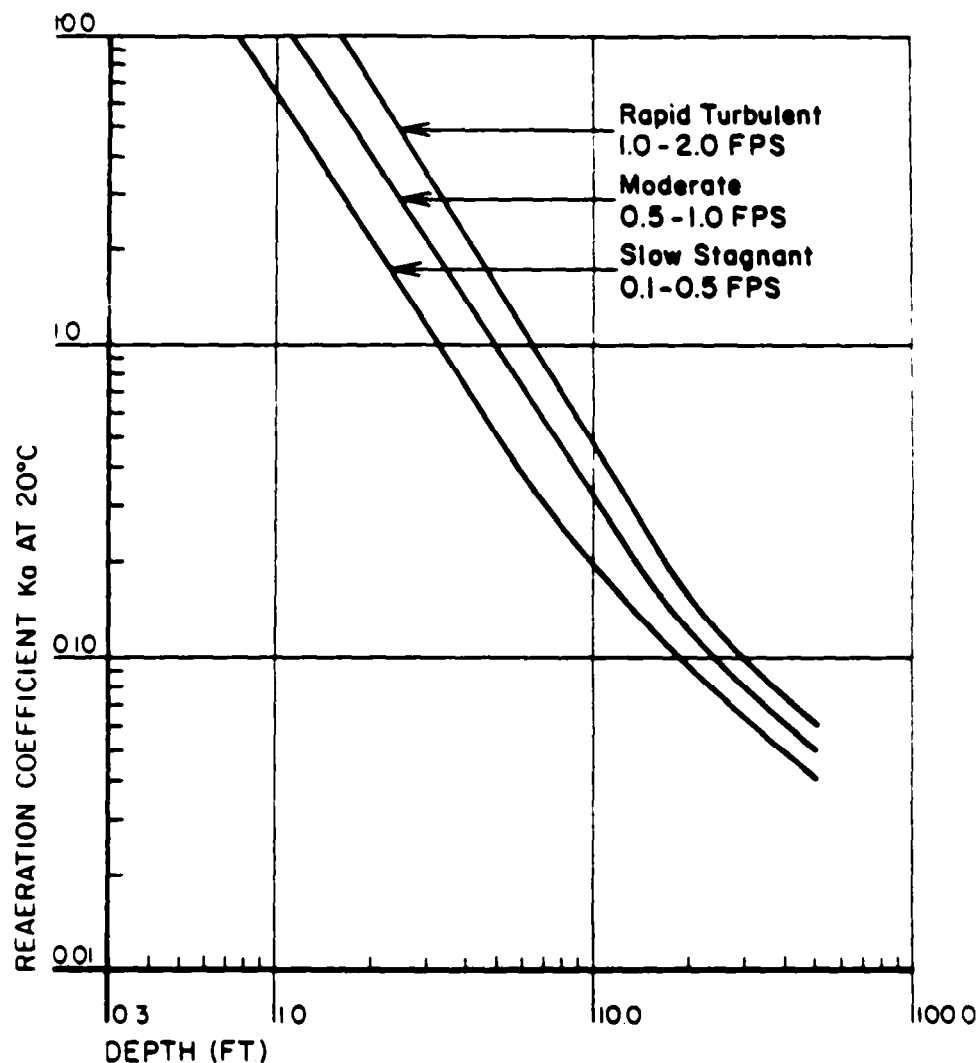
FIGURE IV-15   REAERATION COEFFICIENT AS A FUNCTION OF DEPTH
(FROM HYDROSCIENCE, 1971)

is more accurate. The expression is:

$$
k_a \ (1/day) \ = \begin{cases} 7776. \ US, \ @ \ 25°C, \ Q < 10 \ cfs & (IV-33a) \\ 4665.6 \ US, \ @25°C, \ 10 < Q < 3000 \ cfs & (IV-33b) \\ 2592. \ US, \ @ \ 25°C, \ Q > 3000 \ cfs & (IV-33c) \end{cases}
$$

where

    S = stream slope, ft/ft.

Table IV-13 compares predictions of Tsivoglou-Wallace with observed values for
several small streams in Wisconsin. The agreement is good.

-325-
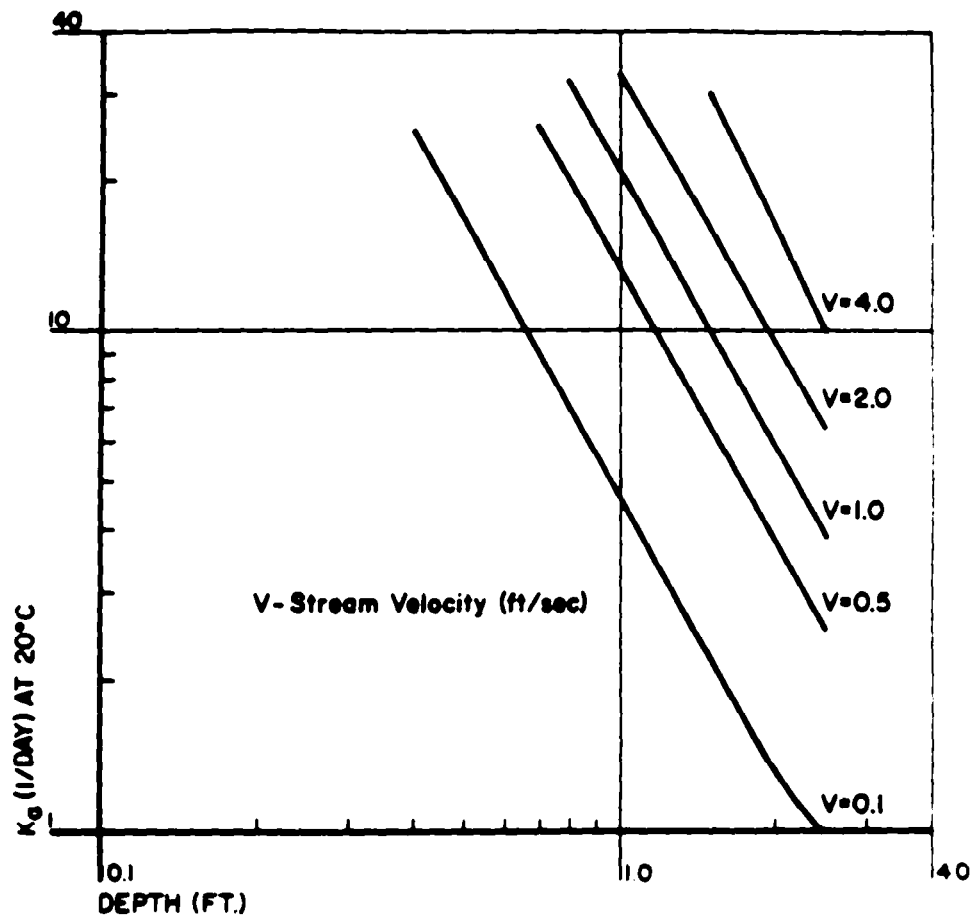
FIGURE IV-16   REAERATION COEFFICIENT FOR SHALLOW STREAMS,
OWEN'S FORMULATION

—·—·—·—·—·—·—·—·—·—· EXAMPLE IV-6 —·—·—·—·—·—·—·—·—·—·—·

Prediction of Reaeration Rates

In September, 1969, a study was conducted to determine the reaeration rate coefficients on the Patuxent River in Maryland during the low flow period. The study was carried out on a seven mile stretch of the river below Laurel, Maryland. The stream was divided into seven segments, and the reaeration rate determined for each segment. A portion of the results are shown in the Table IV-14. Using the hydraulic data in the table predict the reaeration rates using the methods of Tsivoglou-Wallace and of Covar.

Since the method of calculating the reaeration for each reach is the same, an example calculation will be shown for the first reach only. Based on a velocity of 0.39 ft/sec and a slope of 0.0013 ft/ft, the Tsivoglou-Wallace method predicts a reaeration rate of:
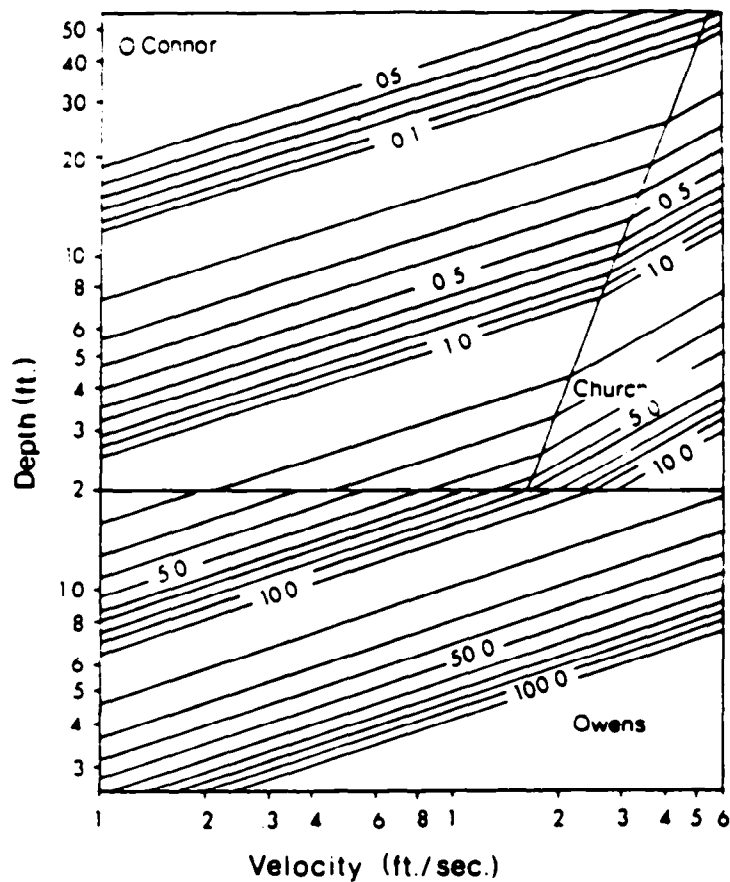
FIGURE IV-17   REAERATION RATE VERSUS DEPTH
AND VELOCITY (FROM COVAR, 1976).

$$k_a = 7776 \times 0.39 \times 0.0013$$
$$= 3.9/\text{day at } 25°C$$

Equation IV-33a is used since Q < 10 cfs.

Using Figure IV-17 and a river depth of 0.8 feet reveals that the Owens formula is applicable. Applying Equation IV-31 shows that:

$$k_a = 21.6 \frac{0.39^{0.67}}{0.8^{1.85}} = 17.4/\text{day at } 20°C$$

TABLE IV-13

COMPARISON OF PREDICTED AND OBSERVED
REAERATION RATES ON SMALL STREAMS IN WISCONSIN*

Stream	Observed k_a (1/day at 25°C)	Predicted k_a Using Tsivoglou's Method (1/day at 25°C)
Black Earth Creek	8.46	7.8
Mud Creek tributary	10.7	4.2
Dodge Branch	33.1	34.6
Isabelle Creek	14.	-
Madison effluent channel	2.06	4.1
Mill Creek	3.31	2.2
Honey Creek	18.4	27.4
West Branch Sugar River	42.5	36.4
Koshkonong Creek	6.09	4.8
Badger Mill Creek	7.98	9.1

*Grant, R.S., 1976. Reaeration-Coefficient Measurements of 10 Small Streams in Wisconsin Using Radioactive Tracers... with a Section on the Energy-Dissipation Model. U.S. Geological Survey. Water Resources Investigations, 76-96.

The results for all the reaches are tabulated below.

REAERATION RATE (1/day)

Reach	Observed (25°C)	Tsivoglou-Wallace (25°C)	Owens (20°C)
1-2	3.9	3.9	17.4
2-3	2.7	1.9	7.8
3-4	3.3	3.8	10.7
4-5	3.5	2.9	9.0
5-6	2.4	1.5	7.2
6-7	4.8	2.2	11.0

The predictions using the Tsivoglou-Wallace method are good for all reaches, while Owens' method predicts values two to three times too large, and provides evidence that Owens' method probably should not be applied to extremely shallow rivers.

TABLE IV-14

TYPICAL HYDRAULIC PROPERTIES

PATUXENT RIVER (SEPTEMBER, 1969)

Reach	Flow cfs	Length ft	Velocity ft/sec	Depth ft	Slope ft/ft	Reaeration Rate (1/day)		
						Observed (25°C)	Tsivoglou-Wallace (25°C)	Cover (20°C)
1-2	9.8	5,400	0.39	0.80	.0013	3.9		
2-3	9.8	4,200	0.22	1.00	.0011	2.7		
3-4	9.8	7,200	0.35	1.00	.0014	3.3		
4-5	19.5	8,400	0.35	1.10	.0018	3.5		
5-6	19.5	6,600	0.25	1.10	.0013	2.4		
6-7	19.5	4,800	0.37	1.00	.0013	4.8		

Temperature changes affect the reaeration rate, and the relationship can be approximated by:

$$(k_a)_T = (k_a)_{20} \; 1.024^{(T-20)}$$

(IV-34)

where

$(k_a)_T$ = the reaeration coefficient at T ^oC.

In addition to temperature, substantial suspended sediment concentrations can appreciably alter the reaeration rate in streams (Alonso et al., 1975). As an approximation, k_a decreases by 9 percent per 1,000 ppm increase in suspended sediment up to a 4,000 ppm load. Beyond that, concentration data are not available to assess the response of k_a. It is suggest: that a 40 percent decrease be used for higher suspended sediment loads. Rivers with high suspended sediment loads are generally found in the western central states. Measured values of k_a for various streams and rivers are included in Bowie et al. (1985).

4.3.4 Effect of Dams on Reaeration

Many rivers or streams have small to moderate sized dams crossing them in one or more places. Reaeration occurs as the water flows over the dam. Based on experimental data (Gameson et al., 1958), and later verified with field data (Barrett et al., 1960), the following relationship for reaeration over dams has been developed:

$$D_a - D_b = \left[1 - \frac{1}{1 + 0.11 \; ab(1 + 0.046T)H} \right] D_a$$

(IV-35)

where

D_a = dissolved oxygen deficit above dam, mg/l

D_b = dissolved oxygen deficit below dam, mg/l

T = temperature, ^oC

H = height through which the water falls, ft

a = 1.25 in clear to slightly polluted water; 1.00 in polluted water

b = 1.00 for weir with free fall; 1.3 for step weirs or cascades.

An alternate equation developed from data on the Mohawk River and Barge Canal in New York State (Mastropietro, 1968) is as follows:

$$D_a - D_b = 0.037H \; D_a$$

(IV-36)

Equation IV-36 is valid for dams up to fifteen feet high and for temperatures in the range of 20° to 25°C.

In handling the problem of a dam, a new reach can be started just below the dam.

O_a can be calculated as the value that occurs at the end of the upstream reach. The new deficit O_b, which will become the deficit at the beginning of the next reach, is calculated using either of the above two formulas.

4.3.5 Dissolved Oxygen Saturation

The rate at which atmospheric reaeration occurs depends not only on k_a, but also on the difference between the saturation concentration C_s and the actual concentration C. The saturation value of dissolved oxygen is a function of temperature, salinity, and barometric pressure. The effect of salinity becomes important in estuarine systems, and to a lesser degree in rivers where high irrigation return flow can lead to substantial salinity values. Table IV-15 depicts the relationship between oxygen saturation and chlorinity. The expression relating salinity and chlorinity concentration is:

$$\text{Salinity } (^0/_{oo}) = 0.03 + 0.001805 \text{ chlorinity (mg l)} \qquad \text{(IV-37)}$$

where

$^0/_{oo}$ = parts per thousand.

The temperature dependence (at zero salinity) can be expressed as:

$$C_s = 14.65 - 0.41022T + 0.00791T^2 - 0.00007774T^3 \qquad \text{(IV-38)}$$

where T is in $^\circ$C. This relationship is also found in Table IV-15 for zero chloride concentration.

Barometric pressure affects C_s as follows:

$$C_s' = C_s \left(\frac{P_b - P_v}{760 - P_v}\right)$$

$$\approx C_s \left(1 - \frac{.027E}{760}\right) \qquad \text{(IV-39)}$$

where

C_s = saturation value at sea level, at the temperature of the water, mg/l

C_s' = corrected value at the altitude of the river, mg/l

P_b = barometric pressure at altitude, mm Hg

P_v = saturation vapor pressure of water at the river temperature, mm Hg

E = elevation, feet.

Table IV-16 illustrates the variability of dissolved oxygen saturation with altitude and temperature. The significant effect of altitude is apparent and should not be neglected. For example, at a temperature of 20°C, the saturation value decreases

TABLE IV-15

SOLUBILITY OF OXYGEN IN WATER (STANDARD METHODS, 1971)

| Temp. in °C | Chloride Concentration in Water - mg/l | | | | | Difference per 100 mg Chloride |
| | 0 | 5,000 | 10,000 | 15,000 | 20,000 | |
	Dissolved Oxygen - mg/l					
0	14.6	13.8	13.0	12.1	11.3	0.017
1	14.2	13.4	12.6	11.8	11.0	0.016
2	13.8	13.1	12.3	11.5	10.8	0.015
3	13.5	12.7	12.0	11.2	10.5	0.015
4	13.1	12.4	11.7	11.0	10.3	0.014
5	12.8	12.1	11.4	10.7	10.0	0.014
6	12.5	11.8	11.1	10.5	9.8	0.014
7	12.2	11.5	10.9	10.2	9.6	0.013
8	11.9	11.2	10.6	10.0	9.4	0.013
9	11.6	11.0	10.4	9.8	9.2	0.012
10	11.3	10.7	10.1	9.6	9.0	0.012
11	11.1	10.5	9.9	9.4	8.8	0.011
12	10.8	10.3	9.7	9.2	8.6	0.011
13	10.6	10.1	9.5	9.0	8.5	0.011
14	10.4	9.9	9.3	8.8	8.3	0.010
15	10.2	9.7	9.1	8.6	8.1	0.010
16	10.0	9.5	9.0	8.5	8.0	0.010
17	9.7	9.3	8.8	8.3	7.8	0.010
18	9.5	9.1	8.6	8.2	7.7	0.009
19	9.4	8.9	8.5	8.0	7.6	0.009
20	9.2	8.7	8.3	7.9	7.4	0.009
21	9.0	8.6	8.1	7.7	7.3	0.009
22	8.8	8.4	8.0	7.6	7.1	0.008
23	8.7	8.3	7.9	7.4	7.0	0.008
24	8.5	8.1	7.7	7.3	6.9	0.008
25	8.4	8.0	7.6	7.2	6.7	0.008
26	8.2	7.8	7.4	7.0	6.6	0.008
27	8.1	7.7	7.3	6.9	6.5	0.008
28	7.9	7.5	7.1	6.8	6.4	0.008
29	7.8	7.4	7.0	6.6	6.3	0.008
30	7.6	7.3	6.9	6.5	6.1	0.008
31	7.5					
32	7.4					
33	7.3					
34	7.2					
35	7.1					

TABLE IV-16

DISSOLVED OXYGEN SATURATION
VERSUS TEMPERATURE AND ALTITUDE

Temperature (°C)	ALTITUDE (ft)				
	0	2,000	4,000	6,000	8,000
0	14.6	13.6	12.5	11.5	10.5
5	12.8	11.9	11.0	10.1	9.2
10	11.3	10.5	9.7	8.9	8.1
15	10.2	9.5	8.8	8.0	7.3
20	9.2	8.5	7.9	7.2	6.6
25	8.4	7.8	7.2	6.6	6.0
30	7.6	7.1	6.5	6.0	5.4
35	7.1	6.6	6.1	5.6	5.1

from 9.2 mg/l to 7.2 mg/l as the altitude increases from sea level to 6000 feet, the approximate elevation of Lake Tahoe and the Truckee River in California and Nevada.

4.3.6 DO-BOD Interactions

A widely used dissolved oxygen predictive equation is the Streeter-Phelps relationship which predicts the dissolved oxygen concentration downstream from a point source of BOD. Assuming a constant river cross-sectional area, the dissolved oxygen deficit $(C_s - C)$ can be expressed as:

$$C = D_0 \exp\left[\frac{-k_a x}{U}\right] + \frac{L_0 k_L}{k_a - k_L} \left[\exp\left(\frac{-k_L x}{U}\right) - \exp\left(\frac{-k_a x}{U}\right)\right] \qquad (IV-40)$$

where

k_a = reaeration coefficient, 1/day

D_0 = initial deficit (at x = 0), mg/l

D = deficit at x, mg/l

L_0 = initial BOD (at x = 0), mg/l

k_L = BOD decay coefficient, 1/day.

L_0 and D_0 are found by proportioning BOD and DO deficit concentrations just upstream

of the waste discharge with the influx from the discharge itself. As presented earlier in the BOD section, L_o is given by:

$$L_o = \frac{W/5.38 + L_u Q_u}{Q_w + Q_u}$$ (IV-41)

where

W = discharge rate of BOD, lb/day

L_u = concentration of BOD in the river upstream of the waste discharge, mg/l

Q_u = river flow rate upstream of discharge, cfs

Q_w = flow rate of waste discharge, cfs

$Q_w + Q_u$ = flow rate of river in the reach under consideration, cfs.

W in Equation IV-41 should be expressed in terms of ultimate BOD, and not 5-day BOD.

The initial deficit is found from:

$$D_o = C_s - \frac{C_w Q_w + C_u Q_u}{Q_w + Q_u} = \frac{D_w Q_w + D_u Q_u}{Q_w + Q_u}$$ (IV-42)

where

C_w = concentration of dissolved oxygen in the waste, mg/l

C_u = concentration of dissolved oxygen upstream of the waste discharge, mg/l

D_w = dissolved oxygen deficit in waste, mq/l

D_u = dissolved oxygen deficit upstream, mg/l.

In cases where information is lacking, D_o can normally be assumed to be in the range 1-2 mg/l.

If NBOD is to be considered as well as CBOD, Equation IV-40 can be modified as follows:

$$D = D_o \exp\left[\frac{-k_a x}{U}\right] + \frac{L_o k_L}{k_a - k_L}\left[\exp\left(\frac{-k_L x}{U}\right) - \exp\left(\frac{-k_a x}{U}\right)\right]$$

$$+ \frac{N_o k_N}{k_a - k_N}\left[\exp\left(\frac{-k_N x}{U}\right) - \exp\left(\frac{-k_a x}{U}\right)\right]$$ (IV-43)

If the decay coefficient of NBOD is approximately equal to that of CBOD, Equation IV-40 can be utilized instead of the more complicated Equation IV-43. In this case, L_o in Equation IV-40 is replaced by the sum of L_o and N_o.

4.3.7 Dissolved Oxygen Calculations

Calculation of dissolved oxygen in rivers can proceed as shown in Figure IV-19. The planner needs to estimate the waste loading scheme for the prototype, whether it be for a 20 year projection or for current conditions. The river system can then be divided into reaches and by repeated use of Equation IV-40, dissolved oxygen calculations can be performed for each reach, starting from a known boundary condition and proceeding downstream. All data and calculations should be succinctly and clearly recorded to minimize errors.

The dissolved oxygen profile downstream from a waste discharge characteristically has a shape shown in Figure IV-18. If the reach is long enough, the dissolved oxygen deficit will increase to some maximum value, D_c, at a distance x_c (termed the critical distance). D_c is called the critical deficit. Within any reach there will always be a minimum dissolved oxygen value that occurs, but it may not be the critical deficit, which is defined as the minimum point on a dissolved oxygen sag. The difference between the minimum and critical values should be kept in mind. As one example of the difference between the values, a reach may have a dissolved oxygen profile where concentrations are monotonically decreasing throughout the reach. The minimum DO will then occur at the downstream end of the reach, but this will NOT be the critical DO value, since DO is still decreasing in the downstream direction.

The travel time to the critical deficit is given by:

$$t_c = \frac{1}{k_a - k_L} \ln \left[\frac{k_a}{k_L} \left(1 - \frac{D_0(k_a - k_L)}{k_L L_0} \right) \right] \qquad (IV-44)$$
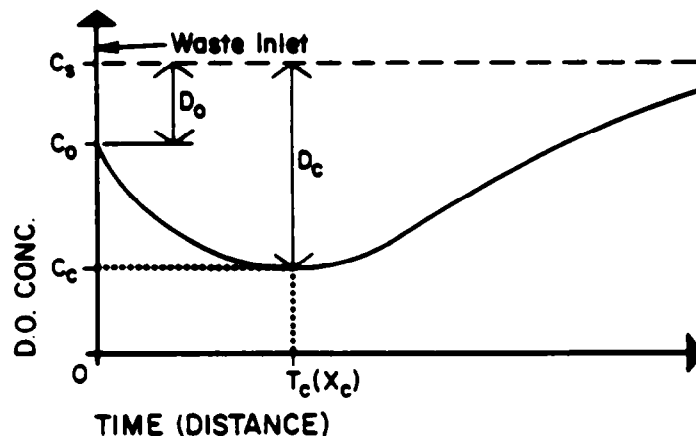
FIGURE IV-18   CHARACTERISTIC DISSOLVED OXYGEN PROFILE DOWNSTREAM FROM A POINT SOURCE OF POLLUTION
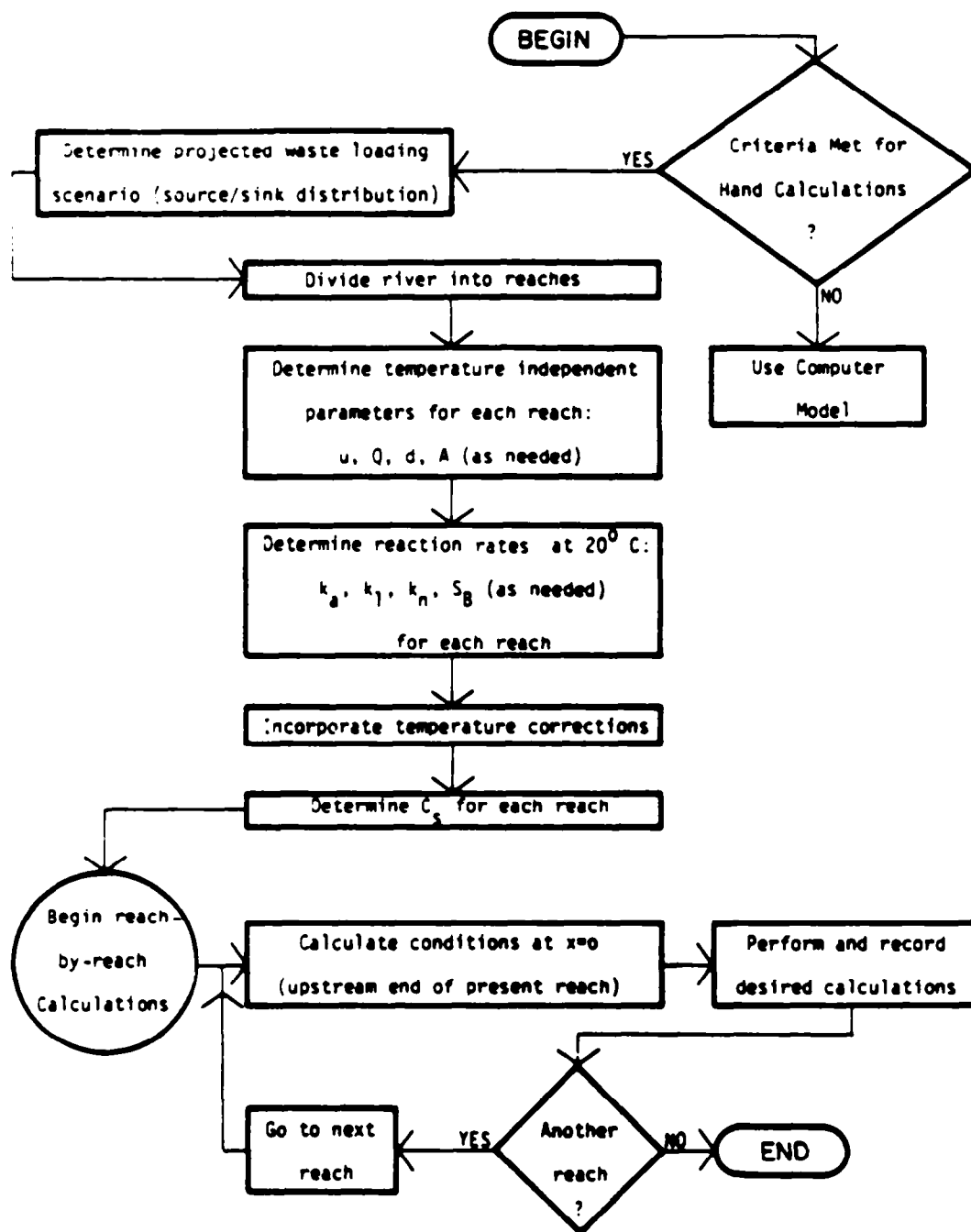
FIGURE IV-19   FLOW PROCESS OF SOLUTION TO DISSOLVED OXYGEN
PROBLEM IN RIVERS

The distance downstream can be computed by knowing the travel time and flow velocity:

$$x_c = U \cdot t_c \qquad \text{(IV-45)}$$

The critical deficit can be found from:

$$D_c = \left(D_0 - \frac{L_0 k_L}{k_a - k_L} \right) \left(\frac{k_a}{k_L} \left(1 - \frac{D_0(k_a - k_L)}{k_L L_0} \right) \right)^{\frac{-k_a}{k_a - k_L}}$$
$$+ \frac{L_0 k_L}{k_a - k_L} \left[\frac{k_a}{k_L} \left(1 - \frac{D_0(k_a - k_L)}{k_L L_0} \right) \right]^{\frac{-k_L}{k_a - k_L}} \qquad \text{(IV-46)}$$

The formulas for the critical dissolved oxygen deficit are not really applicable in the special case when $k_a = k_L$. However, these special cases can readily be handled in one of two ways. First, a small change can be made in either k_a or k_L so that k_a and k_L are approximately equal. Or second, the following expression can be used to predict critical travel time:

$$t_c = \frac{1}{k_a} \left(1 - \frac{D_0}{L_0} \right) \qquad \text{(IV-47)}$$

Then, the critical deficit is given by:

$$D_c = \exp \left[\ln \left(\frac{k_L}{k_a} L_0 \right) - k_L t_c \right] \qquad \text{(IV-48)}$$

Equation IV-48 is valid for all k_a/k_L values, and is not limited to cases where $k_a/k_L = 1$.

Solutions to both Equations IV-46 and IV-44 are presented in Tables IV-17 and IV-18, respectively. There exist practical limitations to the solutions of both equations, governed by the conditions that the solutions be both positive and real. If in solving Equation IV-44 t_c is negative, the minimum dissolved oxygen concentration actually occurs at the point of discharge, and concentrations increase immediately below the discharge.

Tables IV-17 and IV-18 are particularly useful for computing the waste assimilative capacity of a river. Waste assimilative capacity (WAC), as defined here, is the

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TABLE IV-17

D_c/L_o VALUES VERSUS D_o/L_o AND k_a/k_L

k_a/k_L

D_o/L_o	.1	.3	.5	.7	.9	1	1.3	1.5	1.7	1.9	2.1	2.3	2.5	2.7	2.9	3.1	3.3	3.5	3.7	3.9	4	4.3	4.5	4.7	4.9
0.00	77	60	50	44	39	35	32	30	29	26	24	23	22	21	20	19	18	17	17	16	5	5	5	14	
0.02	79	61	51	44	40	36	33	30	28	26	25	23	22	21	20	19	8	9	17	6	6	5	5		
0.04	81	62	52	45	40	36	33	31	29	27	25	24	23	22	21	20	9	9	17	7	6	6	5		
0.06	82	63	53	46	41	37	34	31	29	27	26	24	23	22	21	20	19	9	8	7	7	6	5	5	5
0.08	84	65	54	47	42	38	35	32	30	28	26	25	24	23	21	21	20	9	9	8	7	7	6	5	5
0.10	85	56	55	48	43	39	6	33	31	29	27	26	24	23	22	21	20	9	9	8	7	7			
0.12	37	67	56	49	44	40	36	34	31	29	28	26	25	24	23	22	21	20	9	9	8	7			
0.14	88	68	57	50	45	40	37	34	32	30	28	27	25	24	23	22	21	21	20	9	9	8			
0.16	90	69	58	51	45	41	38	35	33	31	29	27	26	25	24	23	22	21	21	20	9	9	8		
0.18	91	77	59	52	46	42	39	36	33	31	30	28	27	26	25	24	23	22	21	21	20	20	9		
0.20	93	72	60	53	47	43	39	37	34	32	30	29	28	26	25	24	24	23	22	22	21	21	20		
0.22	95	73	62	54	48	44	40	37	35	33	31	30	28	27	26	25	25	24	23	23	22	22			
0.24	96	75	63	55	49	45	41	38	36	34	32	31	29	28	27	26	26	25	25	24	24				
0.26	98	76	64	56	50	46	42	39	37	35	33	31	30	29	28	27	27	26	26						
0.28	99	77	65	57	51	47	43	40	38	36	34	32	31	30	29	29	28	28							
0.30	01	78	66	58	52	48	44	41	39	37	35	34	32	31	31	30	30								
0.32	03	80	67	59	53	49	45	42	40	38	36	35	34	33	32	32									
0.34	04	81	68	60	54	50	46	43	41	39	37	36	35	34	34										
0.36	06	82	70	61	55	51	47	44	42	40	38	37	36	36											
0.38	07	84	71	62	56	52	48	45	43	41	40	39	38												
0.40	09	85	72	63	57	53	49	46	44	42	41	40													
0.42	11	86	73	65	58	54	50	47	45	44	43	42													
0.44	12	88	74	66	60	55	51	49	47	45	44														
0.46	14	99	76	67	61	56	53	50	48	47	46														
0.48	15	90	77	68	62	57	54	51	49	48															
0.50	17	92	78	69	63	59	55	53	51	50															
0.6	25	99	94	76	69	65	62	60																	
0.7	33	06	91	82	76	72	70																		
0.8	41	13	98	89	84	81																			
0.9	50	20	05	97	92	90																			
1.0	58	27	12	04	00																				
1.1	66	35	20	13	10																				
1.2	75	43	28	21																					
1.3	83	50	36	30																					
1.4	92	58	44	40																					
1.5	2.00	66	53																						
1.6	2.09	75	62																						
1.7	2.17	83	71																						
1.8	2.26	91	80																						
1.9	2.34	2.00	90																						
2.0	2.43	2.08																							
2.1	2.52	2.17																							
2.2	2.60	2.26																							

k_a/k_L

D_o/L_o	5.1	5.3	5.5	5.7	5.9	6.1	6.3	6.5	6.7	6.9	7.1	7.3	7.5	7.7	7.9	8.1	8.3	8.5	8.7	8.9	9.1	9.3	9.5	9.7	
0.00	13	13	12	12	12	11	11	11	11	10	10	10	10	10	09	09	09	09	09	09	08	08	08	08	
0.02	13	13	13	12	12	12	11	11	11	11	10	10	10	10	10	09	09	09	09	09	09	08	08	08	08
0.04	14	13	13	13	12	12	12	11	11	11	11	10	10	10	10	10	09	09	09	09	09	09	08	08	08
0.06	14	14	13	13	13	12	12	12	12	11	11	11	11	10	10	10	10	10	09	09	09	09	09	09	
0.08	15	14	14	13	13	13	12	12	12	12	11	11	11	11	11	10	10	10	10	10	10	09	09	09	09
0.10	15	15	14	14	14	13	13	13	12	12	12	12	11	11	11	11	11	11	11	10	10	10	10		
0.12	16	15	15	14	14	14	14	13	13	13	13	12	12	12	12	12	12								
0.14	16	16	16	15	15	15	14	14	14	14	14														
0.16	17	17	17	16	16	16																			
0.18	18	18	18																						

TABLE IV-18

$k_a t_c$ VERSUS D_0/L_0 AND k_a/k_L

k_a/k_L

	.1	.3	.5	.7	.9	1	1.5	1.7	1.9	2.1	2.3	2.5	2.7	2.9	3.1	3.3	3.5	3.7	3.9	4.1	4.3	4.5	4.7	4.9
.00	.26	.52	.79	.93	.95	.05	1.14	1.22	1.29	1.36	1.42	1.47	1.53	1.58	1.63	1.67	1.71	1.75	1.79	1.83	1.87	1.90	1.93	1.97	2.00

D_0/L_0

k_a/k_L

	5	5.3	5.5	5.7	5.9	6	6.3	6.5	6.7	6.9	7.1	7.3	7.5	7.7	7.9	8.1	8.3	8.5	8.7	8.9	9.1	9.3	9.5	9.7	9.9
.00	2.03	2.06	2.08	2.11	2.14	2.16	2.19	2.21	2.24	2.26	2.28	2.30	2.32	2.35	2.37	2.39	2.41	2.43	2.44	2.46	2.48	2.50	2.52	2.53	2.55

D_0/L_0

amount of BOD that can be discharged into a river without causing the minimum dissolved oxygen level to fall below a specified value. In constructing Tables IV-17 and IV-18 extra detail was incorporated for D_0/L_0 values between 0.0 and 0.5. This is necessary because most practical problems fall within this range.

The following steps show how to use Table IV-17.

1. Find the reaeration rate (k_a) and the BOD decay rate (k_L) for the river being investigated.

2. Find the BOD concentration in the river just below the point of mixing (L_0).

3. Find the dissolved oxygen deficit at this location $(D_0 = C_s - C)$.

4. Compute k_a/k_L and D_0/L_0.

5. Using the ratios k_a/k_L and D_0/L_0, find D_c/L_0 where D_c is the critical deficit.

6. Finally, calculate $D_c = (D_c/L_0) L_0$, and $C_{min} = C_s - D_c$.

To use Table IV-18 complete these steps:

1.-4. Repeat steps 1 through 3 above.

5. Using the ratios k_a/k_L and D_0/L_0, find $k_a t_c$.

6. Calculate $t_c = (k_a t_c)/k_a$.

4.3.8 General Dissolved Oxygen Deficit Equation

The most general dissolved oxygen mass-balance formulation to be presented in this chapter is as follows:

$$
D = \left(\frac{k_L}{k_a - k_L}\right) \left(L_0 - \frac{L_{rd}}{k_L}\right) \left[\exp\left(\frac{-j_L}{A_0} f(x)\right) - \exp\left(\frac{-j_a}{A_0} f(x)\right)\right]
$$

$$
+ \left(\frac{k_N}{k_a - k_N}\right) \left(N_0 - \frac{N_{rd}}{k_N}\right) \left[\exp\left(\frac{-j_N}{A_0} f(x)\right) - \exp\left(\frac{-j_a}{A_0} f(x)\right)\right]
$$

$$
+ \frac{R + S_B + L_{rd} + N_{rd} - P}{k_a} \left[1 - \exp\left(\frac{-j_a}{A_0} f(x)\right)\right]
$$

$$
+ D_0 \exp\left(\frac{-j_a}{A_0} f(x)\right) \qquad\qquad (IV-49)
$$

where

P = oxygen production rate due to photosynthesis, mg/l/day

R = oxygen utilization rate due to respiration, mg/l/day

S_B = benthic demand of oxygen, mg/l/day.

The distance function $f(x)$ expresses the cross-sectional area relationship throughout

the reach. The area can increase or decrease linearly or remain constant. The general form of the relationship is:

$$f(x) = A_0 x + \Delta_A \, x^2/2 \, , \quad \Delta_A = \frac{A_f - A_0}{x_L}$$

where

A_f = area at $x = x_L$

A_0 = area at $x = 0$

x_L = length of reach.

For a reach of constant cross-sectional area, $\Delta_A = 0$.

In developing Equation IV-49 the following relationship for CBOD was used (as originally presented in the BOD section):

$$L = \left(L_0 - \frac{L_{rd}}{k_L} \right) \exp\left(\frac{-j_L}{A_0} \, f(x) \right) + \frac{L_{rd}}{k_L} \qquad \text{(IV-22)}$$

An analogous expression for NBOD was also used.

In Equation IV-49, the distributed sources and sinks (P, R, S_B, L_{rd}, N_{rd}) are all mass fluxes, and no volumetric flow rate is associated with any of these sources and sinks of dissolved oxygen.

4.3.9 Photosynthesis and Respiration

The difficulty of accurately assessing the impact of photosynthesis and respiration on the dissolved oxygen resources of streams is not readily apparent from the single terms appearing in Equation IV-49. Of concern are both free floating and attached algae, as well as aquatic plants. The extent to which algae impact the dissolved oxygen resources of a river is dependent on many factors, such as turbidity, which can decrease light transmittance through the water column. Additionally, the photosynthetic rate constantly changes in response to variations in sunlight intensity and is not truly constant as implied by Equation IV-49. Hence if algal activity is known to be a significant factor affecting the dissolved oxygen balance, the use of a computer model is recommended in order to accurately assess such influences. For example, in the Truckee River in California and Nevada, the diurnal variation of dissolved oxygen has exhibited a range of from 150 percent saturation during the daylight hours to 50 percent saturation at night due to algal photosynthesis and respiration, respectively. At the most, hand calculations can give estimates of net dissolved oxygen production rates that then can be compared to the other source/sink terms in Equation IV-28. From this comparison the significance of each can be estimated.

TABLE IV-19

SOME AVERAGE VALUES OF GROSS PHOTOSYNTHETIC PRODUCTION OF
DISSOLVED OXYGEN. (AFTER THOMANN, 1972 AND THOMAS AND O'CONNELL, 1966)

Water Type	Aver Gross Production (grams/m²-day)	Average Respiration (gm/m²-day)
Truckee River - Bottom attached algae	9	11.4
Tidal Creek - Diatom Bloom (62-109.10⁶ diatoms/l)	6	
Delaware Estuary - summer	3-7	
Duwamish River estuary - Seattle, Washington	0.5-2.0	
Neuse River System - North Carolina	0.3-2.4	
River Ivel	3.2-17.6	6.7-15.4
North Carolina Streams	9.8	21.5
Laboratory Streams	3.4-4.0	2.4-2.9

Table IV-19 presents some observed values of photosynthetic oxygen production rates. As shown in the table, dissolved oxygen production is expressed in units of rate per unit area $(gm/m^2\text{-day})$. To convert to units of concentration per unit time, the algal production rate must be divided by river depth:

$$P = \frac{\bar{P}}{H} \qquad (IV-50)$$

where

$\bar{P}$ = production rate of dissolved oxygen, gm/m^2-day

H = average river depth, meters

P = production rate of dissolved oxygen, mg/l-day.

P can now be directly compared to other terms in Equation IV-28.

By using a regression equation developed by Erdmann (1979a, 1979b), the production rate of dissolved oxygen, P, can be determined directly if the diurnal variation of dissolved oxygen is known. When water temperature is fairly constant throughout the day, the photosynthetic oxygen production rate becomes:

$$P = 2\Delta DO \qquad (IV-51)$$
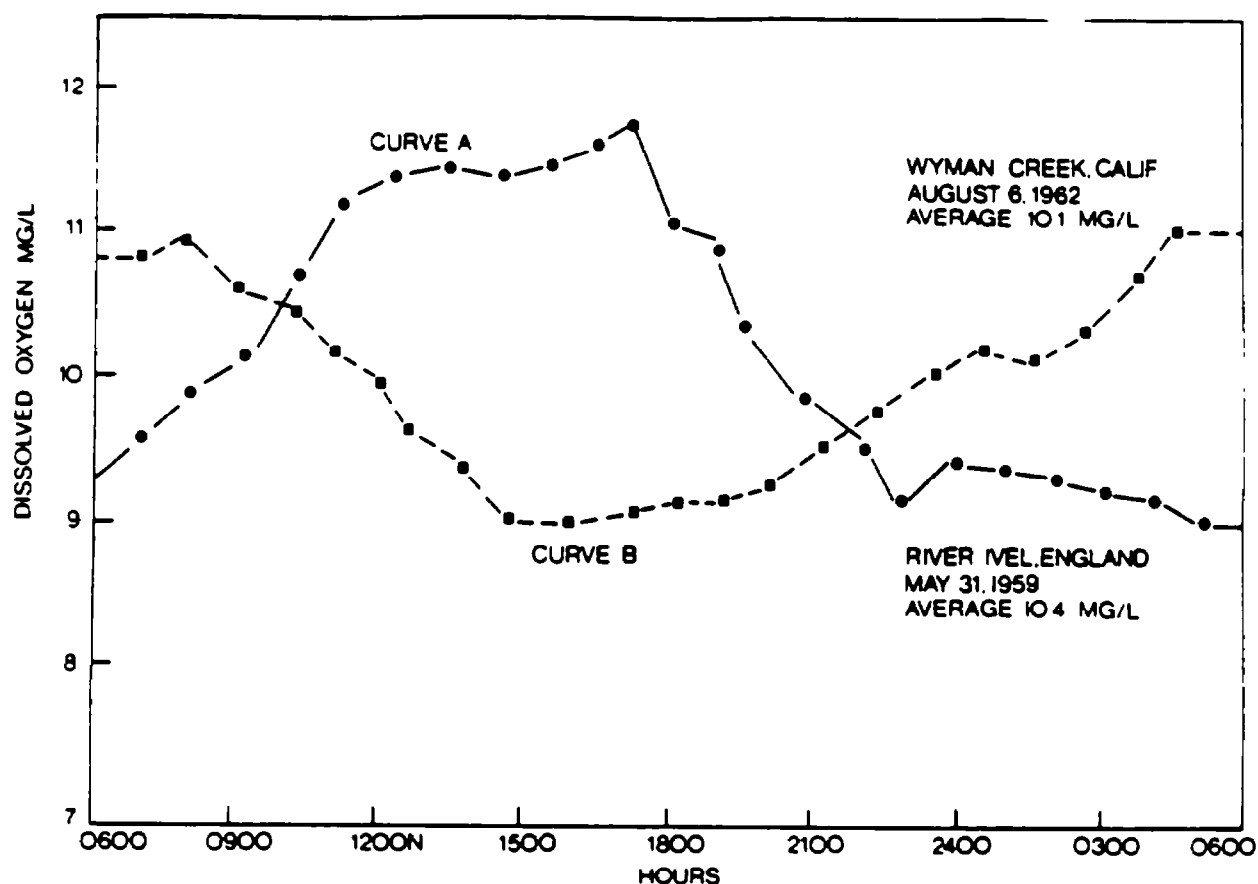
FIGURE IV-20   DAILY DISSOLVED OXYGEN VARIATION IN TWO RIVERS.

where

ΔDO = difference between the daily maximum dissolved oxygen concentrat·
and the daily minimum dissolved oxygen concentration, mg/l.

Since Equation IV-51 is based on regression analysis, the units are not consistent.

The importance of a constant water temperature is illustrated by Figure IV-20. This figure shows the hourly variation of dissolved oxygen over a 24 hour period for Wyman Creek in California and for the Ivel River in England. Both exhibit large diurnal dissolved oxygen variations, although the reasons differ. In Curve A (Ivel River), the dissolved oxygen level gradually increases from 0600 hr to 1800 hr, and then decreases over the next 12 hours. The cause of the changing dissolved oxygen levels is a net photosynthetic oxygen production during the daylight hours, and a net consumption during evening and night. Curve B is almost a mirror image of curve A since the minimum dissolved oxygen levels occur during daylight hours and the maximum during nighttime. The variations exhibited by curve B are principally caused by a changing water temperature. During the day this creek absorbs considerable solar

radiation causing the water temperature to rise and the dissolved oxygen saturation level to decrease. At night the creek cools off and the dissolved oxygen saturation level increases. Curve B then is free from the influence of photosynthetic effects, so it would be erroneous to apply Equation IV-51. Erdmann (1979a, 1797b) and Kelly et al. (1975) provide more sophisticated methods to predict P when both photosynthetic and temperature effects occur concurrently. Example IV-7 illustrates the utility of Equation IV-51.

┌─────────────────────────── EXAMPLE IV-7 ───────────────────────────┐

Prediction of Photosynthetic Oxygen Production Rate

On Mechums River near Charlottesville, Virginia, Kelly et al. (1975) collected the following data:

Time of Day (hours after midnight)	Stream Temperature, °C	Dissolved Oxygen (mg/ℓ)
0.0	23.3	7.6
0.5	23.3	7.6
1.0	23.4	7.6
1.5	23.4	7.5
2.0	23.5	7.4
2.5	23.5	7.2
3.0	23.5	7.3
3.5	23.5	7.3
4.0	23.4	7.3
4.5	23.4	7.3
5.0	23.3	7.3
5.5	23.2	7.3
6.0	23.1	7.3
6.5	23.0	7.3
7.0	22.9	7.4
7.5	22.8	7.4
8.0	22.7	7.5
8.5	22.7	7.6
9.0	22.7	7.7
9.5	22.7	7.8
10.0	22.8	8.0
10.5	23.0	8.1
11.0	23.2	8.4
11.5	23.5	8.5
12.0	23.6	8.7
12.5	24.3	8.9
13.0	24.8	9.0
13.5	25.3	9.1
14.0	25.5	9.2
14.5	25.5	9.3
15.0	25.9	9.2
15.5	26.1	9.2
16.0	26.1	9.2
16.5	26.1	9.1
17.0	26.1	9.0

Time of Day (hours after midnight)	Stream Temperature, °C	Dissolved Oxygen (mg/ℓ)
17.5	25.8	8.9
18.0	25.8	8.8
18.5	25.5	8.6
19:0	25.3	8.5
19.5	25.1	8.3
20.0	24.8	8.2
20.5	24.5	8.0
21.0	24.2	8.0
21.5	24.0	7.9
22.0	23.8	7.6
22.5	23.7	7.7
23.0	23.6	7.7
23.5	23.6	7.6
24.0	23.5	7.5

Using a sophisticated analysis, Kelly et al. found the daily mean photosynthetic oxygen production to be 4.40 mg/l. Using the data shown above and Equation IV-51 estimate the daily photosynthetic oxygen production, P (mg/l/day).

The minimum dissolved oxygen is 7.2 mg/l, which occurs at 0230. The maximum dissolved oxygen is 9.3 mg/l which occurs at 1430. Hence:

$$P = 2\Delta DO = 2(9.3-7.2) = 4.2 \text{ mg/l/day}$$

This compares very well with the value found by Kelly et al. using a more sophisticated analysis, even though the stream temperature varies by a few degrees during the day. Probably one reason for the good agreement is that the maximum and minimum values occur about 12 hours apart, which the method assumes they do.

— — — — — — — — — — END OF EXAMPLE IV-7 — — — — — — — — — — —

Values of photosynthetic respiration vary widely, ranging from 0.5 gm/m²/day to greater than 20 gm/m²/day. One suggested relationship between respiration and chlorophyll a is given as (Thomann, 1972):

$$R(mg/l/day) = 0.024 \text{ (chlorophyll a) } (\mu g/l) \qquad \text{(IV-52)}$$

where

$$1 \mu g/l = 10^{-3} \text{ mg/l}.$$

Chlorophyll a concentration is most commonly expressed in terms of μg/l.

4.3.10 Benthic Demand

In addition to oxygen utilization by respiration of attached algae, benthic

deposits of organic material and attached bacterial growth can utilize dissolved oxygen. Table IV-20 illustrates some uptake rates. As with photosynthesis, the uptake rates are expressed in gm/m²-day. To use these values in Equations IV-28 or IV-49, division by stream depth (in meters) is necessary. Temperature effects can be approximated by:

$$(SB_T) = (S_B)_{20} \; 1.065^{T-20} \tag{IV-53}$$

The areal extent of significant oxygen demanding benthic materials is often limited to the region just below the outfall vicinity. Although the oxygen demand may be great over a short distance, it may be insignificant over larger distances. The response of rivers to areally limited benthic deposits is generally to move the critical deficit upstream, but not to lower its value significantly.

Bowie et al. (1985) contains significantly more data and further discussion of benthic oxygen demand in rivers. Additionally Butts and Evans (1978) conducted extensive studies of sediment oxygen demand on 20 streams in Illinois. They found that benthic oxygen demand could be predicted as:

$$\bar{S}_B = 0.15T + 0.30_s + 0.11 \; logN - 0.56 \tag{IV-54}$$

where

$\bar{S}_B$ = benthic oxygen demand, g/m²-day
T = water temperature, °C
D_s = depth of sediment, inches
N = number of macroinvertebrates per m².

They found that N typically ranged from 10,000 to 1,000,000. Within this range the sum of the last two terms is between ±0.1, and is negligible compared to the first two terms. Under these conditions Equation IV-54 simplifies to:

$$\bar{S}_B = 0.15T + 0.30_s \tag{IV-55}$$

The depths of sediment found during the study of Butts and Evans (1978) ranged from 1 to 17 inches. Consequently Equation IV-55 is applicable to streams which have fairly significant benthic oxygen demands. For cleaner streams Equation IV-55 probably overestimates the benthic oxygen demand.

TABLE IV-20

AVERAGE VALUES OF OXYGEN UPTAKE RATES OF
RIVER BOTTOMS (AFTER THOMANN, 1972)

| Bottom Type and Location | Uptake (gms O_2/m^2-day) @ $20^\circ C$ | |
	Range	Approximate Average
Sphaerotilus - (10 gm dry wt/M^2)	-	7
Municipal Sewage Sludge - Outfall Vicinity	2-10.0	4
Municipal Sewage Sludge - "Aged" Downstream of Outfall	1-2	1.5
Cellulosic Fiber Sludge	4-10	7
Estuarine mud	1-2	1.5
Sandy bottom	0.2-1.0	0.5
Mineral soils	0.05-0.1	0.07

4.3.11 Simplifying Procedures in Dissolved Oxygen Calculations

Using Equation IV-49 might be untenable for several reasons, such as lack of available data, or because of the voluminous calculations required to apply it to a large number of reaches. Several suggestions are offered here that should simplify analysis of dissolved oxygen problems.

Since the general scope of this section is to facilitate the determination of existing or potential problem areas, the analysis should proceed from the simple to the more complicated approach. It may be adequate to analyze the dissolved oxygen response to the most severe loadings first, neglecting those of secondary importance. If such an analysis clearly indicates dissolved oxygen problems, then the inclusion of any other pollutant discharges would only reinforce that conclusion. More rigorous procedures (e.g., a computer model) could then be employed to perform a detailed analysis.

Suppose the improvement of dissolved oxygen levels due to decreased loading from a point source is of interest. This is a common situation since it relates to the design of waste loading abatement schemes. Such improvement can be estimated by:

$$\Delta D = \Delta D_0 \, \exp\left[\frac{-k_a x}{U}\right] + \left(\frac{k_L}{k_a - k_L}\right)\left(\Delta L_0\right)\left[\exp\left(\frac{-j_L}{A_0} f(x)\right)\right.$$

$$\left. - \exp\left(\frac{-j_a}{A_0} f(x)\right)\right] \qquad\qquad (IV-56)$$

where

ΔL_0 = the change in the initial BOD, mg/l

ΔD = change in deficit in response to ΔL_0.

Equation IV-56 was formulated from Equation IV-49 assuming that L_0 and D_0 are the only changes of significance.

Many rivers have a large number of point sources. Although this is not necessarily a complicating factor, a detailed analysis might be too time consuming for hand calculations. There are several possible alternatives to deal with this situation in order to reduce the number of reaches to be analyzed. The first, already mentioned, is to consider only the significant pollutant sources. Second, as was illustrated in Example IV-5, a number of uniformly distributed point sources can be considered as a single distributed source. Third, combining several adjacent point sources is also possible, if the length of the reach under consideration is long relative to the distance of separation between the point sources. Analogously, a distributed source can be approximated as a point source, contributing the same waste loading and located at the center of the distributed source.

It may be that the planner wants only to determine the critical dissolved oxygen concentration in each of a series of reaches. In this case no more than two values of dissolved oxygen per reach need be calculated. Figure IV-21 shows the solution process to be followed.

One final note on dissolved oxygen evaluations should be made here. It may be that if the planner is interested primarily in locating dissolved oxygen problems, he need not perform any computations. This is especially likely where dissolved oxygen data are available at various locations on the river. Plotting dissolved oxygen time trends may reveal when, as well as where, annual dissolved oxygen minima occur.

— EXAMPLE IV-8 —

Determining River Assimilative Capacity from
Tables IV-17 and IV-18

Suppose the user wants to determine waste assimilative capacity (WAC) for a river reach that has the following characteristics:
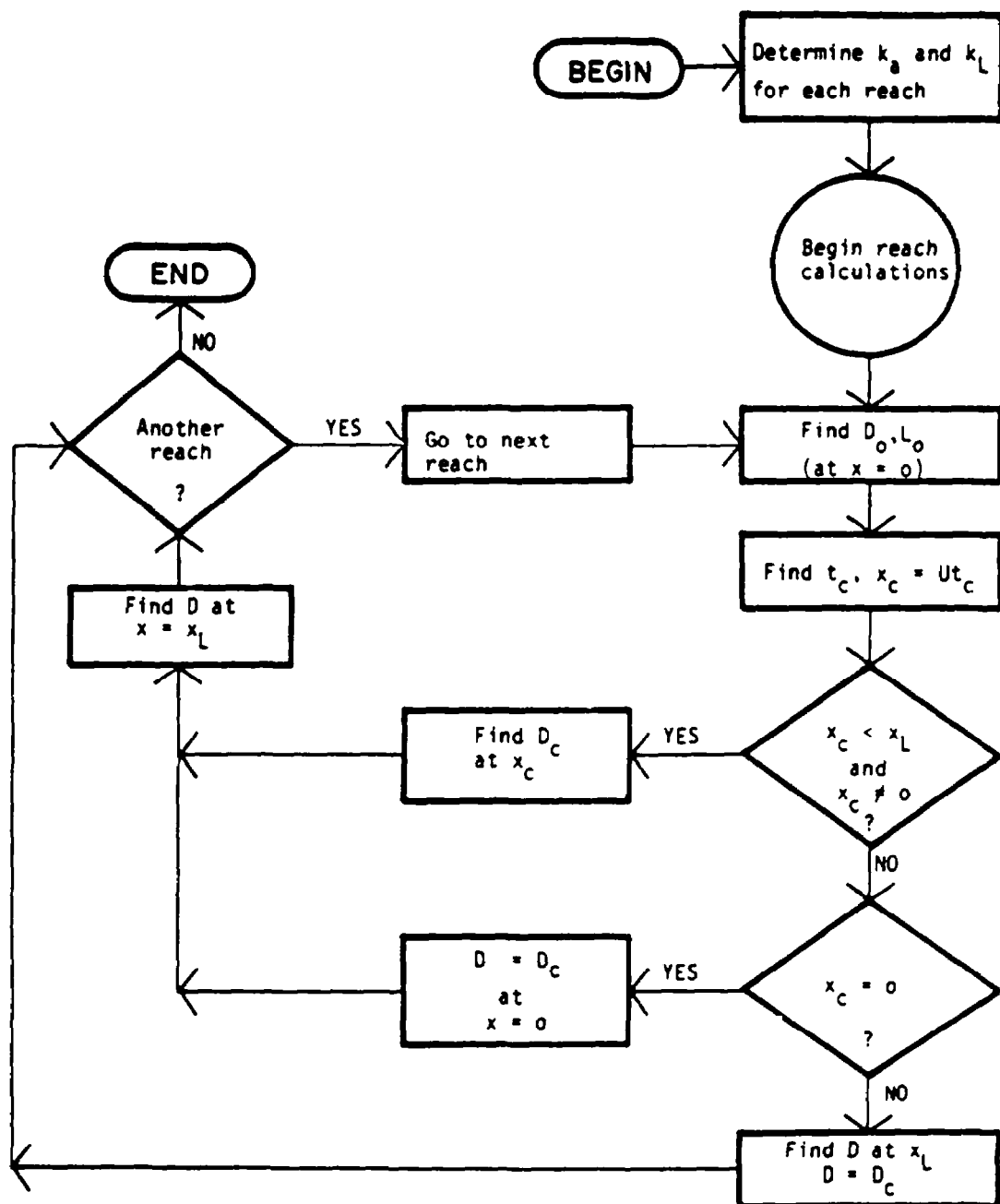
FIGURE IV-21   FLOW PROCESS IN REACH BY REACH SOLUTION TO
CRITICAL DISSOLVED OXYGEN VALUES

Critical dissolved oxygen concentration = 5.0 mg/l (user establishes this)

Initial deficit = 1.0 mg/l

Average velocity = 0.5 fps

Average depth = 4 feet

Chloride concentration = 0

Temperature range = 10°C to 35°C

First, k_a and k_L need to be found. From Figure IV-17, k_a (20°) = 0.8/day, and from Figure IV-11, k_L = 0.4/day. At any other temperature then, k_a and k_L can be found from the temperature relationships previously developed:

$$k_a = (k_a)_{20} \; 1.024^{\,T-20} \qquad\qquad (IV-34)$$

$$k_L = (k_L)_{20} \; 1.047^{\,T-20} \qquad\qquad (IV-17)$$

Using Table IV-15 the dissolved oxygen saturation concentration within the temperature range of interest can be found. This information can then be then compiled into Table IV-21 shown below.

TABLE IV-21

COMPILATION OF INFORMATION IN EXAMPLE IV-8

T (°C)	C_s (mg/l)	C_c (mg/l)	D_c (mg/l)	D_o/D_c	k_a/k_L
10	11.3	5.0	6.3	0.16	2.5
15	10.2	5.0	5.2	0.19	2.2
20	9.2	5.0	4.2	0.24	2.0
25	8.4	5.0	3.4	0.29	1.8
30	7.6	5.0	2.6	0.38	1.6
35	7.1	5.0	2.1	0.48	1.4

Using the values of D_o/D_c and k_a/k_L, L_o can be found, which in this case is the WAC.

Procedure

1. Table IV-21 is entered at the appropriate k_a/k_L column. This is 2.5 at 10°C.

2. Next, the entry within the k_a/k_L column in Table IV-17 is found

such that:

$$\frac{D_o/L_o}{D_c/L_o} = \frac{D_o}{D_c} = 0.16$$

Since the left-most column of Table IV-17 is D_o/L_o and the entries are D_c/L_o, the ratio of these values is calculated until that ratio equals 0.16. For example, try $D_o/L_o = 0.05$. Then $D_c/L_o = 0.23$ and $\frac{0.05}{0.23} = 0.22 > 0.16$; too big.

Try $D_o/L_o = 0.04$. Then $D_c/L_o = 0.23$ and $\frac{0.04}{0.23} = .17$; close enough.

Then $\frac{D_c}{L_o} = .23$, or $L_o = \frac{6.3}{.23} = \underline{\underline{27.4}}$ mg/l

The results are tabulated below for the temperature range 10°C to 35°C.

T(°C)	WAC (mg/l)	D_o/L_o
10	27.4	0.04
15	20.0	0.05
20	15.0	0.07
25	11.3	0.09
30	7.6	0.13
35	5.4	0.19

L_o is directly related to the loading rate of BOD, as expressed earlier in Equation IV-41:

$$WAC = (L_o)_{critical} = \frac{L_u Q_u + W_{critical}/5.38}{Q_u + Q_w}$$

From equation IV-41 the critical waste loading W can be found. If desired, this procedure can be repeated for different river flow rates, and WAC and $W_{critical}$ found for the various flows. To do this, different average depths and velocities will be needed. Generally this analysis is most applicable to minimum flow conditions, as this is the most critical situation, but higher flows may be of interest to assess the benefits of flow augmentation decisions. Novotny and Krenkel (1975) have used a 20 year, 3-day low flow in analyzing the Holston River in Tennessee. For further discussion of low flow calculations refer to Section 4.4.6.

In interpreting the results of this example the user should be looking more at trends rather than particular results. For example, notice how the WAC decreases with increasing temperature. For every 10° increase the WAC is approximately halved. A similar relationship between WAC and flow rate could also be determined.

Finally, using Table IV-18, the travel time t_c can be determined to

the point of critical deficit. The appropriate D_0/L_0 and k_a/k_L values are used to find t_c. Table IV-22 illustrates these results.

TABLE IV-22

CRITICAL TRAVEL TIME RESULTS

$T(^oC)$	k_a/k_L	D_0/L_0	$t_c k_a$	k_a	t_c(days)
10	2.5	0.04	1.4	.63	2.2
15	2.2	.05	1.3	.71	1.8
20	2.0	.07	1.2	.8	1.5
25	1.8	.09	1.13	.9	1.2
30	1.6	.13	1.0	1.0	1.0
35	1.4	.19	0.9	1.1	0.8

— · — · — · — · — · — END OF EXAMPLE IV-8 — · — · — · — · — · — · — · —

— · — · — · — · — · — EXAMPLE IV-9 — · — · — · — · — · — · — · —

Critical Deficit Calculations for Multiple Reaches

Suppose the critical deficit in each of the three reaches of the river illustrated in Figure IV-22 is to be determined. The conditions upstream of the first discharge are:

    T = 27°C   Depth = 5.0 feet

    Q = 600 cfs D_u = 1 mg/l

    U = 0.4 fps L_u = 2 mg/l

Using these data, along with the solution process outlined in Figure IV-21, the following procedure can be used:

1. Determine k_a, k_L for each reach. For this example it will be assumed that the average depth, velocity, and temperature remain relatively constant over the three reaches, so that k_a and k_L are also the same.

    k_a (20) = 0.5, (from Figure IV-17)

    k_L (20) = 0.35, (from Figure IV-11)

Using the temperature correction:

    k_a (27) = 0.60, (from Equation IV-34)

    k_L (27) = 0.48, (from Equation IV-17)
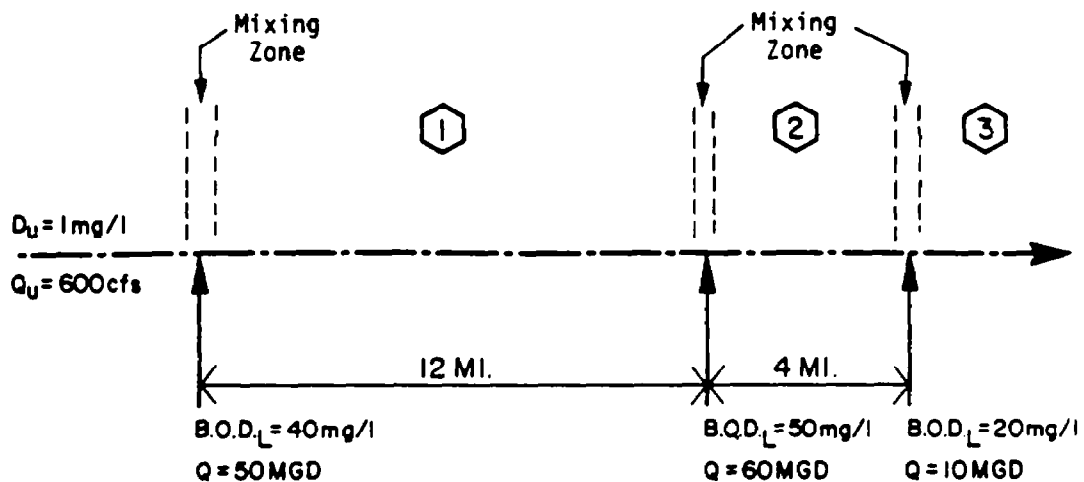
FIGURE IV-22   HYPOTHETICAL RIVER USED IN EXAMPLE IV-9

The saturation dissolved oxygen concentration at 27°C and 0% salinity is (from Table IV-15) 8.1 mg/l.

2. For the first reach, calculate L_o and D_o:

$$L_o = \frac{(2)(600) + (40)(50)(1.55)}{600 + (50)(1.55)}$$

$$= 6.35 \text{ mg/l}$$

For lack of better information about the dissolved oxygen characteristics of the waste, it can be assumed that $D_o = D_u = 1$ mg/l. The location of the critical deficit can now be calculated using Table IV-18, or Equation IV-45. In this example Table IV-18 will be used. To use that table, the following ratios are needed:

$$D_o/L_o = 1/6.35 = 0.16$$

and

$$k_a/k_L = 0.60/0.48 = 1.3$$

From Table IV-18, $k_a t_c = .92$ or

$$t_c = .92/0.6 = 1.53 \text{ days}$$

$$x_c = \frac{(0.4)(1.53)(3600)(24)}{5280} = 10.0 \text{ miles}$$

Since $x_c < 12$, the critical deficit actually exists, and is located 10 miles downstream. From Table IV-17 D_c can be found by entering it with the same ratios used in Table IV-18. The result is:

$$\frac{D_c}{L_o} = .38 \longrightarrow D_c = \underline{2.4} \text{ mg/l}$$

3. Before the critical conditions in reach 2 can be calculated, the conditions at the upstream end of that reach must be established. The conditions at the downstream end of reach 1 are:

D = 2.3 mg/1, from Equation IV-40

L = 2.6 mg/l from Equation IV-42

The conditions at the upstream end of reach 2 are thus:

$$L_o = \frac{(2.6)\ (677)\ +\ (60)\ (1.55)}{677\ +\ 93} = 8.35\ mg/l$$

D_o = 2.3 can be used for lack of better information on the dissolved oxygen concentration in the effluent to reach 2. For use in Table IV-18, it is found that:

$$D_o/L_o = .28$$

so

$$k_a t = .76$$
$$t_c = .76/0.6 = 1.3\ days$$
$$x_c = 8.3\ miles$$

Since reach 2 is only 4.0 miles long, the critical deficit is not reached. Instead the maximum deficit will occur at the downstream end of reach 2, where

D = 3.3 mg/l (Equation IV-40)

L = 6.22 mg/l (Equation IV-22)

4. For the beginning of reach 3, L_o and D_o must be found:

$$L_o = \frac{(20)(10)(1.55)\ +\ (770.5)(6.22)}{770.5\ +\ (10)(1.55)} = 6.5\ mg/l$$

For D_o, it can be assumed that C_w = 5.0 mg/l. From Equation IV-41, then:

$$D_o = 8.1 - \frac{(8.1 - 3.3)\ (770.5)\ +\ (5.0)(10)(1.55)}{770.5\ +\ 15.5} = 3.3\ mg/l$$

The calculations of critical conditions can now be made for this reach, as for the previous two.

—————— END OF EXAMPLE IV-9 ——————————————————

4.4 TEMPERATURE

4.4.1 Introduction

The biota comprising an established aquatic ecosystem generally respond negatively to significant abnormal temperature fluctuations. Anthropogenic modifications of rivers and streams can alter the thermal regime, most often by elevating the maximum and mean water temperatures. Repercussions of elevated temperatures are manifested

through a shift in the ecological balance and in the water quality of rivers. For example, there is a progression in the predominance of algal species from diatoms to green algae to blue-green algae as water temperature increases through a specific range. Thermal discharges can increase the ambient temperature enough to alter the predominant species to the undesirable blue-green algae. Increased metabolic activity of aquatic organisms, such as fish, also accompanies elevated temperature. If the increase is high enough, the results can be lethal. Much data are available today (e.g., Committee on Water Quality Criteria, 1972) which specify lethal threshold temperatures for aquatic organisms.

Water quality may be adversely affected through decreased solubility of dissolved oxygen and increased biochemical reaction rates. Adequate dissolved oxygen levels, particularly at elevated temperatures, are critical because of the increased metabolic activity. Yet, as previously discussed the saturation concentration of dissolved oxygen diminishes with rising temperature. Worse still, is the concurrent low flow condition which is associated, in many parts of the country, with the warm summer months. For example, in a study of 30 river reaches in the U.S. (EPA, 1974), 20 had lower flows in the summer months than in the winter. This situation further reduces assimilative capacity and usually results in the most critical dissolved oxygen levels over the year.

Man can alter the thermal regime of rivers by removing trees, changing the flow regime, and by increasing thermal discharges. Diversions of water from a river can reduce the water depth, and increase the mean and diurnal fluctuation of stream temperature.

In Long Island, modification of the natural environment of streams has increased average stream temperatures during the summertime by as much as 9 to 14°F (Pluhowsi, 1968). Concurrent temperature differences of as much as 14 to 18°F between sites on the same stream were observed on days of high solar radiation. A principal factor involved in these occurrences was the removal of vegetation along the banks of the streams, permitting significantly greater penetration of solar radiation. Other contributing factors cited by Pluhowski included increased stormwater runoff, a reduction in the amount of groundwater inflow, and the introduction of ponds and lakes.

4.4.2 Equilibrium Temperature

If a body of water at a given initial temperature is exposed to a set of constant meteorological conditions, it will tend to approach some other temperature asymptotically. It may warm by gaining heat or cool by losing heat. Theoretically, after a long period of time the temperature will become constant and the net heat transfer will be zero. This final temperature has been called the equilibrium temperature, E. At equilibrium, the heat gained by absorbing solar radiation and

H_s = Shortwave solar radiation (400-2800 BTU ft^{-2} day^{-1})

H_a = Long wave atmospheric radiation (2400-3200 BTU ft^{-2} day^{-1})

H_{br} = Long wave back radiation (2400-3600 BTU ft^{-2} day^{-1})

H_e = Evaporative heat loss (2000-8000 BTU ft^{-2} day^{-1})

H_c = Conductive heat loss or gain (-320-+400 BTU ft^{-2} day^{-1})

H_{sr} = Reflected solar (40-200 BTU ft^{-2} day^{-1})

H_{ar} = Atmospheric reflection (70-120 BTU ft^{-2} day^{-1})
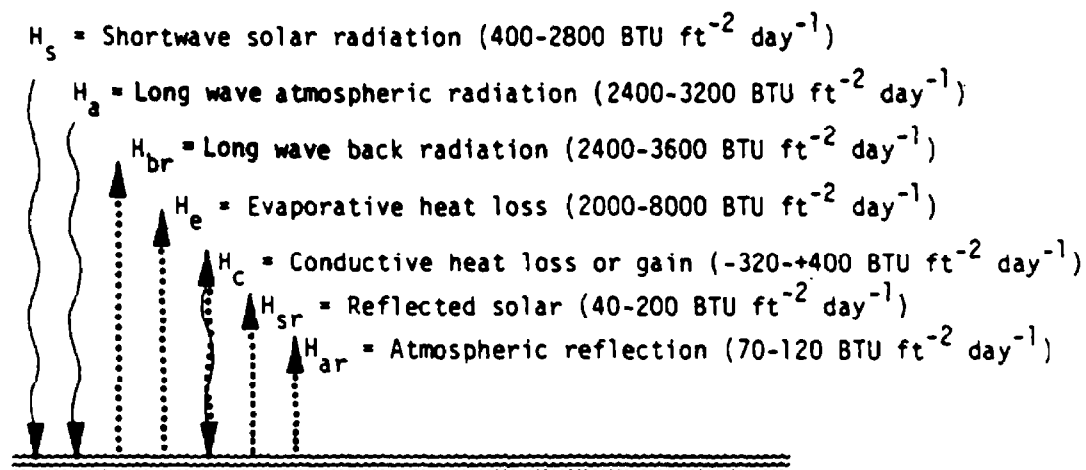
NET RATE AT WHICH HEAT CROSSES WATER SURFACE

$$H_r = \left[(H_s + H_a - H_{sr} - H_{ar}) \quad - \quad (H_{br} \pm H_c + H_e) \right] BTU\ ft^{-2}\ day^{-1}$$

Absorbed Radiation (H_R)
Independent of Water Temperature

Temperature Dependent Terms

$$H_{br} \sim (T_s + 460)^4$$

$$H_c \sim (T_s - T_a)$$

$$H_e \sim W(e_s - e_a)$$

FIGURE IV-23   MECHANISMS OF HEAT TRANSFER ACROSS A
WATER SURFACE (PARKER AND KRENKEL, 1969)

long-wave radiation from the atmosphere will exactly balance the heat lost by back radiation, evaporation, and conduction.

These heat fluxes are illustrated in Figure IV-23 which also shows typical ranges for the fluxes. Some of these terms (H_s, H_a, H_{sr}, H_{ar}) are independent of water temperature, while the remainder (H_{br}, H_c, H_e) are dependent upon water temperature. At equilibrium then, H_n (net transfer) equals zero, or:

$$H_s - H_{sr} + H_a - H_{ar} - H_{br} - H_c - H_e = 0 \qquad (IV-57)$$

In actuality, the water temperature rarely equals the equilibrium temperature because the equilibrium temperature itself is constantly changing with the local meteorological conditions. The equilibrium temperature will rise during

the day when solar radiation is greatest, and fall to a minimum at night when solar radiation is absent.

A daily average equilibrium temperature may be computed using a number of factors including daily average values of radiation, temperature, wind speed, and vapor pressure. The daily average value will reach a maximum in midsummer and a minimum in midwinter. Since the actual water temperature always tends to approach, but does not reach the equilibrium temperature, it will usually be less than equilibrium in the spring when temperatures are rising, and greater than equilibrium in the fall when temperatures are dropping. During a 24 hour period, the equilibrium temperature usually rises above the actual water temperature during the day and falls below the water temperature at night, forcing the water temperature to follow a diurnal cycle.

The amplitude of the actual diurnal water temperature cycle is generally dampened significantly in comparison to the amplitude of the equilibrium temperature cycle due to the large heat capacity of water. A thermal discharge into a water body will usually increase the actual daily amplitude because of the water temperature dependent terms in Equation IV-57. This situation is illustrated in the following example (Edinger, et al., 1968). Figure IV-24 illustrates a flow through a cooling pond into which a thermal effluent is discharged (at Station B).
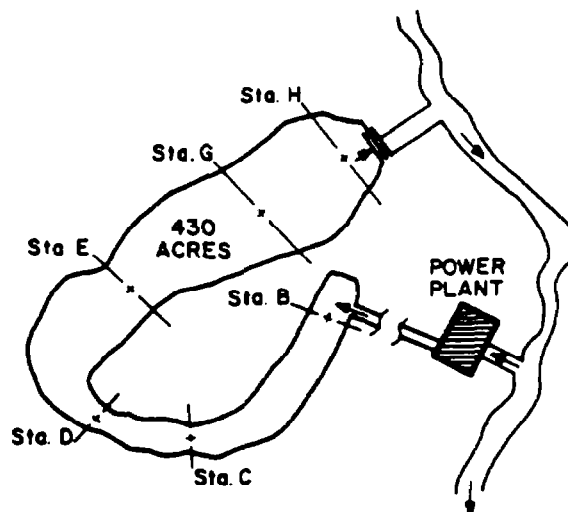
FIGURE IV-24   SCHEMATIC OF SITE No. 3
                 COOLING LAKE (FROM EDINGER,
                 ET AL., 1968)

Temperature observations were recorded at Stations B through H at four-hour periods for one week. The findings are depicted in Figure IV-25.
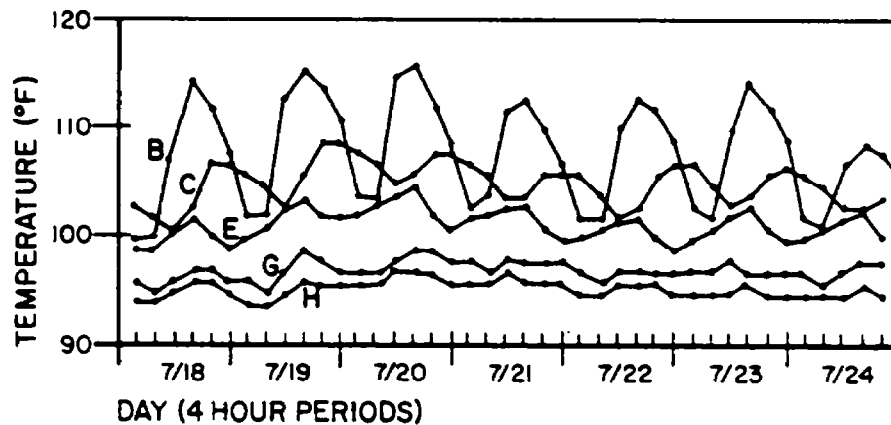
FIGURE IV-25   OBSERVED TEMPERATURES, SITE NO. 3,
                JULY 18 - JULY 24, 1965 (EDINGER,
                ET AL., 1968)

The highest temperatures and largest diurnal temperature variables are recorded at Station B. The peak temperature at Station B occurs just after noon, corresponding to the peak loading from the plant. At Station C the peak temperature is at 1800 hours, indicating the lag in flow time from Stations B to C. The peak temperatures at the remaining stations are more influenced by meteorological conditions, and less by the thermal discharge. The relationship of the observed temperatures to the equilibrium temperature over a 24-hour period is shown in Figure IV-26. Note the amplitude of the equilibrium temperature E (33°F amplitude). The average equilibrium temperature, $\bar{E}$, is approximately 91°F. A progression from Station B to Station H indicates that the daily water temperature tends to approach the average equilibrium temperature.

Stations G and H, and the ambient temperature T_N, all reflect the predominating influence of meteorological conditions. When the ambient water temperature is above the instantaneous equilibrium temperature E, it tends to decrease, and when the temperature is below E, it tends to increase. In the early morning and late evening hours, when E is low, the water temperature decreases at these stations. During midday when E is higher, however, the temperatures at these stations increase.

4.4.3 Calculation of Equilibrium Temperature

Studies (Edinger and Geyer, 1965) have shown that the equilibrium temperature of a well mixed body of water can be estimated by:

$$E = -\frac{0.05E^2}{K} - \frac{H_R - 1801}{K} + \frac{K - 15.7}{K(.26+B)}\left[e_a - C(B) + 0.26\bar{T}_a\right] \qquad (IV-58)$$
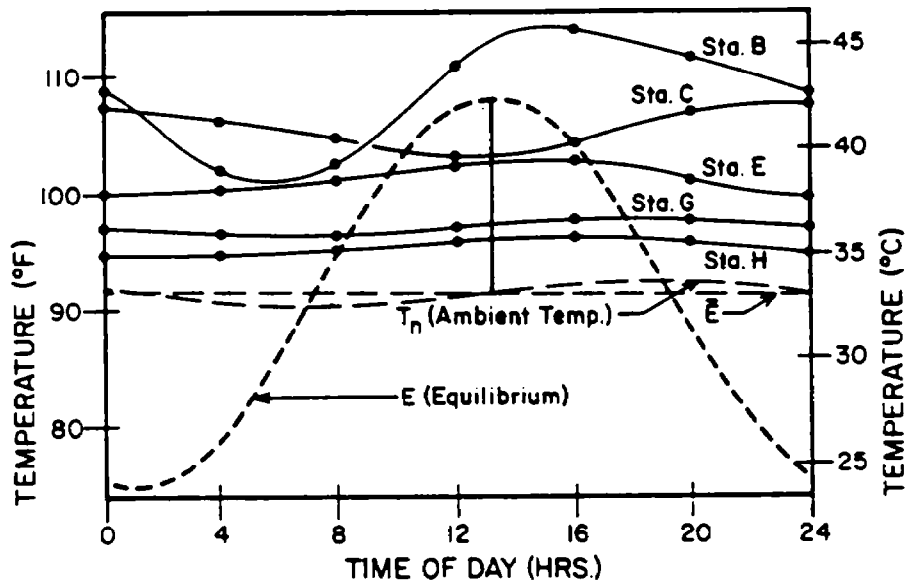
FIGURE IV-26   COMPARISON OF COMPUTED EQUILIBRIUM AND
AMBIENT TEMPERATURES WITH OBSERVED MEAN
DIURNAL TEMPERATURE VARIATIONS FOR SITE
No. 3, JULY 18-JULY 24, 1966 (EDINGER,
ET AL., 1968)

where

E	= equilibrium teperature, °F
K	= thermal exchange coefficient, $BTU/ft^2/day/°F$
H_R	= net incoming short (H_{sn}) and long (H_{an}) wave radiation $BTU/ft^2/day$
T_a	= air temperature, °F
e_a	= water vapor pressure of ambient air at air temperature, mmHg
B	= proportionality coefficient, mmHg/°F
C(B)	= value dependent on B, mmHg.

The thermal exchange coefficient K is expressible as:

$$K = 15.7 + (0.26 + B) f(u)$$ (IV-59)

where

f(u)   = a function of wind speed.

Different relationships for f(u) have been developed. For purposes of hand calculations, the following relationship will be used:

$$f(u) = 11.4u$$ (IV-60)

where

> u = the daily average wind speed in mph.

To calculate E using Equation IV-58 an iterative procedure is needed, since K, B, and C(B) depend on E. The following steps outline a solution procedure.

1. Data needed to start the procedure include T_a, relative humidity, wind speed, and net shortwave solar radiation. Figure IV-27 illustrates daily average solar radiation reaching the continental United States for the months July and August. It is during these months that stream temperatures usually reach their annual maxima. These values do not account for the albedo of water (the percent of incoming solar radiation that is reflected), but since this is small, it can be ignored. Because of the variability caused by topography, vegetative cover, and other factors, local sources of information should be used when possible for solar radiation values.

2. Calculate $H_R = H_{sn} + H_{an}$ (BTU/ft^2/day). If Figure IV-27 is utilized for H_{sn}, convert from langleys/day to BTU/ft^2/day by multiplying by 3.7. H_{an} can be estimated from Table IV-23 by knowing the air temperature and the cloud cover fraction (0.1 to 1.0).

3. Determine e_a from Table IV-24 by entering with T_a and relative humidity.

4. Choose an initial value for E. The air temperature T_a can be the first guess.

5. Enter Table IV-25 for B and C(B) at E (°F).

6. Knowing u, f(u), and B, calculate K from Equation IV-59.

7. From Equation IV-58 make the next estimate of E (E_{new}) by evaluating the right hand side of that equation (call this result F(E)).

8. The next estimate of E is $E_{new} = 0.3E + 0.7 F(E)$.
   (Note: this choice of E_{new} brings about a more rapid convergence to the answer than would use of E alone).

9. If $|E_{new} - E| \leq 1°F$, then $E_{actual} = E_{new}$.
   If $|E_{new} - E| > 1°F$, return to step 5 with E_{new} and repeat the procedure until the convergence criterion is met, namely, $E_{actual} = E_{new}$.

Instantaneous, daily, weekly, or even longer term average equilibrium temperature, $\bar{E}$, can be calculated by using mean meteorological conditions over the period of interest and following the solution procedure just outlined. Calculating the daily average $\bar{E}$ under the most crucial annual meteorological conditions (usually occurring in July or August) yields the highest temperature about which that water body tends to naturally oscillate. The repercussions of man's activities in terms of altering $\bar{E}$ can thus be estimated and analyzed for potential impact.
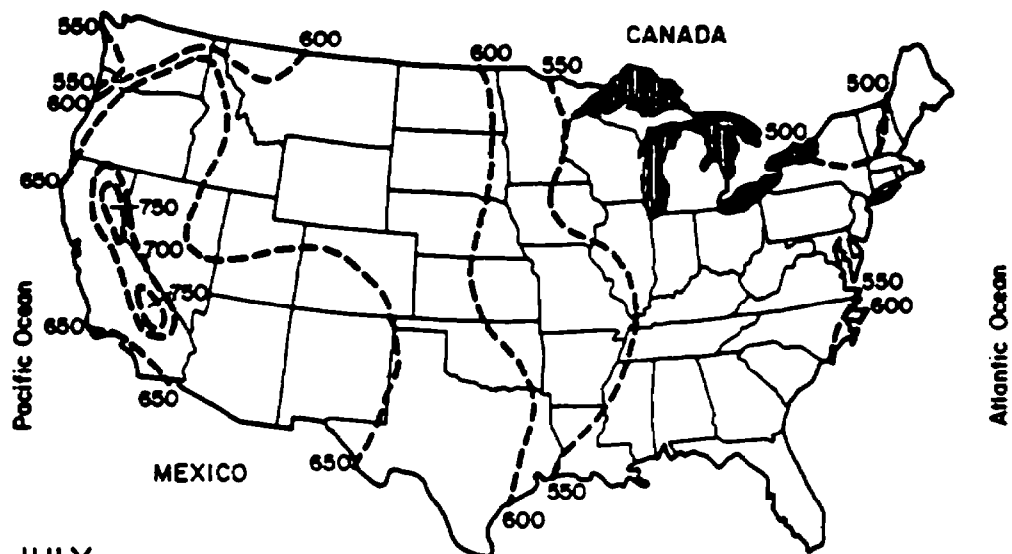
JULY
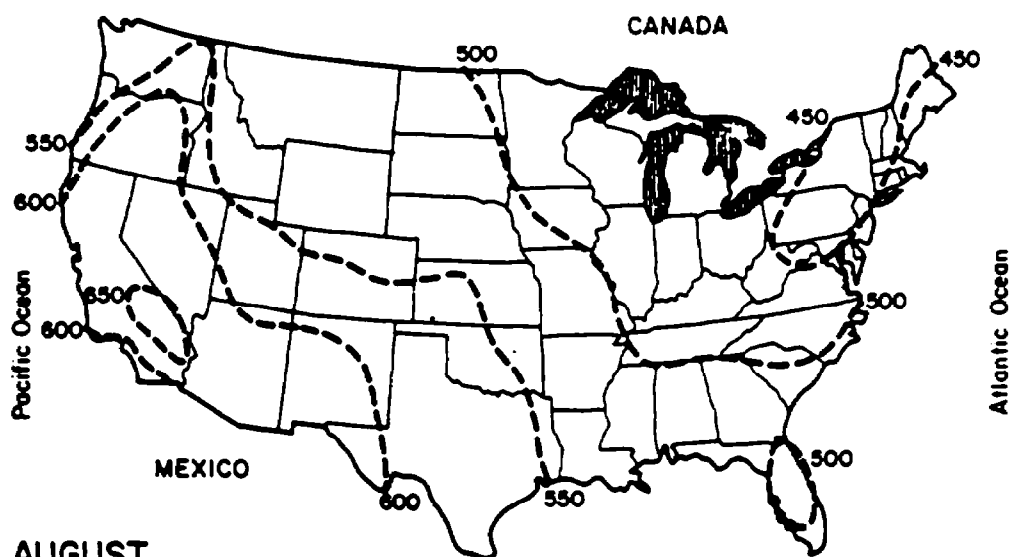
AUGUST

NOTE: To convert Langleys/day to BTU/ft²/day, multiply by 3.7.

FIGURE IV-27   MEAN DAILY SOLAR RADIATION (LANGLEYS) THROUGHOUT
THE U.S. FOR JULY AND AUGUST (U.S. DEPARTMENT
OF COMMERCE, 1968)

TABLE IV-23
NET LONG WAVE ATMOSPHERIC RADIATION, H_{an}

Cloud Cover	Temperature (°F)	H_{an} (BTU/Sq. Ft/Day)	Temperature (°F)	H_{an} (BTU/Sq. Ft/Day)	Temperature (°F)	H_{an} (BTU/Sq. Ft/Day)	Temperature (°F)	H_{an} (BTU/Sq. Ft/Day)	Temperature (°F)	H_{an} (BTU/Sq. Ft/Day)	Temperature (°F)	H_{an} (BTU/Sq. Ft/Day)
.1	35	1685	40	1790	45	1900	50	2016	55	2138	60	2266
	65	2400	70	2540	75	2688	80	2842	85	3004	90	3173
.2	35	1694	40	1799	45	1910	50	2026	55	2149	60	2277
	65	2412	70	2553	75	2701	80	2857	85	3019	90	3190
.3	35	1708	40	1814	45	1926	50	2043	55	2167	60	2296
	65	2432	70	2575	75	2724	80	2881	85	3045	90	3216
.4	35	1728	40	1835	45	1949	50	2067	55	2192	60	2323
	65	2461	70	2605	75	2756	80	2914	85	3080	90	3254
.5	35	1754	40	1863	45	1978	50	2098	55	2225	60	2358
	65	2497	70	2644	75	2797	80	2958	85	3126	90	3303
.6	35	1785	40	1896	45	2013	50	2136	55	2265	60	2400
	65	2542	70	2691	75	2847	80	3011	85	3182	90	3362
.7	35	1822	40	1936	45	2055	50	2180	55	2312	60	2450
	65	2595	70	2747	75	2907	80	3074	85	3249	90	3432
.8	35	1865	40	1981	45	2103	50	2232	55	2366	60	2508
	65	2656	70	2812	75	2975	80	3146	85	3325	90	3513
.9	35	1914	40	2033	45	2158	50	2290	55	2428	60	2573
	65	2725	70	2885	75	3053	80	3228	85	3412	90	3604
1.0	35	1968	40	2091	45	2220	50	2355	55	2497	60	2646
	65	2803	70	2967	75	3139	80	3320	85	3509	90	3707

TABLE IV-24

SATURATED WATER VAPOR PRESSURE, e_s, VERSUS AIR TEMPERATURE, T_a,
AND RELATIVE HUMIDITY

T_a	$e_s^\star$	RELATIVE HUMIDITY									
(°F)	(mmHg)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
35	5.2	0.5	1.0	1.6	2.1	2.6	3.1	3.6	4.2	4.7	5.2
40	6.3	0.6	1.3	1.9	2.5	3.2	3.8	4.4	5.0	5.7	6.3
45	7.6	0.8	1.5	2.3	3.0	3.8	4.6	5.3	6.1	6.8	7.6
50	9.1	0.9	1.8	2.7	3.6	4.6	5.5	6.4	7.3	8.2	9.1
55	11.0	1.1	2.2	3.3	4.4	5.5	6.6	7.7	8.8	9.9	11.0
60	13.1	1.3	2.6	3.9	5.2	6.6	7.9	9.2	10.5	11.8	13.1
65	15.6	1.6	3.1	4.7	6.2	7.8	9.4	10.9	12.5	14.0	15.6
70	18.6	1.9	3.7	5.6	7.4	9.3	11.2	13.0	14.9	16.7	18.6
75	22.0	2.2	4.4	6.6	8.8	11.0	13.2	15.4	17.6	19.8	22.0
80	26.0	2.6	5.2	7.8	10.4	13.0	15.6	18.2	20.8	23.4	26.0
85	30.5	3.1	6.1	9.2	12.2	15.3	18.3	21.4	24.4	27.5	30.5
90	35.8	3.6	7.2	10.7	14.3	17.9	21.5	25.1	28.6	32.2	35.8
95	41.8	4.2	8.4	12.5	16.7	20.9	25.1	29.3	33.4	37.6	41.8
100	48.7	4.9	9.7	14.6	19.5	24.4	29.2	34.1	39.0	43.8	48.7

TABLE IV-25

B AND C(B) AS FUNCTIONS OF TEMPERATURE

Temperature ($^{\circ}$F)	B (mmHg/$^{\circ}$F)	C(B) (mmHg)	Temperature ($^{\circ}$F)	B (mmHg/$^{\circ}$F)	C(B) (mmHg)
45	.286	-5.5	70	.660	-22.9
46	.296	-4.5	71	.680	-23.6
47	.306	-4.1	72	.701	-24.4
48	.317	-4.2	73	.722	-25.4
49	.328	-4.6	74	.743	-26.5
50	.340	-5.4	75	.765	-27.8
51	.352	-6.3	76	.787	-29.3
52	.365	-7.5	77	.810	-31.0
53	.378	-8.7	78	.833	-33.0
54	.391	-10.0	79	.857	-35.1
55	.405	-11.2	80	.881	-37.6
56	.419	-12.5	81	.905	-40.3
57	.433	-13.6	82	.930	-43.2
58	.448	-14.7	83	.955	-46.4
59	.464	-15.8	84	.980	-49.7
60	.479	-16.7	85	1.006	-53.3
61	.496	-17.6	86	1.033	-57.1
62	.512	-18.3	87	1.060	-61.0
63	.529	-19.0	88	1.087	-64.9
64	.547	-19.6	89	1.114	-68.9
65	.564	-20.1	90	1.142	-72.9
66	.583	-20.7	91	1.171	-76.7
67	.601	-21.2	92	1.200	-80.4
68	.620	-21.7	93	1.229	-83.8
69	.640	-22.3	94	1.259	-86.8
			95	1.289	-89.3

—————————— EXAMPLE IV-10 ——————————

Calculation of Equilibrium Temperature

On Long Island, New York, studies done by Pluhowski (1968) have indicated that shading of streams by a natural vegetative canopy can drastically affect the shortwave solar radiation reaching those streams. The results of some of his findings are presented in Table IV-26. In the summer, when leaves are on the trees, the actual solar radiation reaching the Connetquot River can be as low as 29% of that reaching unobstructed sites at nearby Mineola or Brookhaven.

Suppose the user is interested in predicting how the removal of the riparian

TABLE IV-26

SUMMARY OF SOLAR-RADIATION DATA
FOR MINEOLA, BROOKHAVEN, AND THE CONNETQUOT RIVER SITES

| Solar Site | Dates | Mean-Daily Solar Radiation in Langleys: for the Indicated Periods | | | | Ratio= Connetquot River Observed |
| | | Mineola | Brookhaven | Connetquot River Estimated | Connetquot River Observed | Connetquot River Unobstructed |
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	Jan. 30, 31, 1967	235	244	240	148	0.62
2	Jan. 28, 29, 1967	148	130	137	96	.70
3	Jan. 25, 26, 1967	135	135	135	104	.77
1	Apr. 21-23, 1967	466	464	465	343	.74
	Apr. 16-18, 1968	452	502	502	389	.77
2	Apr. 19, 20, 1967	436	386	429	384	.90
3	Apr. 24-26, 1967	408	411	410	401	.98
1	June 9-11, 1967	600	599	599	254	.42
2	June 7, 8, 1967	664	671	669	531	.79
3	June 12-14, 1967	527	523	525	443	.84
1	Aug. 26-28, 1967	275	260	266	78	.29
2	Aug. 22-24, 1967	277	328	308	162	.53
3	Aug. 29, 30, 1967	504	484	492	338	.69
1	Nov. 28, 29, 1967	204		204	86	.42

Notes:

Solar site 1 is typically heavily forested, solar site 2 is moderately to heavily forested, and solar site 3 is moderately forested.

Radiation data in column 5 are estimated unobstructed horizon values for Connetquot River based on data from Mineola and Brookhaven (cols. 3,4).

vegetative cover might effect $\bar{E}$. Consider the period 22-24 August, 1967, when the Connetquot River received 162 langleys/day of a possible 308 langleys/day of shortwave solar radiation. Representative meteorological conditions at this time were:

$$T_a = 65°F$$
$$u = 2 \text{ mph}$$

Cloud cover fraction = 0.5

Relative humidity = 80%

The steps in solving for $\bar{E}$ are as follows:

1. Data have been gathered, as previously listed.

2. $H_{sn} = 162 (3.7) = 600$ BTU/ft^2/day. This value assumes that the vegetative canopy blocks 47% of the solar radiation. From Table IV-23, H_{an} is (.5 cloud cover at 65°F) 2497 BTU/ft^2/day. Thus,
$$H_R = 2497 + 600 = 3097 \text{ BTU/ft}^2\text{/day}.$$

3. At 80% relative humidity and an air temperature of 65°F, $e_a = 12.5$ mmHg from Table IV-24.

4. As an initial guess of E, assume $E_1 = 65°F$, the air temperature.

5. From Table IV-25, B = .56, C(B) = -20.1

6. $K = 15.7 + (.26 + .56) (11.4) (2) = 34.4$

7. $F(E_1) = \dfrac{-0.05(65)^2}{34.4} + \dfrac{3098 - 1801}{34.4} + \dfrac{34.4 - 15.7}{34.4(.26 + .56)}$

 $X [12.5 + 20.1 + .26(65)] = -.6.1 + 37.7 + 33.0 = 64.6$

8. $E_2 = .3(65) + .7(64.6) = 64.7$

9. Since $|E_2 - E_1| < 1°F$ $\quad$ $\underline{\underline{\bar{E} = 64.7°F}}$

Now suppose the user wants to find $\bar{E}$ for no reduction in H_{sn} due to shading. Steps 1 through 9 again are repeated, using $H_{sn} = 308(3.7) = 1140$ BTU/ft^2/day, with otherwise the same meteorological conditions. Without detailing the calculations here, it is found that $\bar{E} = 74.7°$, a 10°F increase.

It is evident then that altering the solar radiation penetrating to the stream can significantly change $\bar{E}$. Even more severe cases of repression of shortwave radiation (as noted by the 71% reduction on 26-28 August, 1967, Table IV-26) are possible, exemplifying the large differences which may be observed.

─────────────── END OF EXAMPLE IV-10 ───────────────

The approach illustrated in Example IV-10 for predicting equilibrium temperature is obviously time consuming, and has been programmed for hand held calculators in Mills et al. (1979) . A simplified approach is also available for predicting equilibrium temperature (Brady et al., 1969) and is described below. The predictions are usually within 3°F or less of those found by the more complicated approach.

The data required for the simpler approach are:

T_d, dewpoint temperature (°F)

U, mean daily wind speed (mph)

H_{sn}, net incoming shortwave radiation (Btu/ft²/day).

Short wave solar radiation data were previously shown in Figure IV-27. The Climatic Atlas (U.S. Department of Commerce, 1968) contains compilations of dewpoint temperature and windspeed. Figures IV-28 and IV-29 show these data for the months of July and August. Figures IV-27 through IV-29 provide the user with all the data needed to predict equilibrium temperature using the approach of Brady et al.

To find the equilibrium temperature the following equations are applied sequentially:

COMPUTE ONCE ⟶
$$F(U) = 70 + 0.7 \, U^2 \qquad \text{(IV-61)}$$

$$T = \left(E_i + T_D\right)/2 \qquad \text{(IV-62)}$$

ITERATE OVER THESE EQUATIONS
$$B = 0.255 - 0.0085T + 0.000204T^2 \qquad \text{(IV-63)}$$

$$K = 15.7 + \left(B + .26\right) F(u) \qquad \text{(IV-64)}$$

$$E_{i+1} = T_D + H_s / K \qquad \text{(IV-65)}$$

The wind speed function f(U) is found once from Equation IV-61. The dewpoint temperature (T_d) is a convenient starting choice as an initial guess of the equilibrium temperature. T can then be calculated from Equation IV-62; B from Equation IV-63; K from Equation IV-64; and finally a new equilibrium temperature (E_{i+1}) from Equation IV-65. If E_i and E_{i+1} differ by more than 1°F, return to Equation IV-62 with E_{i+1} and repeat the procedure until convergence is attained (usually within 2 or 3 cycles).

—·—·—·—·—·—·—·—·—·— EXAMPLE IV-11 —·—·—·—·—·—·—·—·—·—·—·—

Equilibrium Temperature Using Simplified Approach

Determine the average daily surface water equilibrium temperature for Little Rock, Arkansas during the month of August. Based on Figures IV-27 through IV-29 the following data are found:

T_d = 68°F

U = 7 mph

H_{sn} = (525)(3.7) = 1943 Btu/ft²/day
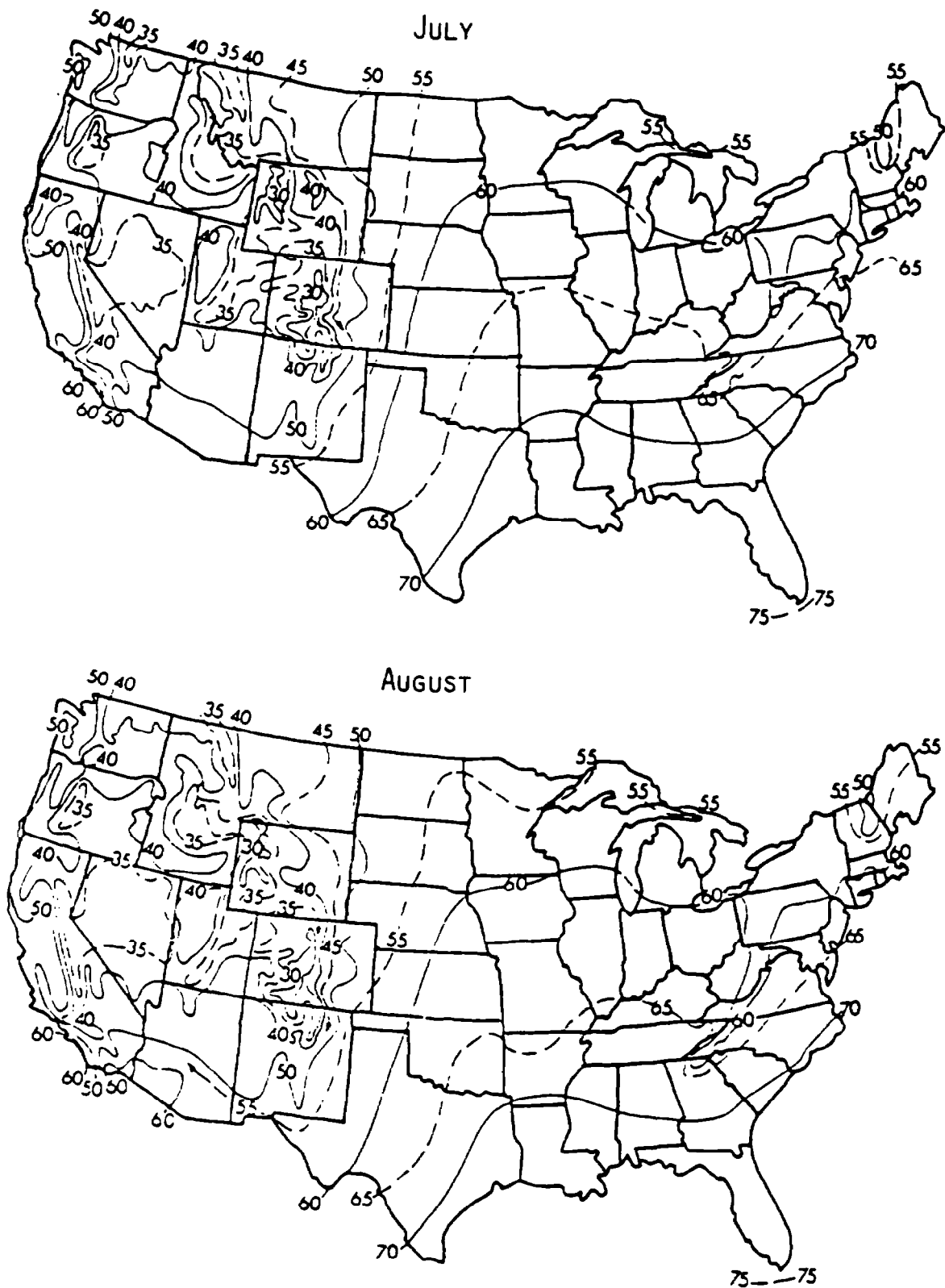
FIGURE IV-28 MEAN DEWPOINT TEMPERATURE (°F) THROUGHOUT THE
UNITED STATES FOR JULY AND AUGUST (U.S. DEPART-
MENT OF COMMERCE, 1968)
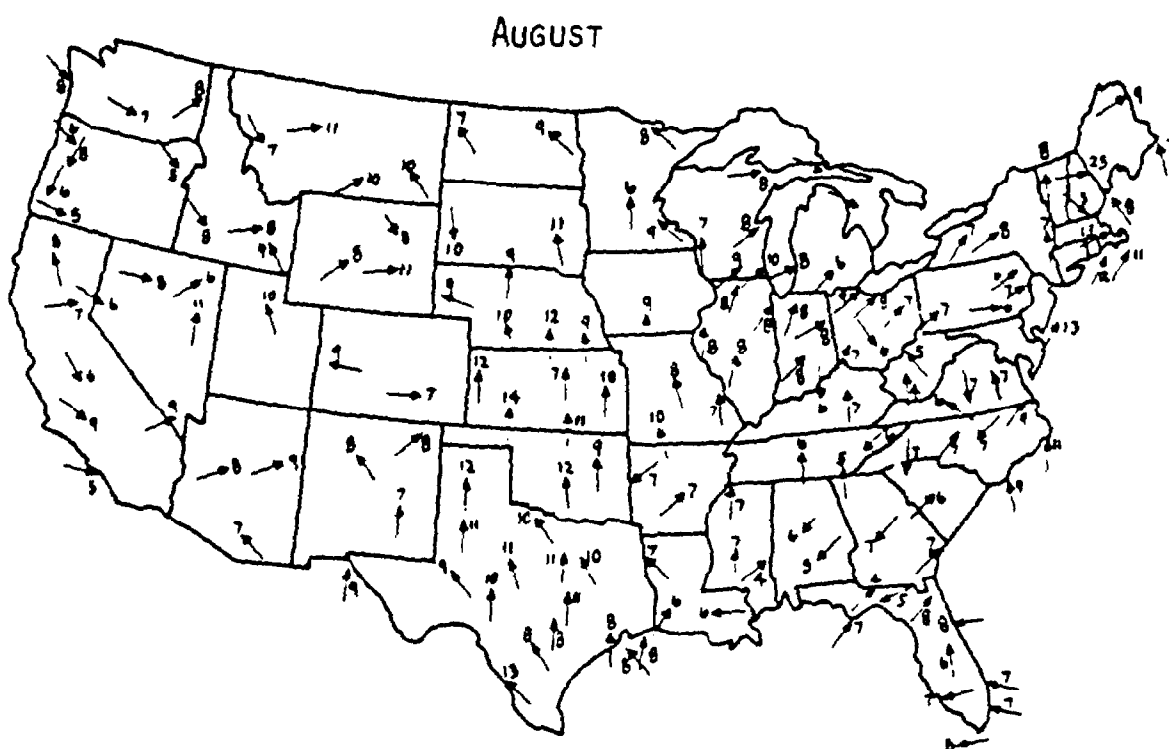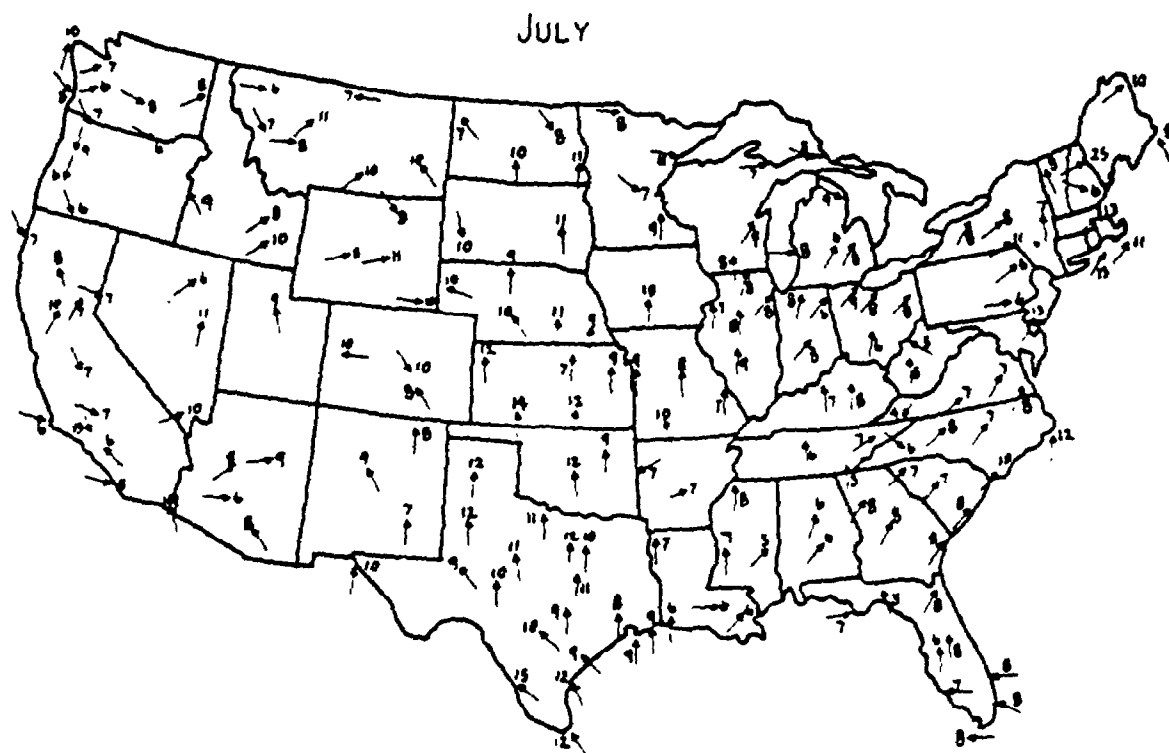
JULY

AUGUST

FIGURE IV-29 MEAN DAILY WIND SPEEDS (MPH) THROUGHOUT THE
UNITED STATES FOR JULY AND AUGUST (U.S. DEPARTMENT
OF COMMERCE, 1968)

Assume as a first guess that $E = T_d = 68°F$
then:

$$f(U) = 70 + .7 (7)^2 = 104.$$
$$T = (T_d + T_d)/2 = 68°$$
$$B = .62$$
$$K = 15.7 + (.62 + .26) (104) = 107.$$
$$E = 68 + 1943/107 = 86°F$$

For the second iteration:

$$T = (86 + 68)/2 = 77$$
$$B = 0.81$$
$$K = 127$$
$$E = 83.3°F$$

At the end of a third iteration $E = 83.7°F$, so convergence has been attained by three iterations.

As a comparison, the equilibrium temperature will also be calculated using the longer approach. The required data are:

$$T_a = 80°F$$
$$T_d = 68°F$$
$$U = 7.$$
$$H_{sn} = 1943$$
$$\text{sky cover} = 0.5 \text{ (from climatic atlas)}$$

A summary of the procedure is:

1. $H_{an} = 2958$
   $H_R = 1943 + 2958 = 4901$
2. Since $T_d = 68°$, $e = 17.4$
3. Choose $E = T_a = 80°F$
4. $B = .881$
   $C(B) = -37.6$
5. $f(U) = 70 + 0.7 (7)^2 = 104$
   $K = 15.7 + (0.26 + .881) (104) = 134$
6. $F(E) = 79.3$
7. $E = .3(80) + .7 (79.3) = 80°F$, after one pass.

Since the starting guess of 80°F is virtually identical with the calculated value at step 7, a second iteration is not required. The two procedures predict equilibrium temperatures which differ by about 4°F.

—————————————— END OF EXAMPLE IV-11 ——————————————

To estimate the effects of shading, the incoming solar radiation should be calculated first assuming no shading, but otherwise using existing meteorological conditions for the time of the year of interest. The effects of shading should be superimposed upon this result as a percent reduction. The following (Pluhowski, 1968) can serve as guidelines in estimating solar radiation reduction:

- 0-25 percent reduction: shading generally restricted to early morning and late afternoon.

- 25-50 percent reduction: some sunshine penetration in morning and evening. Considerable sunshine between 1000 and 1400 hours.

- 50-75 percent reduction: very little sunshine penetration in morning or late afternoon. Some sunshine between 1000 and 1400 hours.

- Greater than 75 percent reduction: very little penetration even at noon.

4.4.4 Screening of Thermal Discharges

4.4.4.1 Introduction

This section presents a set of procedures which can be used to determine whether the thermal discharge at a proposed power plant site or the discharge from the expansion of an existing site is likely to violate thermal standards. Procedures are presented to test for contravention of the following types of standards:

- The ΔT Criterion: The increase in temperature of water passing through the condenser must not exceed a specified maximum.

- The Maximum Discharge Temperature Criterion: The temperature of the heated effluent must not exceed a specified maximum.

- The Thermal Block Criterion: The cross-sectional area of a river occupied by temperatures greater than a specified value must not exceed a specified percentage of the total area.

- The Surface Area Criterion: The surface area covered by isotherms exceeding a specified temperature increment (above ambient) must not exceed a specified maximum.

Actual values associated with the above standards vary by political jurisdiction. Accordingly, regulations must be consulted.

The thermal discharge screening procedures are designed to address the following questions:

- Is the power plant, as proposed, acceptable at the candidate location?

- What is the largest power plant that can be placed at the candidate location? Equivalently, can an existing power plant at the candidate location be expanded?

The methods do not analyze interactions among multiple powerplants on the same river. Such an analysis can be rather more complex. A report by Tetra Tech (1978)

Intake Channel

Power Plant

T_i

$T_0 = T_i + \Delta T$

Outlet Channel

Q_0 — Skimmer Wall

A

w_R

Q_r

River

A

PLAN VIEW
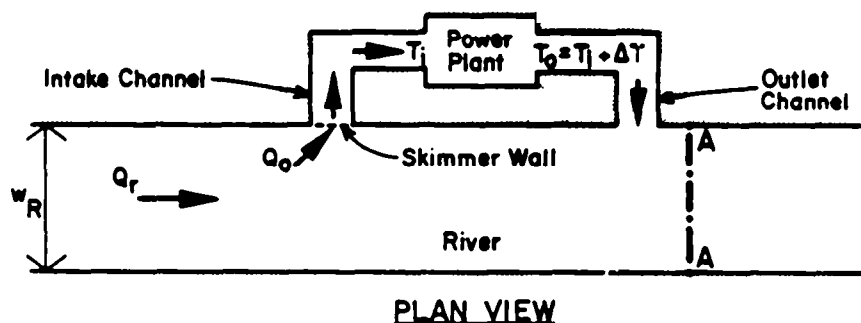
FIGURE IV-30   IDEALIZATION OF A RUN-OF-THE-RIVER POWER PLANT

addresses that question.

The methods developed to evaluate instream thermal criteria use heat balance equations assuming a steady-state, well mixed system at low flow. The power plants are assumed to employ once through cooling, as shown in Figure IV-30.

The selection of well mixed conditions appears to be justified. Studies by Stefan and Gulliver (1978) on the Mississippi and Missouri Rivers have dealt with the lateral mixing of thermal plumes which were released at the shoreline and were not initially well mixed across the river. The investigators found that over a short distance, thermal losses were negligible and that the well-mixed isotherm (the isotherm that would result were the plume initially well-mixed laterally and vertically) eventually extended across nearly the entire width of the river, albeit at some distance downstream. This indicates that if the thermal block criterion is not met for the well mixed case, it is not likely to be met for the shoreline discharge either. A similar conclusion can be reached regarding the surface area constraint. Thus, at this level of analysis, it is not necessary to consider the consequence of incomplete lateral or vertical mixing adjacent to the shoreline discharge.

One simplification which can be used at the option of the user for the surface area calculation should be mentioned. Surface water that is undisturbed by anthropogenic influences (in a thermal sense) approaches the equilibrium temperature. This temperature is dictated by natural meteorological conditions. Surface water temperature in rivers, especially during steady low-flow periods, can be near equilibrium. In calculating the surface area occupied by isotherms exceeding a specified temperature, it is necessary to know the equilibrium temperature. However, since the procedure for calculating equilibrium temperature is fairly complicated, considerable savings in computational effort can be obtained by assuming the ambient water is at its equilibrium temperature.

Some circumstances, in addition to anthropogenic influences, tend to produce ambient temperatures different from equilibrium. For example:

- Locally, large quantities of groundwater may discharge into the river
- Hypolimnionic releases from large reservoirs may occur nearby
- Snow melt may supply a substantial amount of inflow.

As a result of the first two influences, the stream water temperature may be lower than equilibrium since the source of the water comprising the stream flow has been shielded from the heating effect of solar radiation. Snow melt, although not likely to influence the river's thermal regime during the late summer, can be important through spring and into early summer in areas where high-mountain snowpack exists over most, or all, of the year.

The screening procedure that follows assumes the river water, once it has been heated by the thermal plume, is above equilibrium. This means that the water temperature will then decrease in the downstream direction, which is generally, but not always, true.

Table IV-27 shows the data needed to apply the thermal screening methods. The symbols are defined in the table and suggested default values are given for variables where appropriate. The variables are introduced in the table in the order they occur in the screening procedure.

4.4.4.2 Evaluating the Thermal Block Criterion

The initial temperature elevation that results when the thermal plume becomes well mixed with the river water is given as:

$$\Delta T_{wm} = \frac{Q_p}{Q_r} \Delta T \qquad (IV-66)$$

$$= \frac{1}{Q_r} \cdot \frac{e_c}{e_p} \, MWe \cdot \frac{1}{\rho C_p} \cdot \frac{3.414 \times 10^6}{3600} \qquad (IV-67)$$

where

ΔT_{wm} = temperature elevation of the initially well mixed isotherm (°F)

Q_p = flowrate of cooling water (m³/s)

ΔT = $T_e - T_r$ (°F)

T_e = temperature of heated effluent (°F)

T_r = temperature of river water upstream of power plant (°F).

All other terms are defined in Table IV-27.

To find ΔT_{wm}, Equation IV-67 is solved. If ΔT_{wm} is less than the thermal block temperature increment (ΔT_{tb}), the thermal block criterion is not contravened. Otherwise, it is.

-373-

TABLE IV-27

DATA NEEDED FOR THERMAL DISCHARGE SCREENING

Variable	Term Definition	Default Value
MWe	Capacity of power plant in megawatts electric (bus bar)	--
e_p	Percent of total energy produced that goes to electricity production	new fossil fuel plants:38 nuclear plants:32
e_c	Percent of total energy produced that is dissipated through the cooling water	new fossil fuel plants:48 nuclear plants:68
Q_r	River·flow rate above power plant (m^3/s)	$7Q_{10}$
ρ	Mass density of water (kg/m^3)	1000
C_p	Specific heat of water ($Btu/°F-kg$)	2.2
ΔT_{tb}	Temperature rise in the river cross section that constitutes a thermal block (°F)	5
ΔT_{max1}	Maximum legal allowable temperature rise across the condenser (°F)	20
ΔT_{max2}	Maximum allowable temperature rise across the condenser such that $T_e \leq (T_e)_{max}$ (°F)	--
T_e	Temperature of heated effluent (°F)	--
$(T_e)_{max}$	Maximum legal allowable temperature of heated effluent (°F)	86
ΔT_{maxmin}	The lesser of ΔT_{max1} and ΔT_{max2} (°F)	--
$(Q_p)_{max}$	The maximum allowable flow rate through the cooling system (m^3/s)	$.25Q_r$
ΔT_{sa}	The isotherm defining the boundary of the surface area for which legal limits have been established (°F)	4
V	Mean velocity of the river (m/s)	
d	Mean hydraulic depth of river in reach under consideration (m)	--
E	Equilibrium temperature (°F)	--
K	Surface thermal transfer coefficient ($Btu/d · °F · m^2$)	--

TABLE IV-27 (continued)

Variable	Term Definition	Default Value
A	Surface area of river down to ΔT_{sa} isotherm (m²)	--
A_{sa}	Legal maximum surface area limit which can be covered by the ΔT_{sa} and greater isotherms (m²)	--
W	Average surface width of river down to ΔT_{sa} isotherm (m)	--
T_{ra}	River temperature just above where a tributary joins the mainstem (°F)	--
T_t	Temperature of tributary (°F)	--
Q_t	Flow rate of tributary (m³/s)	--
T_a	Air Temperature (°F)	--
Relative humidity	--	--
u	Wind speed at 7 meters above surface (m/s)	--
H_{sn}	Net shortwave solar radiation (Btu/m² · d)	--
H_{an}	Net long wave solar radiation (Btu/m² · d)	--

4.4.4.3 Acceptability of the Temperature Rise Across the Condenser and of the Temperature of the Heated Effluent

Whether these criteria are met or not depends on a number of factors, such as the cooling water flow rate. Since the cooling water flow rate can be designed to be within a specified range, it is determined here whether a feasible range exists such that the two above mentioned criteria are met.

The minimum acceptable flow rate such that both temperature criteria do not exceed their standards is as follows:

$$(Q_p)_{min} = \frac{e_c}{e_p} \cdot MWe \cdot \frac{1}{\rho C_p \Delta T_{maxmin}} \cdot \frac{3.414 \times 10^6}{3600} \qquad (IV-68)$$

where

$(Q_p)_{min}$ = minimum flow rate such that the two temperature criteria are not exceeded (m³/s).

By evaluating Equation IV-68 the minimum cooling water flow can be determined.

As an example of how ΔT_{maxmim} is chosen, suppose the following conditions exist:

Maximum legal temperature rise across the condenser = 20°F

Maximum legal temperature of the heated effluent = 86°F

Ambient river temperature = 74°F.

From these conditions, ΔT_{max2} (the allowable temperature increase across the condenser such that the temperature of the effluent does not exceed the legal maximum) = 86°F - 74°F = 12°F. So T_{maxmin} = minimum (20°F, 12°F) = 12°F. 12°F must be chosen, then, as the maximal temperature rise across the condenser.

Once Equation IV-68 has been solved, the ratio of cooling water to river flow should be checked so that the value is within acceptable limits. Equation IV-66 can be rewritten as:

$$\frac{Q_p}{Q_r} = \frac{\Delta T_{wm}}{\Delta T}$$

(IV-69)

Since ΔT_{wm} has been calculated from Equation IV-67 and ΔT has been calculated as ΔT_{maxmim}, the flow rate fraction can be calculated from Equation IV-69. If this fraction exceeds a certain percent (e.g., 25 percent or some user defined value), then the cooling water flow rate is too large to be acceptable. If the flow rate fraction is not excessive, the actual flow rate can be chosen so that:

$$(Q_p)_{min} \leq Q_p \leq (Q_p)_{max}$$

(IV-70)

where

$(Q_p)_{max}$ = maximum allowable cooling water flow rate (m³/s)

4.4.4.4 Evaluating the Surface Area Constraint

The evaluation of this criterion may require the user to perform considerably more calculations than for any of the other prescreening criteria. The two major complicating factors that are encountered are: 1. determining the river equilibrium temperature, and 2. evaluating the effects of tributaries.

If it is the case that ΔT_{wm} does not exceed ΔT_{sa} the surface area criterion will not be contravened and no calculations have to be performed. If ΔT_{wm} exceeds ΔT_{sa}, the criterion might be exceeded. In this case it is necessary to determine the distance from the location of the thermal discharge to the downstream location of the ΔT_{sa} isotherm. This distance is given by:

$$x_{sa} = \frac{-\rho C_p V d}{K} \ln \left(\frac{T_{sa} - E}{T_{wm} - E} \right) 24 \cdot 3600$$

(IV-71)

where

$$T_{sa} = \Delta T_{sa} + T_r$$
$$T_{wm} = \Delta T_{wm} + T_r$$

Section 4.4.3 discusses procedures for predicting K and E. Once K and E are found, x_{sa} can be determined from Equation IV-71. If one or more tributaries exist with the distance x_{sa}, then x_{sa} should be recalculated as discussed in Section 4.4.4.5.

The surface area included within this reach is:

$$A = x_{sa} \cdot W \qquad (IV-72)$$

where

A = surface area of the river from the point of thermal discharge to x_{sa} (m^2)

W = average river width in this reach (m).

If $A < A_{sa}$ then the surface area criterion is not contravened. Otherwise, it is.

4.4.4.5 Evaluating the Effects of a Tributary in Mitigating Temperature Within a Thermal Plume

Tributaries, when they join a river subjected to the influences of a thermal plume, generally act to reduce the elevated river temperature. They may therefore prevent the surface area constraint from being exceeded when it otherwise would.

Equation IV-71 assumes no tributaries exist throughout the reach defined by x_{sa}. If it is found that $x_{sa} > x_t$ (x_t is defined below under Equation IV-73) then it is necessary to examine the impact of the tributary flow on the surface area constraint. This is done by computing the water temperature (°F) just above the location where the tributary joins the mainstream using the following equation:

$$T_{ra} = \left(T_{wm} - E\right) \exp\left(\frac{-Kx_t}{\rho C_p Vd \cdot 24 \cdot 3600}\right) + E \qquad (IV-73)$$

where

T_{ra} = river temperature just upstream of tributary (°F)

x_t = distance from power plant discharge to tributary (m).

After the river has mixed with the tributary the new river temperature (°F) is given by:

$$\left(T_r\right)_{new} = \frac{T_{ra}Q_r + T_t Q_t}{Q_r + Q_t} \qquad (IV-74)$$

where

$\quad T_t$ = temperature of the tributary (°F)

$\quad Q_t$ = flow rate of tributary (m³/s).

If:

$$\left(T_r\right)_{new} \leq \Delta T_{sa} + T_{ra} \qquad\qquad (IV\text{-}75)$$

then this location marks the downstream location of the ΔT_{sa} isotherm and the surface area A can be calculated using the distance x_{sa} as the distance down to the tributary, x_t. Otherwise the ΔT_{sa} isotherm is located further downstream. In this case Equation IV-71 is reapplied (first making appropriate adjustments to V and d) where the initial temperature is $(T_r)_{new}$ (which was T_{wm} in Equation IV-71) and the final temperature is still T_{sa}. The distance x_{sa} is determined by adding this additional distance to x_t.

4.4.4.6 Determining Whether the Thermal Block or the Surface Area Constraint Is the More Limiting

One of these two constraints may cause a greater limitation on power plant size than the other. If $\Delta T_{tb} < \Delta T_{sa}$ the thermal block constraint will be more limiting, and there is no need to continue with the analysis in this part. If, however, $\Delta T_{tb} > \Delta T_{sa}$, the surface area constraint may be more limiting. To determine if it is, find ΔT_{wm} (call it ΔT_{wmsa}) using the following equation:

$$\Delta T_{wmsa} = E + \left(T_{sa} - E\right) \exp\left(\frac{-Kx_{sa}}{\rho C_p Vd \cdot 24 \cdot 3600}\right) - T_r \qquad (IV\text{-}76)$$

where

$$T_{sa} = \Delta T_{sa} + T_r \qquad\qquad (IV\text{-}77)$$

$$x_{sa} = \frac{A_{sa}}{W} \qquad\qquad (IV\text{-}78)$$

If a tributary exists in the reach delineated by x_{sa}, recompute x_{sa} as outlined in Section 4.4.4.5.

If $\Delta T_{wsma} < \Delta T_{tb}$ the surface area constraint is more restrictive, so set $\Delta T_{wm} = \Delta T_{wmsa}$. Otherwise set $\Delta T_{wm} = \Delta T_{tb}$.

4.4.4.7 Determining the Maximum Plant Capacity

The maximum power plant capacity can be determined based upon the maximum well mixed temperature elevation and the river flow rate. It is given by:

$$(MWe)_{max} = \frac{e_p}{e_c} \cdot \rho C_p \cdot (Q_p \Delta T)_{max} \frac{3600}{3.414 \times 10^6} \qquad (IV\text{-}79)$$

$$= \frac{e_p}{e_c} \cdot \rho C_p \cdot \Delta T_{wm} Q_r \cdot \frac{3600}{3.4.4 \times 10^6} \qquad (IV\text{-}80)$$

By using Equation IV-80 and the maximum allowable ΔT_{wm}, the maximum capacity can be found.

4.4.4.8 Readjusting the Maximum Cooling Water Flow Rate

If the minimum acceptable flow rate is greater than the maximum allowable, the power plant size must be reduced. To do this, set:

$$Q_p = (Q_p)_{max} \qquad (IV\text{-}81)$$

where

Q_p = actual cooling water flow rate (m^3/s)

$(Q_p)_{max}$ = maximum allowable cooling water flow rate (m^3/s).

ΔT_{wm} is recalculated by:

$$\Delta T_{wm} = \Delta T_{maxmin} \frac{(Q_p)_{max}}{Q_r} \qquad (IV\text{-}82)$$

where

ΔT_{maxmin} = ΔT calculated earlier.

(Note: the surface area and thermal block constraints are still met and need not be recomputed.)

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┌─ ·—·—·—·—·—·—·—·—·— EXAMPLE IV-12 —·—·—·—·—·—·—·—·—·—·—·—·—┐
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Estimating ΔT Across a Power Plant Heat Exchange Unit

Suppose the user wants to determine ΔT for the Hartford Electric Light Company's South Meadow Steam Electric Power Plant (a fossil fuel plant) located on the Connecticut River. Data available are (Jones et al., 1975):

Capacity . . . . 217 WM

Cooling water flow rate. . . . . 341 ft³/sec

Waste heat discharged to cooling water . . . 422 MW

Since the waste heat being dissipated through the cooling water is known, ΔT can be calculated directly using that value in conjunction with the known flow rate. Assume, however, that the waste heat being discharged is not known. It can be estimated from the plant capacity as follows. First, assume the plant efficiency is 33 percent. The rate at which fuel is burned when at capacity is then:

$$\frac{217}{.33} = 658 \text{ MW}$$

If 10 percent of the total energy is lost up the stacks, then approximately 58 percent is dissipated through the cooling water, or:

$$658 (.58) = 382 \text{ MW}$$

Compared with the known 422 MW of heat discharged to the cooling water, the above calculation would underestimate ΔT.

ΔT is calculated by:

$$\Delta T = \frac{\text{thermal loading rate to cooling water in megawatts}}{\gamma C_p Q_o} \times$$

$$(3.414)\left(10^6 \frac{BTU}{hr/_{MW}}\right)\left(\frac{1 \ hr}{3600 \ sec.}\right) \qquad (IV\text{-}83)$$

where

$$\gamma C = 62.4 \ BTU/ft^3/°F$$

$$Q_o = \text{flow rate, } ft^3/sec.$$

Substituting the appropriate values into the above equation, it is found that (using the known thermal loading to the cooling water):

$$\Delta T = \frac{(422) \ (3.414) \ (10^6)/3600}{(62.4) \ (341)} = 18.8°F$$

Equation IV-83 is not feasible to use when the thermal loading rate to the cooling water is unknown. As an alternative approach, the following expression can be employed:

$$\Delta T = \frac{1}{Q_o} \cdot \frac{e_c}{e_p} \ MWe \cdot \frac{1}{\rho C_p} \cdot \frac{3.414 \times 10^6}{3600} \qquad (IV\text{-}84)$$

where

e_p = percent of total energy produced that is transmitted as electricity. For new fossil fuel plants: 38 percent; for nuclear plants: 32 percent

e_c = percent of total energy produced that is dissipated through cooling water. For new fossil fuel plants: 48 percent; for nuclear plants: 68 percent

MWe = capacity of power plant in megawatts electric.

Equation IV-84 predicts that ΔT is:

$$\frac{1}{341} \cdot \frac{58}{32} \cdot .217 \frac{1}{62.4} \cdot \frac{3.414 \quad 10^6}{3600} = 17.5°F$$

ΔT is only about 1°F less than predicted by Equation IV-83.

─── END OF EXAMPLE IV-12 ───

4.4.5 Longitudinal Temperature Variation

If the temperature at a particular location in a river is known, the steady-state temperature distribution downstream from that point can be estimated by:

$$\frac{T - E}{T_m - E} = \exp \left(\frac{-.061 \cdot Kx}{\rho C_p Ud} \right) \qquad (IV-85)$$

where

T_m = temperature at x = 0, °F

T = stream temperature at a distance x, where x is measured in miles

E = equilibrium temperature, °F

K = thermal transfer coefficient, $BTU/ft^2/day/°F$

U = stream velocity, ft/sec

d = stream depth, feet

ρ = water density, lb/ft^3

C_p = heat capacity of water, BTU/lb/°F (ρC_p = 62.4 $BTU/ft^3/°F$).

An important fact is revealed upon inspection of Equation IV-85. Suppose that a thermal discharge heats the ambient water to a temperature T_m, but T_m is less than the instantaneous equilibrium temperature E. In that instance the stream temperature will continue to rise exponentially downstream, approaching E. The rate at which T approaches E is dependent on the thermal transfer coefficient, as well as stream velocity and depth. Equation IV-66 is graphically illustrated in Figure IV-31.

─── EXAMPLE IV-13 ───

Use of Figure IV-31

Suppose an average daily thermal transfer coefficient, K, of 200 $BTU/ft^2/day$ has been calculated. The river of interest has an initial temperature "excess" (i.e., $T_m - E > 0$). How far downstream will that excess be 50 percent of the
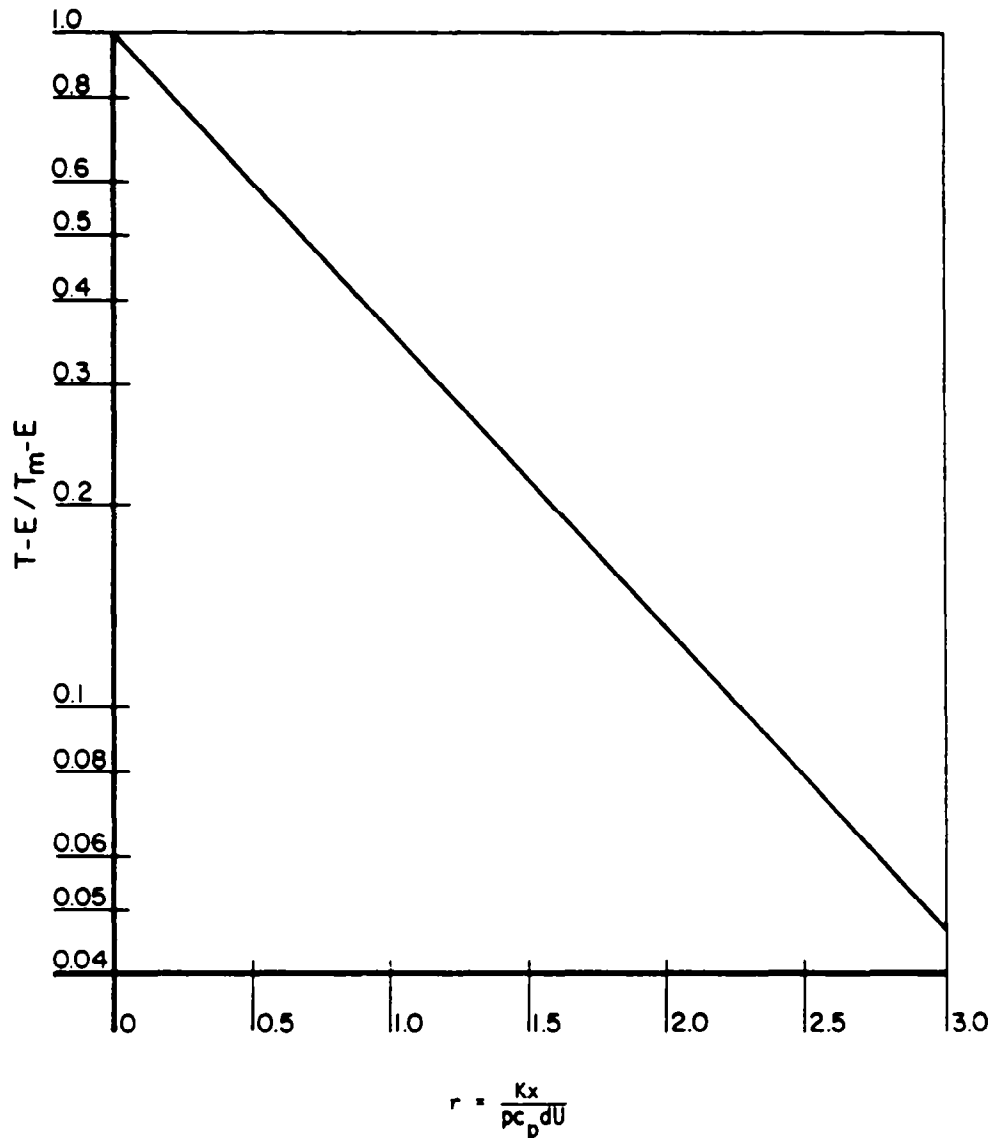
FIGURE IV-31   DOWNSTREAM TEMPERATURE PROFILE FOR COMPLETELY
MIXED STREAM, T-E/T_M-E VS. r (FROM EDINGER,
1965)

original? Other stream data:

    U   = .5 fps
    d   = 4 feet
    ρC_p = 62.4 BTU/ft^3/°F

From Figure IV-31, r is to be found such that:

$$\frac{T - E}{T_m - E} = .5$$

The correct r equals 0.68. Solving for x in terms of r it is found:

$$x = \frac{r c C_p dU}{K} = \frac{(0.68)(62.4)(4)(.5)(24)(3600)}{200}$$

$$= 3.6 \times 10^4 \text{ feet} = 6.9 \text{ miles}$$

The associated travel time is $T = \frac{3.6 \times 10^4}{.5} \times \frac{1}{3600} \text{ hr} = 20.4 \text{ hours}$

—·—·—·—·—·—·—·— END OF EXAMPLE IV-13 —·—·—·—·—·—·—·—·—·—

4.4.6 Diurnal Temperature Variation

Although it is beyond the scope of this report to analyze diurnal stream temper-
ature variations, a few brief statements should be made. Diurnal stream temperature
variations on Long Island, New York, were mentioned in Section 4.4.1. Documentation of
large diurnal temperature variations is not limited to New York. For example, studies
in Oregon (Brown, 1969), Hawaii (Hathaway, 1978) and California have revealed that
solar radiation entering shallow streams and rivers produces a significant difference
between maximum and minimum daily temperatures. Figure IV-32 shows one such example on
the Santa Ana River near Mentone, California. The water temperature varied by 17°F
over a period of 24 hours. One significant effect of the temperature variation is its
effect on dissolved oxygen levels. Figure IV-33 shows the measured dissolved oxygen
concentrations and predicted saturation levels over the same time period at the same
location on the Santa Ana River. The dissolved oxygen concentrations ranged from a
high of 9.2 mg/l to a low of 8.0 mg/l. The variations were caused predominantly by the
temperature changes. This illustrates several points:

- *Temperature data concomitant with dissolved oxygen data might be
  needed to properly interpret the cause of dissolved oxygen variations in
  shallow rivers receiving large amounts of solar radiation*
- *Removing riparian vegetation around shallow rivers tends to increase the
  daily maximum temperature and decrease the daily minimum temperature*
- Impacts on the dissolved oxygen levels and indigenous biota can be
  significant.

4.4.7 Low Flow and Temperature

Evidence has previously been cited in this chapter to show that in many parts of
the country high temperature conditions are concomitant with low flow. The planner
needs to be able to quantify better the nebulous term "low flow" to fruitfully use
this concept as a planning tool. For example, suppose a decision is made based on
the low flow condition of this year. What are the chances that this low flow will be
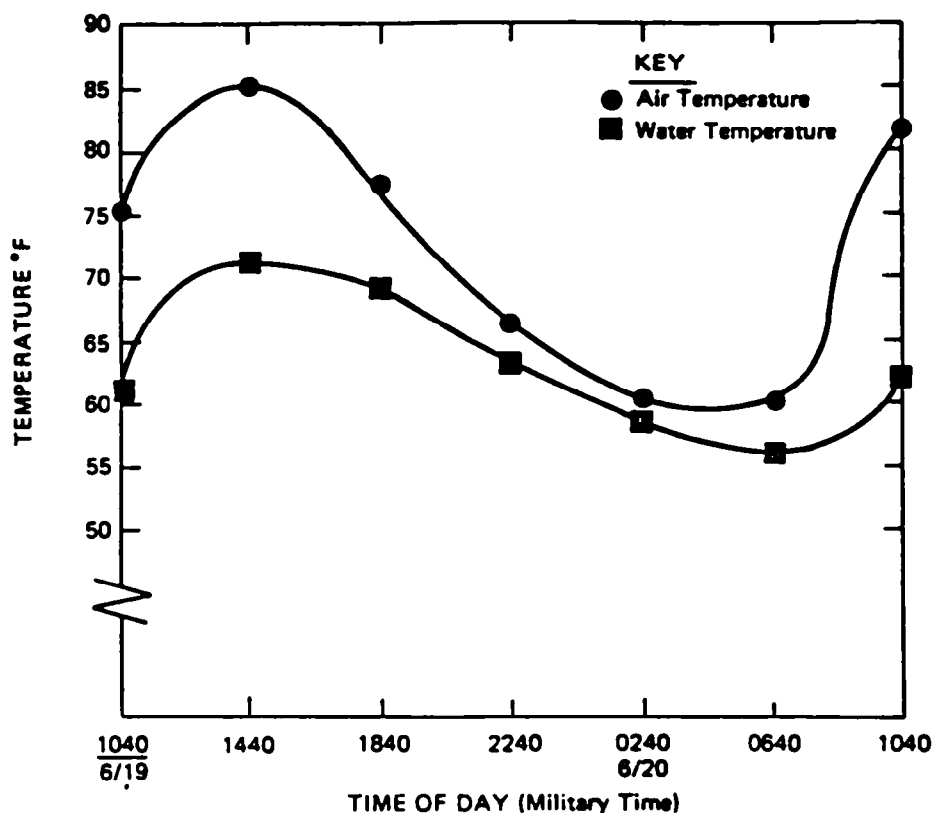
FIGURE IV-32   MEASURED AIR AND WATER TEMPERATURES FOR
THE SANTA ANA RIVER NEAR MENTONE, CALIFORNIA,
IN JUNE 1979.

exceeded in the future? If they are high, then any decision (e.g. at particular
level of waste abatement at a sewage treatment plant) based on the observed conditions
could have unexpected deleterious results at a future time. It is paramount then, to
predict how often flow will fall below a specified rate.

Two measures or indices of low flow that have been found useful are flow
duration and low-flow frequency. Although it is beyond the scope of this report to
explain in detail how to develop these measures, examples of each will be presented
that explain their utility. The majority of the material in this section is from
Cragwall (1966) who provides a discussion on low flow, and cites additional references.
Many texts on engineering hydrology (e.g., Linsley et al., 1958) also discuss low
flow. Figure IV-34 shows a flow duration curve for the Hatchie River at Bolivar,
Tennessee. The vertical axis is the daily discharge and the horizontal is the
percent of time a flow is equaled or exceeded. For example, 95 percent of the time
from 1930-58 the flow exceeded 177 cfs. It can also be assumed that this flow (177
cfs) will probably be exceeded 95 percent of the time in other years. Thus this
concept offers one means by which to quantify "low flow".
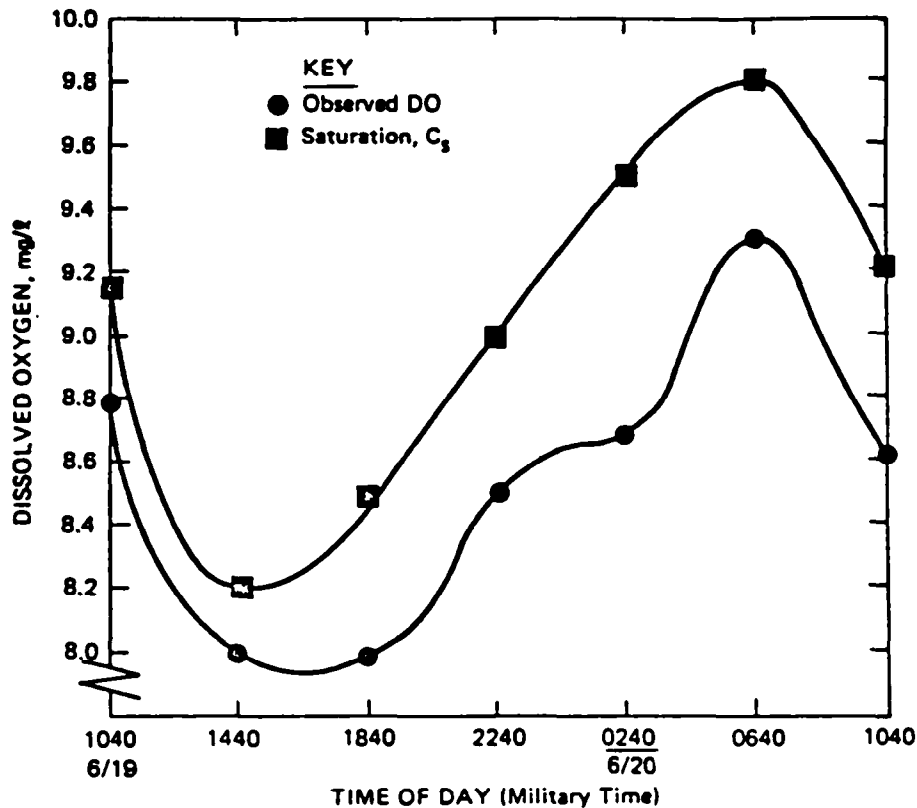
FIGURE IV-33   MEASURED DISSOLVED OXYGEN CONCENTRATION
AND PREDICTED SATURATION CONCENTRATION FOR
THE SANTA ANA RIVER NEAR MENTONE, CALIFORNIA,
IN JUNE 1979.

A second concept is the low flow frequency curve, illustrated in Figure IV-35. This depicts the relationship between discharge and recurrence interval of different duration flows. For example the 7 day mean flow of 100 cfs can be expected to occur once each 19 years. Stated another way, since probability is the reciprocal of recurrence interval, in any one year there is about a 5 percent probability that a seven day mean flow of less than 100 cfs will occur. A commonly used flow for analyses is the 7 day mean flow at a recurrence interval of 10 years, or 7Q10.

4.4.8   Interrelationships Between Temperature Prediction Tools

The three major temperature prediction tools presented in Section 4.4 are:

- Water temperature alterations caused by a power plant
- Equilibrium temperature
- Longitudinal river temperature profile.

10,000

DAILY DISCHARGE (cfs)

1,000

100

1930-58

PERCENT OF TIME INDICATED DISCHARGE
WAS EQUALLED OR EXCEEDED

0.1 0.2 0.5 1 2 5 10 20 30 40 50 60 70 80 90 95 98 99 99.5 99.8 99.9
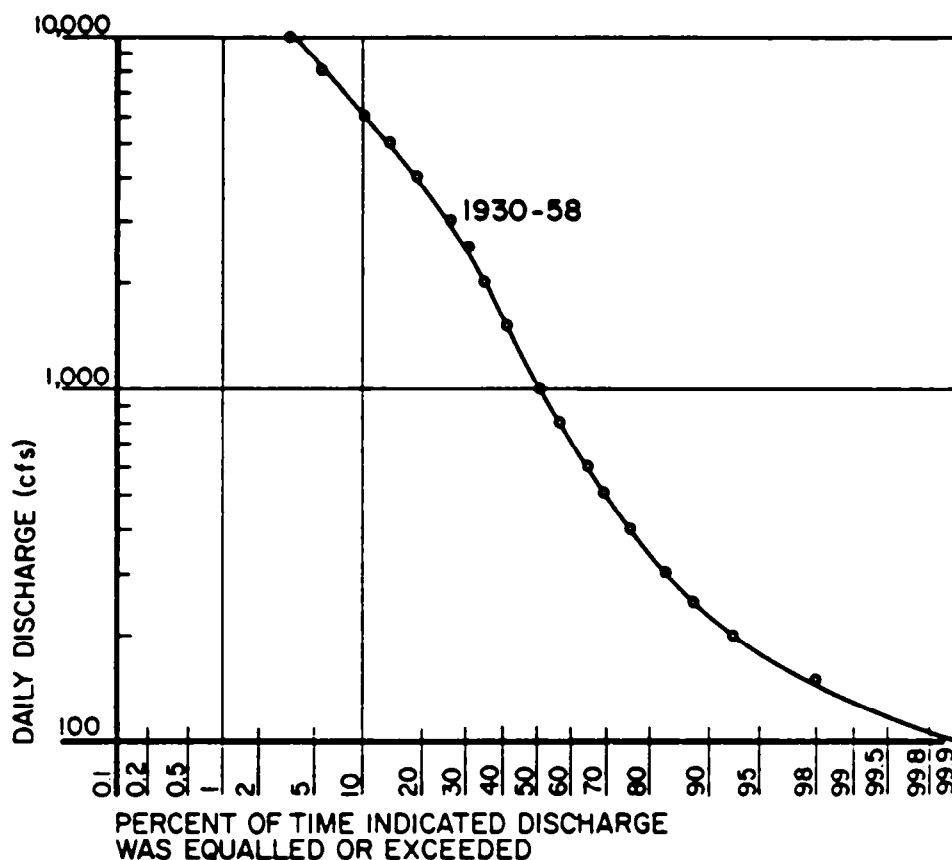
FIGURE IV-34   FLOW DURATION CURVE, HATCHIE RIVER AT
BOLIVAR, TENN. (FROM CRAGWALL, 1966)

Figure IV-36 shows three river temperature profiles which illustrate how these
tools can be used jointly. Curve A represents a temperature profile of a river
where a power plant is located a distance D below some reference point. The tempera-
ture on the river above the power plant is T_2 which is slightly below the equi-
librium temperature. Due to the thermal discharge from the power plant, the river's
temperature is increased to T_4, above the equilibrium temperature. Below the
mixing zone area, the water temperature gradually decreases toward equilibrium, as
the excess heat is dissipated into the atmosphere.

Curve B illustrates the temperature profile of a river whose water comes
predominantly from the hypolimnion of a reservoir. While in the reservoir the
water is insolated from the solar radiation, so the temperature is below the equi-
librium temperature. As the water is withdrawn from the reservoir and begins to flow
downstream, its temperature increases due to solar radiation and atmospheric heating.
The temperature tends to approach the same equilibrium temperature (the two rivers
are assumed to be in the same geographic area).

Curve C shows the temperature profile of river B which now has a power plant,

-386-
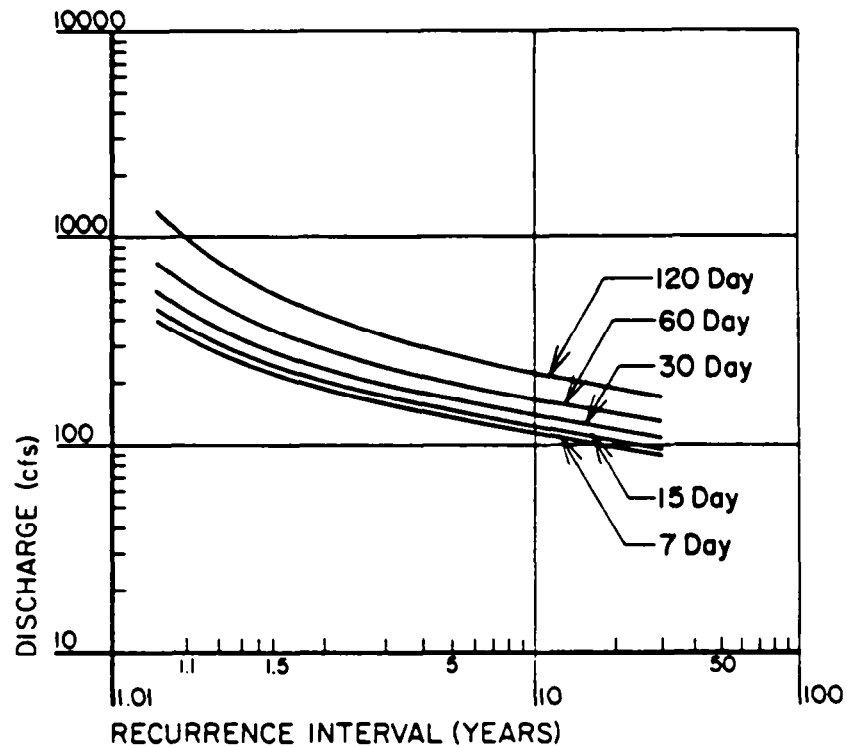
FIGURE IV-35   FREQUENCY OF LOWEST MEAN DISCHARGES OF
                INDICATED DURATION, HATCHIE RIVER AT
                BOLIVAR, TENN. (FROM CRAGWALL, 1966)

similar to the one on river A, discharging into it. If the flow rates of the two
rivers are the same, so is the initial temperature increase (i.e., $T_3 - T_1 =$
$T_4 - T_2$). However, the temperature of the river continues to increase,
in contrast to profile A, because T_3 is less than E. This illustrates an
unusual, but entirely possible, situation where river temperature continues to
increase below a thermal discharge.

4.5   NUTRIENTS AND EUTROPHICATION POTENTIAL

4.5.1   Introduction

Within the past decade the elements most often responsible for accelerat-
ing eutrophication - nitrogen and phosphorus - have shown generally increasing
levels in rivers (EPA, 1974). Median concentrations increased in the period from
1968 to 1972 over the period from 1963 to 1967 in 82 percent of the reaches sampled
for total phosphorus, 74 percent for nitrate, and 56 percent for total phosphate.

These increasing concentrations afford more favorable conditions for eutrophica-
tion, although many rivers with high nutrient levels do not have algal blooms. Algal
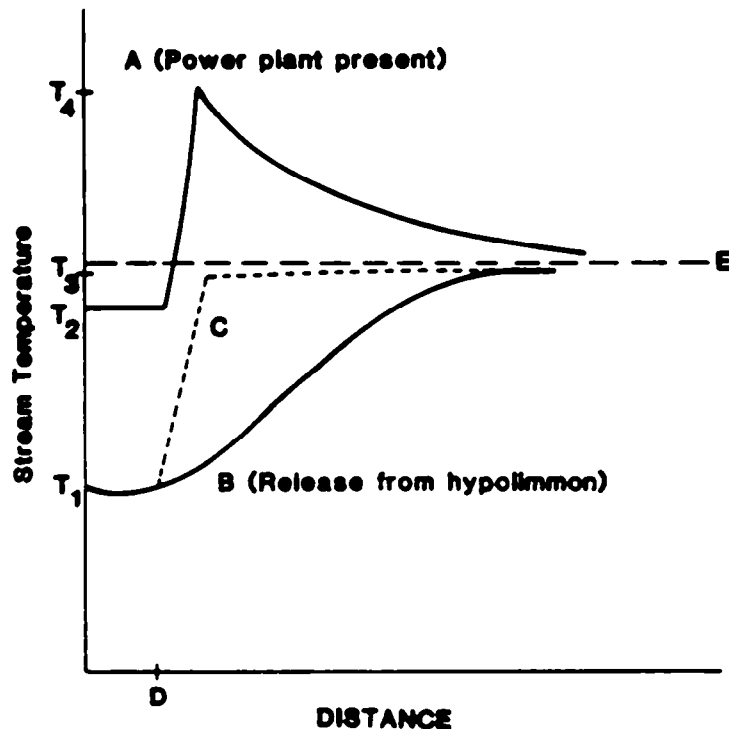
FIGURE IV-36   THREE RIVER TEMPERATURE PROFILES

growth can be inhibited in numerous ways. For example, turbidity can decrease light transmittance through water and effectively stop growth. Decreasing turbidity could, however, have a deleterious side effect of promoting excessive algal growth, unless stream nutrient levels are concurrently decreased. High water velocity can also prevent algae from reaching bloom proportions before they are carried out of the river system. The eutrophication problem, then, is transferred to the water body into which the river empties.

4.5.2 Basic Theory

Stumm and Morgan (1970) have proposed a representation for the stoichiometry of algal growth:

$$106CO_2 + 16NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+ (+ \text{ trace}$$

elements; energy)

P ↑↓ R   (IV-86)

$$\{C_{106}H_{263}O_{110}N_{16}P_1\} + 138 \ O_2$$

algal protoplasm

-388-
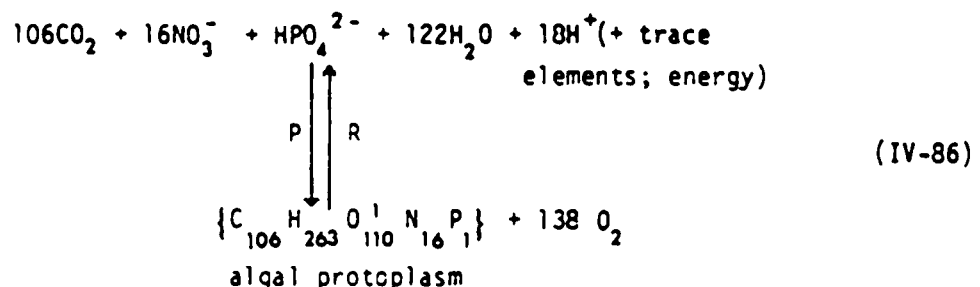
where

       P = photosyntehsis

       R = respiration.

Observe that in the algal protoplasm the ratio of C:N:P is:

$$C:N:P = 106:16:1, \text{ by atomic ratios} \qquad \text{(IV-87)}$$

$$C:N:P = 41:7:1, \text{ by weight ratios} \qquad \text{(IV-88)}$$

From the above two equations it can be inferred that only small amounts of phosphorus are needed to support algal growth in relation to the amounts of carbon and nitrogen required. If phosphorus is not present in the amount required for algal growth then algal production will be curtailed, regardless of how much of the other nutrients is available. Phosphorus is then termed growth limiting. It is possible for other elements, particularly nitrogen, and occasionally carbon or trace metals, to be growth limiting as well (Stumm and Stumm-Zollinger, 1972).

Nitrogen uptake by algae is generally in the nitrate form if nitrate is available. However, different types of fresh water algae can utilize either organic nitrogen or inorganic nitrogen in the form of ammonia, depending on which is available (Stumm and Stumm-Zollinger, 1972). Algae typically require phosphorus in an inorganic form, usually as orthophosphate ion (Kormondy, 1969).

Some indication of whether nitrogen or phosphorus is growth limiting may be made by determining the weight ratio of the appropriate forms of nitrogen and phosphorus found in a river, and comparing that with the stoichiometric ratio required for growth. This gives an idea regarding the nutrient on which control efforts should focus. Specifically, let:

$$R = \frac{[TN]}{[OPO_4-P]} \qquad \text{(IV-89)}$$

where

      $[TN]$ = concentration of total nitogren in river, mg-N/l

      $[OPO_4-P]$ = concentration of orthophosphate, mg-P/l.

If R>10, phosphorus is more likely to limit than N.

If R<5, nitrogen is more likely limiting than P.

If 5<R<10, a determination cannot be made.

Since the N:P ratio in algal biomass can vary from species to species, this makes the determination of the limiting nutrient somewhat uncertain, and leads to the indetermination range of 5<R<10. If local data include an inventory of algal species present, then the N:P ratio of the known species should be used in lieu of Equation IV-88.

Both Lehman, et al. (1975) and Lund (1965) provide specific algal data as well as further discussions.

The following table (Table IV-28) shows an approximate relationship between total nitrogen and total phosphorus concentrations and the potential algal biomass that can result. Both nitrogen and phosphorus must be present in the amounts shown for the resultant growth to occur.

TABLE IV-28

EUTROPHICATION POTENTIAL AS A
FUNCTION OF NUTRIENT CONCENTRATIONS

P (mg-P/l)	N (mg-N/l)	Dry Algal Cells (mg/l)	Significance
0.013	0.092	1.45	Problem threshold
0.13	0.92	14.5	Problem likely to exist
1.3	9.2	145.0	Severe problems possible

4.5.3 Estimating Instream Nutrient Concentrations

Because of the transformations that occur among the different nitogren and phosphorus compounds it is not possible to conveniently track any particular form of nitrogen or phosphorus through a stretch of river. However, if total nitrogen and total phosphorus can be considered conservative, a mass balance approach can be easily formulated for these constituents. In reality this assumption may not be met for a variety of reasons.

For example, algae utilize nutrients, die, and settle to the bottom. Although there is a recycling of algal cell-bound nutrients, the settling rate may surpass the rate of recycling. Assuming total nitrogen and total phosphorus to be conservative should give an estimate of the upper limit of the instream concentrations of these nutrients.

The instream concentration of total nitorgen (TN) or total phosphorus (TP) resulting from a point discharge is (formulas will be presented for TN only; those for TP are exactly analogous):

$$TN_o = \frac{TN_u Q_u + TN_w Q_w}{Q_u + Q_w} \qquad (IV-90a)$$

$$TN_o = \frac{TN_u Q_u + W_p/5.38}{Q_u + Q_w} \qquad (IV-90b)$$

where

TN_u = instream TN upstream of discharge, mg-N/l

TN_w = concentration of TN in point discharge, mg-N/l

Q_u = flow in river upstream of point discharge, cfs

Q_w = flow rate of point discharge, cfs

TN_o = resulting instream TN concentration, mg-N/l

w_p = loading rate of point source, lb/day.

The expression for TN_o is given by either Equation IV-91A or IV-91B. The appropriate form to use will depend on the form of the available data.

To determine the instream concentration of total nitrogen due to a distributed discharge, use:

$$TN = TN_o + \frac{\Delta_Q x}{Q} (TN_r - TN_o) \qquad \text{(IV-91a)}$$

or

$$TN = \frac{TN_o Q_o}{Q} + \frac{wx}{5.38\,Q} \qquad \text{(IV-91b)}$$

where

TN_r = TN entering with the distributed flow, mg-N/l

TN_o = instream TN at x = 0, mg-N/l

x = distance downstream from the point source discharge

Q = stream flow rate at x, cfs

Q_o = stream flow rate at x = 0, cfs

Δ_Q = incremental flow increase per unit distance, cfs/mile

w = mass flux of TN entering the stream through the distributed source, lb/day/mile.

The choice of whether to use Equation IV-91a of IV-91b depends on the available data. Based on the approach detailed in Chapter III, the mass flux of nutrient entering the stream (in units of lb/day/mile) can be generated. When this approach is used, then Equation IV-91b is applicable.

To use Equation IV-91a the concentration of pollutant from the nonpoint source has to be known. This can be accomplished using the approach of Omernik (1977). Nonpoint source nitrogen and phosphorus concentrations are predicted as fractions of land use type or based on color coded maps if land use categories are not known. The data used to predict nitrogen and phosphorus concentrations were generated in a National Eutrophication Survey (NES) program wherein a nationwide network of 928 nonpoint-source watersheds were monitored. This method accounts for only the nonpoint source contribution. Consequently, if point source exist within the watershed, their contributions must be included as well in order to accurately predict instream concentrations.

Table IV-29 summarizes the predictive formulas developed by Omernik for total phosphorus, orthophosphorus, total nitrogen, and inorganic nitrogen. The formulas are regionalized by eastern, central, and western United States. Agricultural, urban, and forested lands comprise the independent variables in the formulas.

Omernik's analysis of the NES data indicates that:

● Streams draining agricultural watersheds had considerably higher nutrient concentrations than those draining forested watersheds.

● Nutrient concentrations were generally directly proportional to the percent of the land in agriculture and inversely proportional to the percent of land in forest.

● Mean concentrations of total phosphorus and total nitrogen were nearly nine times greater in streams draining agricultural lands than in streams draining forested lands.

● Mean phosphorus concentrations in streams draining forested watersheds in the west were generally twice as high as those in the east.

● Total and inorganic nitrogen in streams draining agricultural watersheds were considerably higher in the heart of the corn belt than elsewhere.

As an alternative to the equations shown in Table IV-29, Omernik provides three colored maps of nonpoint source related concentrations of nutrients in streams. They can be used where detailed information necessary for more accurate prediction is unavailable.

4.5.4 Nutrient Accounting System

It may be desirable to determine the impact of each nutrient source on the total instream concentration in order to distinguish among the major sources. An accounting procedure utilizing Equations IV-90 and IV-91 can be developed to do this. The following steps outline the procedure.

1. Segment River. Divide the river into major segments. These segment divisions may reflect waste loading distributions or another convenient division scheme chosen at the discretion of the planner. The segments are not necessarily the same as the reaches that have previously been discussed (see Section 4.1). The delineation of reaches as described earlier is based upon lengths of river having uniform hydraulic conditions. Segments, as used here, are purely a convenient subdivision of the river.

2. Quantify and Locate Sources of Nutrients. The quantification of point, nonpoint, and natural sources on the mainstem and tributaries should be accomplished using the best available data. Tabulation can be performed for each different season to reflect the discharge pattern characteristic of each season. The quantification should include total nitrogen and total phosphorus. Tabulate data in terms of average daily input (lb/day).

TABLE IV-29

REGIONAL STREAM NUTRIENT CONCENTRATION PREDICTIVE MODELS

Nutrient Form Region — Model, Correlation Coefficient and Multiplicative Standard Error

Total phosphorus

East $\quad$ $\log_{10}$ (PCONC) = -1.8364 + 0.00971 (% agric + % urb)

$$r = 0.74, \ f = 1.85$$

Central $\quad$ $\log_{10}$ (PCONC) = -1.5697 + 0.00811 (% agric + % urb) -0.002312 (% for)

$$r = 0.70, \ f = 2.05$$

West $\quad$ $\log_{10}$ (PCONC) = -1.1504 + 0.00460 (%agric + %urb) -0.00632 (% for)

$$r = 0.70, \ f = 1.91$$

Orthophosphorus

East $\quad$ $\log_{10}$ (OPCONC) = -2.2219 + 0.00934 (% agric + % urb)

$$r = 0.73, \ f = 1.86$$

Central $\quad$ $\log_{10}$ (OPCONC) = -2.0815 + 0.00868 (% agric + % urb)

$$r = 0.63, \ f = 2.05$$

West $\quad$ $\log_{10}$ (OPCONC) = -1.5513 + 0.00510 (% agric + % urb) -0.00476 (% for)

$$r = 0.64, \ f = 1.91$$

Total nitrogen

East $\quad$ $\log_{10}$ (NCONC) = -0.08557 + 0.00716 (% agric + % urb) -0.00227 (% for)

$$r = 0.85, \ f = 1.51$$

Central $\quad$ $\log_{10}$ (NCONC) = -0.01609 + 0.00399 (% agric + % urb) -0.00306 (% for)

$$r = 0.77, \ f = 1.50$$

West $\quad$ $\log_{10}$ (NCONC) = -0.03665 + 0.00425 (% agric + % urb) -0.00376 (% for)

$$r = 0.61, \ f = 1.75$$

Inorganic nitrogen

East $\quad$ $\log_{10}$ (INCONC) = -0.3479 + 0.00858 (% agric + % urb) -0.00584 (% for)

$$r = 0.84, \ f = 1.93$$

Central $\quad$ $\log_{10}$ (INCONC) = -0.5219 + 0.00482 (% agric + % urb) -0.00572 (% for)

$$r = 0.71, f = 2.06$$

West $\quad$ $\log_{10}$ (INCONC) = -0.6339 + 0.00789 (% agric + % urb) -0.00657 (% for)

$$r = 0.65, \ f = 2.45$$

From: Omernik (1977)

Characterize the location of the nutrient sources by river mile. For
nonpoint sources characterize by river mile at both the beginning
and end of the source.

3. **Perform Mass-Balance.** Sum the known sources to determine the total
nutrient loading to each segment. Then make the following comparisons:

   a. Compare the total loading with the nutrient input from the mainstem
   at the upstream end of the segment. This direct comparison permits
   an assessment of the collective impact of the nutrient sources
   entering a segment and the upstream contribution of the mainstem.

   b. Perform an intersource comparison to ascertain the relative impact
   of each nutrient source. Express the results for each source as a
   percent of the total loading.

When a tributary has a high percent contribution steps 1 through 3 can be
repeated for the tributary itself to track the sources of the nutrients.

Apply Equations IV-90 and IV-91 to each reach within the segment to determine
the instream nutrient concentration throughout the segment. Once this is done that
step can be repeated for the next reach.

By applying this analysis one can determine the relative impact of any discharge,
determined jointly by the flux of the nutrient and the discharge location. Section
4.1.10 provided a detailed example problem which illustrates the procedure. A brief
example also follows.

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┌─ · — · — · — · — · — · — · — EXAMPLE IV-14 · · — · — · — · — · — · — · — ┐
```

Computing Total Nitrogen Distribution

This example illustrates the use of Equations IV-90b and IV-91b in calculating
the total nitrogen distribution in a river. Suppose the user has been able to
estimate the point and nonpoint loading of total nitrogen in a river as shown in
Table IV-30.
If these loading rates are estimated over a year, then the flow rates used
should also be average annual flows. To compute the concentration at mile
0, Equation IV-90b can be used:

$$TN_o = \frac{(0)(Q_u) + \frac{400}{8.34}}{\frac{300}{1.55}} = 0.25 \text{ mg-N/l}$$

where the following conversions were used:

1 MGD = 1.55 cfs

1 mg/l = 8.34 lb/MG

To determine the concentration at milepoint 9.99, use Equation IV-91b:

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TABLE IV-30

TOTAL NITROGEN DISTRIBUTION IN A RIVER IN
RESPONSE TO POINT AND NON-POINT SOURCE LOADING

Reach Number	River Mile-Point	TN Added* (lbs/day)	TN Cumulative (lbs/day)	Q Cumulative (cfs)	TN Concentration (mg-N/l)
1	0	400 L	400	300	0.25
	9.99	500 D	900	400	0.42
2	10.0	0	900	400	0.42
	14.99	700 D	1,600	600	0.50
3	15.0	800 L	2,400	700	0.64
	20.99	650 D	3,050	900	0.62
4	21.0	0	3,050	900	0.62
	26.0	900 D	3,950	1,000	0.73

* "L" indicates a localized or point source. "D" indicates a diffuse or non-point source whose range of input is over the entire reach.

$$TN = (0.25)\frac{300}{400} + \frac{\frac{500}{8.34}}{\frac{400}{1.55}} = 0.42 \text{ mg-N/l}$$

Note that wx in Equation IV-91 is the 500 lb/day shown in Table IV-30. By reapplying these two basic equations for each reach the user can work downstream through the four reaches. Also note that the total nitrogen concentration has decreased slightly through reach 3, even though more TN has been added. This is because the incoming flow has served to lower the concentration by dilution.

————— END OF EXAMPLE IV-14 —————

4.6 TOTAL COLIFORM BACTERIA

4.6.1 Introduction

Total coliform bacteria are considered an indicator of the presence of pathogenic organisms, and as such relate to the potential for public health problems. Allowable levels of total coliform bacteria in rivers vary from state to state and according to the water use description characterizing the particular river segment. For example, in Montana (Montana State Dept. of Health and Environmental Sciences, 1973) the raw

water supply may not have more than an average of 50 MPN/100 ml* total coliforms if
it is to be used as a potable water supply following simple disinfection. In water
suitable for bathing, swimming and recreation, as well as growth and marginal propa-
gation of salmonid fishes, an average of 1,000 MPN/100 ml is allowable.

Concentrations of total coliforms vary with the season of the year. Often
the heaviest loadings occur during the summer months, but this impact is somewhat
offset due to the more rapid die-off at higher temperatures and more intense solar
radiation. In the Willamette River (Figure IV-37), for example, the highest counts
of 1971-72 were actually observed from November through May (EPA, 1974).

Treated municipal sewage comprises a major source of coliform pollution.
Urban stormwater runoff can also be significant, especially through combined sewer
outflows. Rural storm water runoff transports significant fecal contamination from
livestock pastures, poultry and pig feeding pens, and feedlots. Wildlife both within
refuges and in the wilds can contribute as well. For guidance in the interpretation
of preliminary coliform analyses, Table IV-31 can be used.

4.6.2 Mass Balance for Total Coliforms

The mass balance equations applicable to total coliform organisms are exactly
analogous to Equations IV-18, IV-21, and IV-23A and IV-23B, since first order decay
is used for both. For purposes of hand computations, the following decay coefficient
is acceptable:

$$k_{tc} = 1.0 + 0.02 \ (T-20) \tag{IV-92}$$

where

$\qquad k_{tc}$ = decay coefficient for total coliforms, 1/day
$\qquad T$ = water temperature, °C.

Those equations with the widest applicability are listed below. For a point source
of coliforms:

$$TC = TC_0 \ \exp \left[\frac{-j_{tc}}{A_0} \ \left(A_0 \ x + \Delta_A \ \frac{x^2}{2} \right) \right] \tag{IV-93}$$

---

*MPN means "Most Probable Number". Coliform organisms are not counted individually,
but their densities are statistically determined and the results stated as MPN/100
ml.

SEASONAL RIVER PROFILES
WILLAMETTE RIVER
Total Coliforms
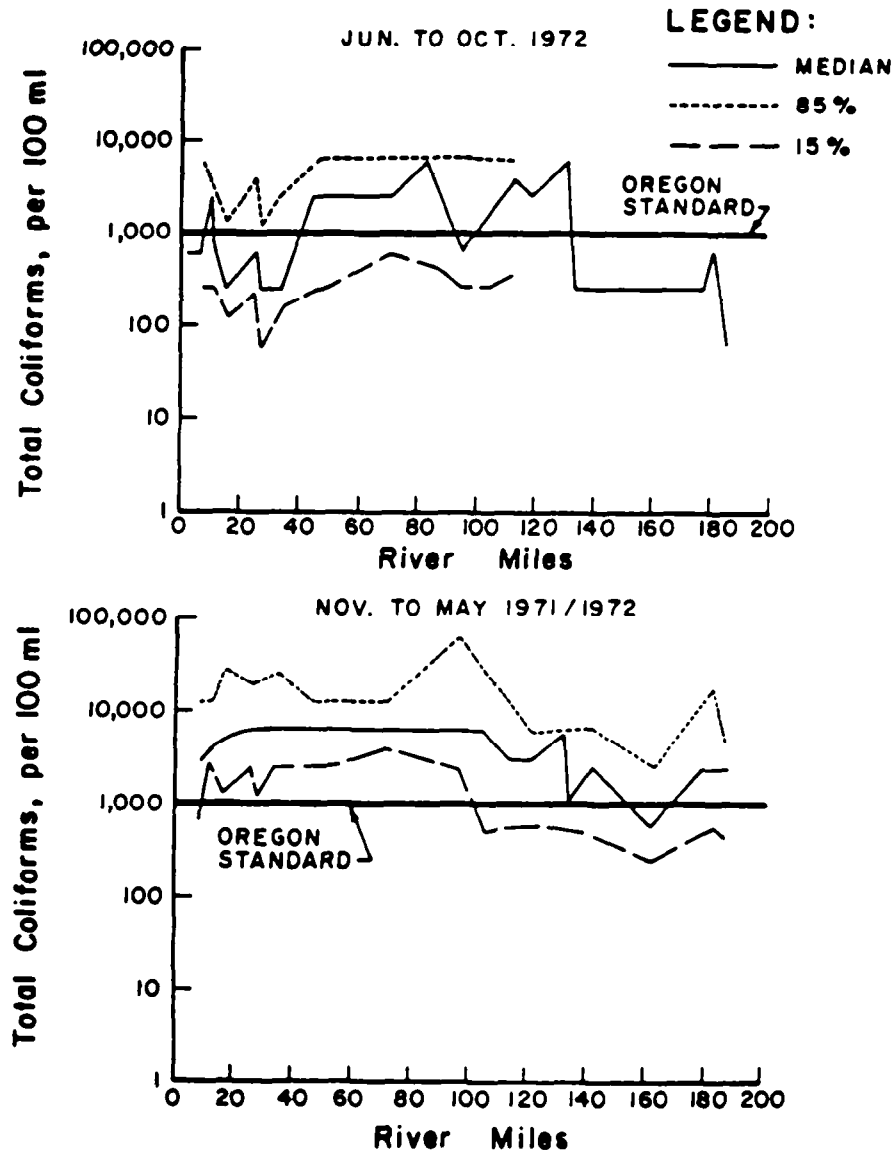
FIGURE IV-37 TOTAL COLIFORM PROFILES FOR THE WILLAMETTE RIVER (EPA, 1974)

TABLE IV-31

TOTAL COLIFORM ANALYSIS (EPA, 1976)

If the Calculated Concentration is:	Probability of a Coliform Problem
Less than 100/100 ml	Improbable
Less than 1,000/100 ml	Possible
More than 1,000/100 ml	Probable
More than 10,000/100 ml	Highly Probable

For both point and distributed sources of coliforms:

$$TC = \frac{TC_r}{E_{tc}} + \left(TC_0 - \frac{TC_r}{E_{tc}}\right)\left(\frac{Q_0}{Q}\right)^{E_{tc}} \qquad (IV-94)$$

For a change in coliform concentration due to a point source modification:

$$\Delta TC = \begin{cases} \Delta TC_0 \; \exp\left[\frac{-j_{tc}}{A_0}\left(A_0 x + \Delta_A \frac{x^2}{2}\right)\right] & (IV-95a) \\[2em] \Delta TC_0 \left(\frac{Q_0}{Q}\right)^{E_{tc}} & (IV-95b) \end{cases}$$

where

TC	=	total coliform concentration, MPN/100 ml
TC_0	=	initial total coliform concentration, MPN/100 ml
j_{tc}	=	$\frac{k_{tc}}{U_0}$
TC_r	=	total coliform level in distributed flow, MPN/100 ml
E_{tc}	=	$\frac{k_{tc}A_0 + \Delta_Q}{\Delta_Q}$

Because of the potential variability in coliform loadings, seasonal analyses may be warranted. Typically the summer months are of primary concern because loadings often increase during this time period and water contact recreation is at its maximum. Major storm events may also be of interest, because of the large coliform loading that may be associated with them.

─ · ─ · ─ · ─ · ─ · ─ · ─ EXAMPLE IV-15 ─ · ─ · ─ · ─ · ─ · ─ · ─

Estimating the Change in Total Coliform Levels
in Response to a Waste Loading Change

Compare the change in total coliform levels, ΔTC, produced by a change ΔTC_0 at a given location in a river. Further, determine how this change is affected by a distributed flow entering the river. Relevant data for the river are as follows:

$$U_0 = 1 \text{ fps}$$
$$T = 20°C$$
$$Q_0 = 500 \text{ cfs}$$
$$Q_f = 800 \text{ cfs}$$

$$x_L = 10 \text{ miles}$$
$$k_{tc} = 1.0/\text{day at } 20°C$$

First the computations will be performed assuming no distributed flow. Equation IV-95A is then applicable. Computing the expondent $j_{tc}x$ (at a flow distance of 10 miles):

$$j_{tc}x = \frac{(1.0)\ (10)\ (5280)}{(24)\ (3600)\ (1)} = 0.611$$

so

$$\frac{\Delta TC}{\Delta TC_0} = \exp(-.611) = 0.54$$

or

$$\Delta TC = 0.54\ \Delta TC_0$$

For example if $\Delta TC_0 = -1,000$ MPN/100 ml then $\Delta TC = -540$ MPN/100 ml (negative ΔTC_0 indicates that the coliform level has decreased from what it previously was).

Now suppose the distributed flow of 300 cfs is included in the computation. Then:

$$E_{tc} = \frac{k_{tc}A_0 + \Delta_Q}{\Delta_Q}$$

$$A_0 = Q_0/U_0 = 500/1 = 500 \text{ ft}^2$$

$$\Delta_Q = \frac{300}{10(5280)} = 0.0057 \text{ ft}^2/\text{sec}$$

$$E_{tc} = \frac{(1.0)\ (500)}{(24)\ (3600)\ (0.0057)}$$
$$= 2.02$$

Then

$$\frac{\Delta TC}{\Delta TC_0} = \left(\frac{500}{800}\right)^{2.02} = 0.39$$

or

$$\Delta TC = 0.39\ \Delta TC_0$$

For $\Delta TC_0 = 1,000$ MPN/100 nml, $\Delta TC = -390$ MPN/100 ml.
Note that this decrease is 150 MPN/100 ml less than if no distributed flow existed.

To determine the absolute total coliform level, simply add to the original level the resulting change caused by the waste loading modification.

— · — · — · — · — · — · — · END OF EXAMPLE IV-15 — · — · — · — · — · — · — · —

4.7 CONSERVATIVE CONSTITUENTS

4.7.1 Introduction

Conservative constituents are those which are not reactive and remain either in solution or in suspension. They are advected through the water column at the velocity of the river with no loss of mass. The analysis of nutrients, already discussed in this report, was performed assuming they acted conservatively. Other substances, such as salinity, can also be considered as conservative. Chapter 3 contains information on salinity in irrigation return flow for many rivers with salinity problems.

4.7.2 Mass Balance for Conservative Constituents

Two simple mass balance equations are sufficient for analyzing conservative constituents. The first relates the instream concentration due to a point source loading:

$$S = \frac{S_u Q_u + W/5.38}{Q_u + Q_w} \qquad (IV-96)$$

where

S = resulting pollutant concentration, mg/l

S_u = upstream concentration, mg/l

Q_u = upstream flow rate, cfs

Q_w = point source flow rate, cfs

W = loading rate of pollutants, lb/day.

When a distributed flow is present along some length of the river, then the distribution of the conservative pollutant is given by:

$$S = \frac{S_o Q_o}{Q} + \frac{wx}{5.38\ Q} \qquad (IV-97)$$

where

w = distributed loading rate, lb/day/mi

x = distance downstream, miles

S_o = initial concentration (at $x = 0$), mg/l.

S_o in Equation IV-97 is identical with S in Equation IV-96.

EXAMPLE IV-16

Calculating Salinity Distribution in a River

Salinity problems are receiving increased attention in the western United States, particularly relating to the economic issues in the Colorado River Basin and international compacts with Mexico. In the Colorado River high salinity levels in the lower reaches adversely affect nearly twelve million people and approximately one million acres of fertile irrigated farmland (Bessler and Maletic, 1975). The salinity now averages approximately 865 mg/l at Imperial Dam and is projected to be 1,160 mg/l or more by the year 2000, unless firm control actions are taken.

Consider the river shown in Figure IV-38. Predict the salinity distribution based on the inflows and withdrawals shown. Assume the data are averaged over a period of a year. These data, along with the salinity concentrations at different river mileposts are shown in Table IV-32.

To calculate S (salinity at milepoint 100) use Equation IV-96:

$$S = \frac{0.500 + (2 \times 10^6)(1.55/8.34)}{2000}$$

$$= 186 \text{ mg/l}$$

At milepost 199.9, Equation IV-97 is appropriate and S is given by:

$$S = \frac{(186)(2000)}{5000} + \frac{(4 \times 10^6)(1.55/8.34)}{5000}$$

$$= 223 \text{ mg/l}$$
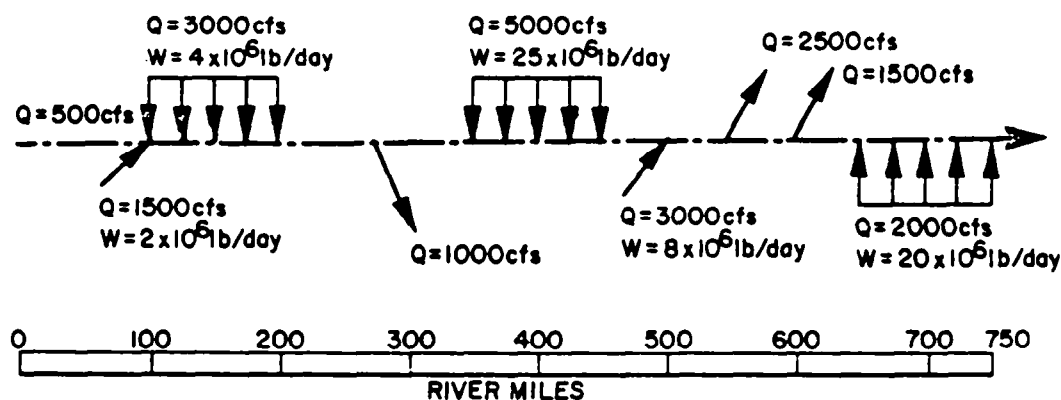
FIGURE IV-38   SALINITY DISTRIBUTION IN A HYPOTHETICAL RIVER

TABLE IV-32

SALINITY DISTRIBUTION IN A HYPOTHETICAL RIVER

Reach Number	River Mile Point	Salinity Added* (lbs/day)		Salinity Cumulative (lbs/day)	Q Cumulative (cfs)	Salinity Concentration (mg/l)
1	0	0		0	500	0
	99.9	0		0	500	0
2	100	2×10^6	L	2×10^6	2000	186
	199.9	4×10^6	D	6×10^6	5000	223
3	200	0		6×10^6	5000	223
	279.9	0		6×10^6	5000	223
4	280	-1.2×10^6	L	4.8×10^6	4000	223
	359.9	0		4.8×10^6	4000	223
5	360	0		4.8×10^6	4000	223
	449.9	25×10^6	D	29.8×10^6	9000	615
6	450	0		29.8×10^6	9000	615
	499.9	0		29.8×10^6	9000	615
7	500	$8 \ 10^6$	L	37.8×10^6	12000	585
	524.9	0		37.8×10^6	12000	585
8	525	-7.9×10^6	L	29.9×10^6	9500	585
	599.9	0		29.9×10^6	9500	585
9	600	-4.7×10^6	L	25.2×10^6	8000	585
	649.9	0		25.2×10^6	8000	585
10	650	0		25.2×10^6	8000	585
	750	20×10^6	D	45.2×10^6	10000	840

*'L' indicates a localized or point source at the milepoint shown in the same row.

'D' indicates a diffuse or non-point source ending at the milepoint shown in the same row and beginning at the milepoint in the above row.

At milepoint 280, 1,000 cfs of flow leaves the mainstem (perhaps for irrigation purposes). The concentration of salinity in this flow is the same as that in the mainstem. So the mass rate of withdrawal is:

$$W = \frac{-8.34}{1.55} (223 \times 1000)$$

$$= -1.2 \times 10^6 \ \text{lb/day}$$

A negative sign is used to signify a withdrawal. Completing the remainder of the table is solely a matter of reapplying these basic concepts.

———————— END OF EXAMPLE IV-16 ————————————

4.8 SEDIMENTATION

4.8.1 Introduction

One of the more difficult classes of hydraulic engineering problems associated with rivers involves the erosion, transportation, and deposition of sediment. Sedi-

mentation is important economically, particularly relating to filling of reservoirs and harbors, and to maintaining channel navigability and stability. Table IV-2, located in Section 4.1, documents some suspended solids problems encountered in eight major U.S. waterways.

The sediment load carried in a river can be divided into two components: the bed material load and the wash load. The bed material load is composed of those solid particles represented in the bed. The transport of this material is accomplished both along the bed (bed load) and suspended within the water (suspended load). Although there is no sharp demarcation delineating bed load from suspended load, many researchers have developed individual expressions for each transport component. The total bed material load is the sum of the bed load and the suspended load. Other researchers have developed a unified theory from which the total bed material load can be predicted from a single expression.

The wash load is usually produced through land erosion, rather than channel scour. Wash load is composed of grain sizes finer than found in the bed material. It readily remains in suspension and is washed out of the river without being deposited. A definite relationship between the hydraulic properties of a river and the wash load capacity apparently does not exist, making it difficult to advance an analytical method for washload prediction (Graf, 1971). Not all the erodible material entering a stream is transported as wash load, but a large portion may become part of the bed material and be transported as bed material load.

Figure IV-39 provides a graphical illustration of the difference between wash load and bed material load. For a particular flow condition in a particular river, the river has the capacity to transport a certain quantity of sediment (q_s) which generally decreases as particle size increases. At some large particle size the river cannot exert enough force to transport particles of that size or larger. This situation would occur at some point to the right of point D on curve COD. This same river might be supplied with sediment at a rate AOB, which is unrelated to transport capacity.

To the left of point O the river is transporting all the material of that size range being supplied to it. Sediment having diameters less than d* are classified as wash load, because the amount being transported is supply limited, and not transport limited. To the right of point O, supply exceeds transport capacity. The amount given by the curve OD is transported, and the difference in OB and OD is deposited in the stream bed. The methods to be presented in the following sections are generally concerned with predicting curve OD (i.e. the bed material load), although Section 4.8.2 does provide a brief description of how to estimate long-term sediment supply rates.

As a guide in evaluating whether a river is carrying a significant quantity of suspended sediment, Table IV-33 can be consulted. 100 mg/l is the delinea-
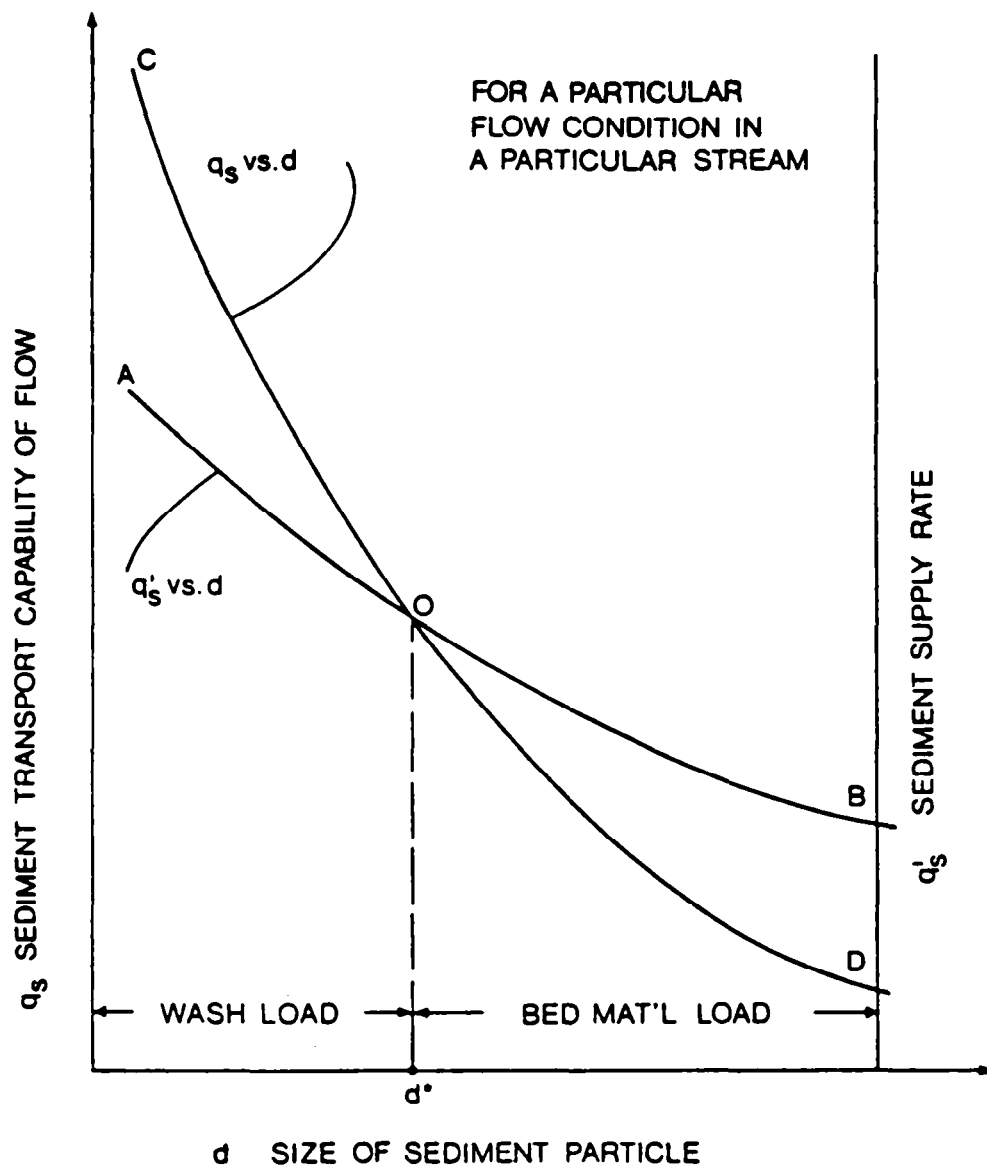
FIGURE IV-39 DIVISION BETWEEN WASH LOAD AND BED MATERIAL
              LOAD (FROM: COLORADO STATE UNIVERSITY, 1979)

TABLE IV-33

RELATIONSHIP OF TOTAL SUSPENDED SEDIMENT CONCENTRATION
TO PROBLEM POTENTIAL (AFTER EPA, 1976)

If Calculated Concentration is:	Probability of a Problem
Less than 10 mg/l	Improbable
Less than 100 mg/l	Potential
More than 100 mg/l	Probable

tion between a potential and probable problem. In a table previously introduced (Table IV-1), a reference level of 80 mg/l was set for protection of aquatic life.

4.8.2 Long-Term Sediment Loading from Runoff

The procedures outlined in Chapter 3 will permit an assessment of the sediment loading to a river on a long-term basis. When using those procedures care should be taken to incorporate the entire drainage area of the watershed. As an estimate, the loading can be assumed conservative (i.e. all sediment that comes into the river will be washed out of the river over an extended time period). Under that assumption the procedure outlined in Section 4.7 can be utilized for an estimate of average yearly suspended solids concentrations at locations throughout the river system. This result should be interpreted as an indicator of the impact of the runoff on sediment loads within a river and not as actual suspended solids concentrations. Not all of the incoming sediment will be transported as suspended load since a large fraction can be transported as bed load. The transport process is generally of an intermittent nature with higher concentrations occurring during periods of high flow.

Care should be taken not to apply the conservative assumption at points on a river where that assumption is clearly violated, such as at reservoirs which can be efficient sediment traps. An example for the computation of sediment loading to rivers has been considered in Chapter 3.

4.8.3 Bed Material Load

As previously mentioned, the estimation of bed material transport poses a difficult problem, and is an area where there is no consensus regarding the best predictive relationship to use. Numerous bed material load relationships (Task Committee on Preparation of Sedimentation Manual, 1971) have been developed over the past century, some requiring considerably more input data than others. In this report the DuBoys relationship (Task Committee on Preparation of Sedimentation Manual, 1971) will be used in part because of its simplicity. The relationship, which is restricted to uniform flow in alluvial channels, is:

$$g_b = \psi_o (\tau_o - \tau_c)$$ (IV-98)

where

g_b = bed load, lb/sec/ft of width of river
ψ = coefficient depending on grain size, $ft^3/lb/sec$
τ_0 = $\gamma R_H S$, bed shear stress, lb/ft^2
γ = specific weight or water, lb/ft^3
R_H = river hydraulic radius, ft

S = slope of stream, ft/ft

τ_c = critical shear stress, lb/ft^2.

The values of ψ and τ_c can be expressed as functions of the median size (by weight) of the bed sediment (d_{50}). These relationships are expressed graphically in Figure IV-40. To aid in determining d_{50} Table IV-34 is presented to show the size range of sediment and each associated class name. If the class name of the predominant sediment type comprising a stream bed is known, then the sediment size (in mm) can be estimated.
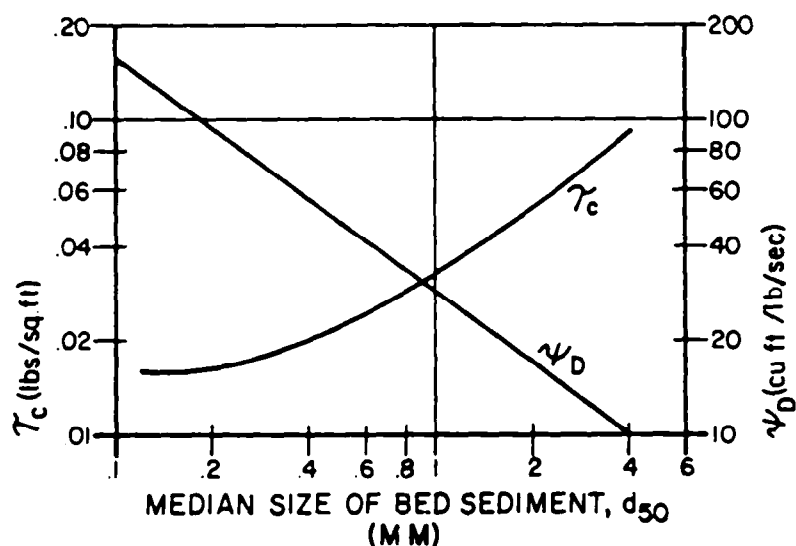
FIGURE IV-40 ψ AND τ_c FOR DuBoys RELATIONSHIP AS FUNCTIONS OF MEDIAN SIZE OF BED SEDIMENT (TASK COMMITTEE ON PREPARATION OF SEDIMENTATION MANUAL, 1971)

Once d_{50} is estimated, then ψ and τ_c can easily be evaluated, leaving only τ_o to compute. A summary of hydraulic radii (the ratio of cross-sectional area to wetted perimeter) for different channel geometries is shown in Figure IV-41. For very wide, shallow channels, the hydraulic radius approximately equals the depth of flow. Many river cross-sections can be approximated by a parabolic section. To calculate "c" in the relationship for hydraulic radius of a parabolic section, refer to Table IV-35.

If the bed slope is unknown it can be estimated by using a topographic map and finding contour lines approximately five hundred feet above and below the point on the river where the measurement is to be made. Dividing this elevation difference by the horizontal distance over which the difference is measured, produces the slope.

TABLE IV-34

SEDIMENT GRADE SCALE (TASK COMMITTEE ON PREPARATION OF SEDIMENTATION MANUAL, 1971)

Class Name	Size Range			Approximate Sieve Mesh Openings Per Inch	
	Millimeters	Microns	Inches	Tyler	United States Standard
Very large boulder	4096-2048		160-80		
Large boulders	2048-1024		80-40		
Medium boulders	1024-512		40-20		
Small boulders	512-256		20-10		
Large cobbles	246-128		10-5		
Small cobbles	128-64		5-2.5		
Very coarse gravel	64-32		2.5 -1.3		
Coarse gravel	32-16		1.3 -0.6		
Medium gravel	16-8		0.6 -0.3	2-1/2	
Fine gravel	8-4		0.3 -0.16	5	5
Very fine gravel	4-2		0.16-0.08	9	10
Very coarse sand	2-1	2.000-1.000	2000-1000	16	18
Coarse sand	1-1/2	1.000-0.500	1000-500	32	35
Medium sand	1/2-1/4	0.500-0.250	500-250	60	60
Find sand	1/4-1/8	0.250-0.125	250-125	115	120
Very fine sand	1/8-1/16	0.125-0.062	125-62	250	230
Coarse silt	1/16-1/32	0.062-0.031	62-31		
Medium silt	1/32-1/64	0.031-0.016	31-16		
Fine silt	1/64-1/128	0.016-0.008	16-8		
Very fine silt	1/128-1/256	0.008-0.004	8-4		
Coarse clay	1/256-1/512	0.004-0.0020	4-2		
Medium clay	1/512-1/024	0.0020-0.0010	2-1		
Fine clay	1/1024-1/2048	0.0010-0.0005	1-0.5		
Very fine clay	1/2048-1/4096	0.0005-0.00024	0.5-0.24		

TABLE IV-35

COMPUTING D/T FOR DETERMINING THE HYDRAULIC RADIUS OF A PARABOLIC SECTION (FROM KING, 1954)

$\frac{D}{T}$*	.00	.01	.02	.03	.04	.05	.06	.07	.08	.09
.0	.667	.667	.666	.665	.664	.662	.660	.658	.656	.653
.1	.650	.646	.643	.639	.635	.631	.626	.622	.617	.612
.2	.607	.602	.597	.592	.586	.581	.575	.570	.564	.559
.3	.554	.548	.543	.537	.532	.526	.521	.516	.510	.505
.4	.500	.495	.490	.485	.480	.475	.470	.465	.460	.455
.5	.451	.446	.442	.437	.433	.428	.424	.420	.416	.412
.6	.408	.404	.400	.396	.392	.388	.385	.381	.377	.374
.7	.370	.367	.364	.360	.357	.354	.351	.348	.344	.341
.8	.338	.335	.333	.330	.327	.324	.321	.319	.316	.313
.9	.311	.308	.306	.303	.301	.298	.296	.294	.291	.289

*$\frac{D}{T} = c$

Adequate methods that are within the scope of this report and which would provide a straightforward estimation of suspended sediment discharge presently do not exist. Most relationships require a known reference level concentration at some depth within the river to predict the concentration at another depth (Morris and Wiggert, 1972). To determine the suspended sediment load, then, a summation of contributions at each depth must be made. Since these formulas apply to one grain size this procedure should be repeated for all grain sizes present. Einstein (Graf, 1971) has developed a method for computing suspended sediment discharge that does not require knowledge of a reference concentration, but it is an advanced approach. For this report the contribution of the suspended load will be estimated from the bed material load by the relationship given in Table IV-36. The relationship in Table IV-36 is valid for graded channels (by graded is meant that the slope is stable over time, being neither steepened nor flattened by flow or other influence). Once the width to depth ratio for the stream in question is determined, the suspended load can then be approximated after first computing the bed material load, and then using Table IV-36.

Once the suspended load discharge is estimated the average concentrations at a section can be computed by:

$$C_{ss} = \frac{G_{ss}}{Q} 1.6 \times 10^4 \qquad \text{(IV-99a)}$$
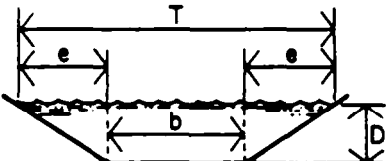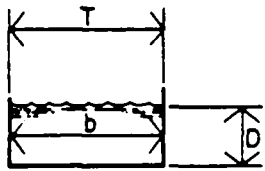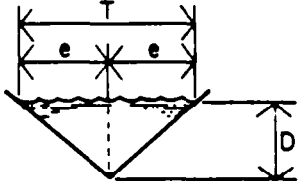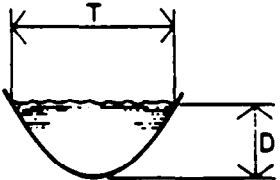
CHANNEL SLOPE	HYDRAULIC RADIUS
Trapezoidal	$\dfrac{(1 + zx)\ D}{1 + 2\ x\ \sqrt{1 + x^2}}$, $x = D/b$, $z = e/D$
Rectangular	$\dfrac{bD}{b + 2D}$
Triangular	$\dfrac{zD}{2\sqrt{1 + z^2}}$ $z = e/D$
Parabolic	cD (for c, see Table IV-35)

FIGURE IV-41   HYDRAULIC RADII FOR DIFFERENT CHANNEL SHAPES (FROM KING, 1954)

TABLE IV-36

RELATIONSHIP BETWEEN WIDTH TO DEPTH RATIO OF A GRADED STREAM AND
THE SUSPENDED AND BED LOAD DISCHARGE (AFTER FENWICK, 1969)

Suspended Load % of Total Bed Material Load	Bed Load % of Total Bed Material Load	Width-Depth Ratio
85-100	0-15	7
65-85	15-35	7-25
30-65	35-70	25

or

$$C_{ss} = \frac{g_{ss}}{q} \, 1.6 \times 10^4 \qquad \text{(IV-99b)}$$

where

C_{ss} = average suspended solids concentration, mg/l

G_{ss} = suspended solids discharge, lb/sec

Q = flow rate, cfs

g_{ss} = suspended solids discharge per unit width, lb/sec/ft

q = flow rate per unit width, cfs/ft.

The procedures discussed in this section can be summarized as follows:

1. Determine the bed load discharge g_b (lb/sec/ft) using Equation IV-98. The required input data are channel slope, hydraulic radius (see Figure IV-41), and the median sediment size, d_{50}. Once d_{50} has been estimated the unknown parameters τ_c and ψ can be found from Figure IV-40.

2. Multiply g_b by the river width to find the total bed load discharge.

3. Determine the width/depth ratio.

4. Use Table IV-36 to determine the suspended load.

5. To determine the suspended sediment concentration use Equation IV-99.

6. Compare the suspended sediment concentration against the data in Table IV-33 to find out if a problem potentially exists.

7. The total bed material load is sum of the total bed load (step 2) and the total suspended load (step 4).

The user may be primarily concerned with the total bed material load rather than either bed load or suspended load individually. Total bed material load can be directly calculated using a number of predictive formulas. The method of Yang (1976) based on unit stream power is presented here. Yang's method has been verified for the following parameter ranges:

Median bed size: from 0.16 mm to 1.0 mm

Channel depth: from 0.2 ft to 49.9 ft

Water temperature: from 0°C to 29.4°C

Stream velocity: from 1.23 fps to 7.82 fps

Flow rate: from 2.7 cfs to 470,000 cfs

Slope: from 0.0000428 to 0.00188

Total sediment concentration (excluding wash load): from 2.8 ppm to 2,440 ppm.

The input data are the same as for the DuBoy's method, with the addition of water temperature. The predictive formula, however, is considerably more complicated,

so the method has been programmed on a hand held calculator and the program is included. The predictive expression is:

$$\log C_t = 5.435 - 0.286 \log \frac{wD}{\nu} - 0.457 \log \frac{U_*}{w}$$

$$+ (1.799 - 0.409 \log \frac{wD}{\nu} - 0.314 \log \frac{U_*}{w}) \log (\frac{US}{w} - \frac{U_{cr}S}{w}) \quad (IV-100)$$

where

C_t = total sediment concentration in parts per million by weight

D = median sieve diameter

S = water surface slope or energy slope

U_* = shear velocity

U = average water velocity

U_{cr} = critical average water velocity at incipient motion

ν = kinematic viscosity

w = terminal fall velocity.

The term $\frac{U_{cr}}{w}$ can be calculated as:

$$\frac{U_{cr}}{w} = \frac{2.5}{\log(\frac{U_* D}{\nu}) - 0.06} + 0.66 \text{ when } 1.2 < \frac{U_* D}{\nu} < 70 \quad (IV-101)$$

and

$$\frac{U_{cr}}{w} = 2.05 \text{ when } 70 \leq \frac{U_* D}{\nu} \quad (IV-102)$$

Figure IV-42 shows the required user instructions to execute the program on a TI-59. Figure IV-43 contains the program listing and a sample input/output. This program was written by Colorado State University (1979).

EXAMPLE IV-17

Estimation of Bed Material Load

Table IV-37 shows characteristics of the Colorado River at Taylor's Ferry, California, and of the Niobrara River near Cody, Nebraska. Suppose one desires to calculate the bed load for the Colorado River at this location for flow ranges of 8-35 cfs/ft. The following data will be used:

d_{50} = 0.33 mm

γ = 62.4 lb/ft^3, at 60°F

S = 0.000217 ft/ft

PROGRAM DESCRIPTION

Program: Yang's Sediment Transport Equation

USER INSTRUCTIONS

STEP!	PROCEDURE	ENTER	PRESS		DISPLAY
1	Enter kinematic viscosity, $v\left(\frac{ft^2}{sec}\right)$	v	A		v
2	Enter slope S_o (ft/ft)	S_o	B		S_o
3	Enter median sediment diameter, d_s (ft)	d_s	C		d_s
4	Enter flow velocity, U ($\frac{ft}{sec}$)	U	D		U
5	Enter flow depth, Y (ft)	Y	E		Y
6	Compute sediment concentration (ppm)		2nd	A´	C_t
7	To input new data, repeat steps 1 through 6.				

FIGURE IV-42   USER INSTRUCTIONS FOR YANG'S SEDIMENT TRANSPORT EQUATION.

Using Figure IV-40 one finds:

ψ = 64

τ_c = 0.019

All that remains is the computation of the hydraulic radius. Since the width is much greater than the depth, assume R_H = D:

$$R_H = \begin{cases} 4 \text{ ft at } q = 8 \text{ cfs/ft} \\ 12 \text{ ft at } q = 35 \text{ cfs/ft.} \end{cases}$$

Using Equation IV-98 it is found that the bed 'load is:

$$g_b = \begin{cases} 0.12 \text{ lb/sec/ft at } q = 8\text{cfs/ft} \\ 1.5 \text{ lb/sec/ft at } q = 35 \text{ cfs/ft.} \end{cases}$$

The actual bed material load observed at Taylor's Ferry has been compared with the DuBoys prediction for a range of flow rates (Task Committee on Preparation of Sedimentation Manual, 1971). This relationship is shown in Figure IV-44 (The

000	76	LBL									
001	77	GE	051	34	√X	101	02	2	151	70	RAD
002	93	.	052	75	-	102	65	×	152	76	LBL
003	00	0	053	06	6	103	43	RCL	153	89	π
004	00	0	054	65	×	104	04	04	154	02	2
005	00	0	055	43	RCL	105	65	×	155	93	.
006	02	2	056	06	06	106	43	RCL	156	00	0
007	32	X:T	057	54	)	107	01	01	157	05	5
008	43	RCL	058	55	÷	108	54	)	158	42	STO
009	02	02	059	43	RCL	109	34	√X	159	08	08
010	77	GE	060	02	02	110	42	STO	160	76	LBL
011	88	DMS	061	54	)	111	05	05	161	70	RAD
012	33	X²	062	42	STO	112	65	×	162	53	(
013	65	×	063	00	00	113	43	RCL	163	53	(
014	02	2	064	92	RTN	114	02	02	164	05	5
015	93	.	065	76	LBL	115	55	÷	165	93	.
016	09	9	066	11	A	116	43	RCL	166	04	4
017	05	5	067	42	STO	117	06	06	167	03	3
018	01	1	068	06	06	118	54	)	168	05	5
019	07	7	069	22	INV	119	42	STO	169	75	-
020	55	÷	070	52	EE	120	07	07	170	93	.
021	43	RCL	071	92	RTN	121	32	X:T	171	03	2
022	06	06	072	76	LBL	122	07	7	172	08	8
023	95	=	073	12	B	123	00	0	173	06	×
024	42	STO	074	42	STO	124	32	X:T	174	65	×
025	00	00	075	01	01	125	77	GE	175	53	(
026	92	RTN	076	92	RTN	126	89	π	176	43	RCL
027	76	LBL	077	76	LBL	127	53	(	177	00	00
028	88	DMS	078	13	C	128	53	(	178	65	×
029	53	(	079	42	STO	129	02	2	179	43	RCL
030	53	(	080	02	02	130	93	.	180	02	02
031	53	(	081	92	RTN	131	05	5	181	55	-
032	43	RCL	082	76	LBL	132	55	÷	182	43	RCL
033	03	02	083	14	D	133	53	(	183	06	06
034	45	Y^x	084	42	STO	134	43	RCL	184	54	)
035	03	3	085	03	03	135	07	07	185	28	LOG
036	65	×	086	92	RTN	136	28	LOG	186	42	STO
037	03	3	087	76	LBL	137	75	-	187	09	09
038	06	6	088	15	E	138	93	.	188	75	-
039	93	.	089	42	STO	139	00	0	189	93	.
040	00	0	090	04	04	140	06	6	190	04	4
041	06	6	091	92	RTN	141	54	)	191	05	5
042	04	4	092	76	LBL	142	54	)	192	07	7
043	85	-	093	16	A'	143	65	×	193	65	×
044	03	3	094	71	SBR	144	93	.	194	53	(
045	06	6	095	77	GE	145	06	6	195	43	RCL
046	65	×	096	53	(	146	06	6	196	05	05
047	43	RCL	097	53	(	147	54	)	197	55	÷
048	06	06	098	03	3	148	42	STO	198	43	RCL
049	33	X²	099	02	2	149	08	08	199	00	00
050	54	)	100	93	.	150	61	GTO	200	54	)

FIGURE IV-43   PROGRAM LISTING AND SAMPLE INPUT/OUTPUT FOR
YANG'S SEDIMENT TRANSPORT EQUATION

-413-

201	28	LOG	228	10	10
202	42	STO	229	54	)
203	10	10	230	65	×
204	54	)	231	53	(
205	85	+	232	43	RCL
206	53	(	233	03	03
207	53	(	234	65	×
208	01	1	235	43	RCL
209	93	.	236	01	01
210	07	7	237	55	÷
211	09	9	238	43	RCL
212	09	9	239	00	00
213	75	−	240	75	−
214	93	.	241	43	RCL
215	04	4	242	08	08
216	00	0	243	65	×
217	09	9	244	43	RCL
218	65	×	245	01	01
219	43	RCL	246	54	)
220	09	09	247	28	LOG
221	75	−	248	54	)
222	93	.	249	54	)
223	03	3	250	22	INV
224	01	1	251	28	LOG
225	04	4	252	98	ADV
226	65	×	253	99	PRT
227	43	RCL	254	92	RTN

v = .0000111

S_o = .0017

d_s = .000623

U = 2.89

Y = 0.51

Output:

C_t = 2117.066395

FIGURE IV-43   (CONTINUED)

DuBoys curve in Figure IV-44 does not quite match the calculations in this example because slightly different data were used). Observe that the DuBoys relationship overpredicts the bed material load for nearly all flow ranges. This pattern is repeated for the Niobrara River (Figure IV-45). This suggests that the bed material load estimated by the DuBoys relationship will in general exceed the actual bed material load. This is further substantiated by other work (Stall et al., 1958). The more accurate predictions of bed material load occur under high flow conditions, which is generally when the prediction of bed material load is most important.

To estimate the suspended load contribution first calculate the width-depth ratio:

$$W/D = \begin{cases} 88 \text{ at } q = 8 \text{ cfs/ft} \\ 29 \text{ at } q = 35 \text{ cfs/ft.} \end{cases}$$

TABLE IV-37

CHARACTERISTICS OF THE COLORADO AND NIOBRARA RIVERS
(TASK COMMITTEE ON PREPARATION OF SEDIMENTATION MANUAL, 1971)

Data	Stream	
	Colorado River (Taylor's Ferry)	Niobrara River (Cody, Neb.)
Depth range, ft	4-12	0.7-1.3
Range in q, in cubic feet per second per foot of width	8-35	1.7-5
Mean width, in feet	350	110
Slope, in feet per foot		
Minimum value	0.000147	0.00116
Maximum value	0.000333	0.00126
Value used in calculations	0.000217	0.00129
Water temperature, in degrees Fahrenheit		
Minimum value	48	33
Maximum value	81	86
Value used in calculations	60	60
Geometric mean*sediment size, in millimeters	0.320	0.283
d_{35}, in millimeters	0.287	0.233
d_{50}, in millimeters	0.330	0.277
d_{65}, in millimeters	0.378	0.335
d_{90}, in millimeters	0.530	0.530
Mean size, d_m, in millimeters	0.396	0.342

*The geometric mean of a set of values X_n is $\left(\prod_{i=1}^{n} X_n\right)^{1/n}$. Thus the geometric mean of the values 1, 2, 3, and 4 is $(1 \times 2 \times 3 \times 4)^{1/4} = 2.213$. Compare with arithmetic mean of 2.5.

**COLORADO RIVER
AT TAYLORS FERRY**
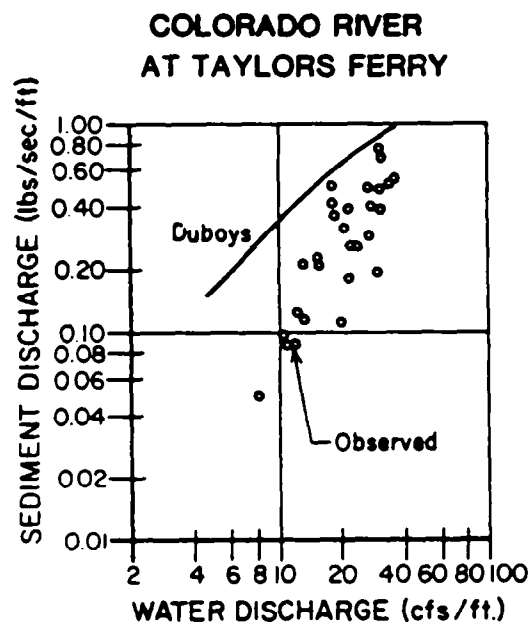
FIGURE IV-44   SEDIMENT DISCHARGE AS A FUNCTION OF WATER DISCHARGE
FOR THE COLORADO RIVER AT TAYLOR'S FERRY (TASK
COMMITTEE ON PREPARATION OF
SEDIMENTATION MANUAL, 1971)
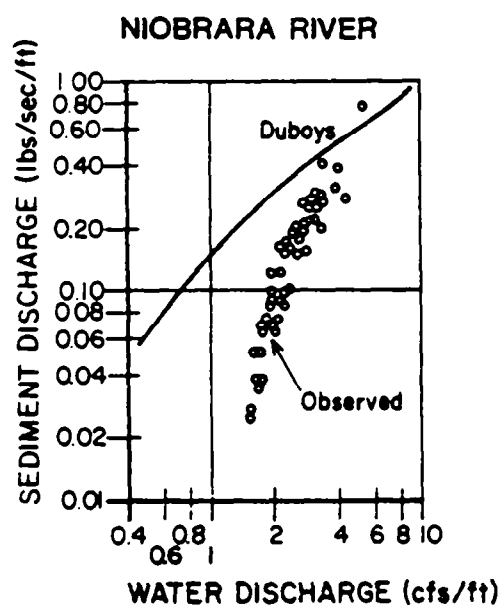
NIOBRARA RIVER

FIGURE IV-45   SEDIMENT DISCHARGE AS A FUNCTION OF WATER DISCHARGE
FOR THE NIOBRARA RIVER AT CODY, NEBRASKA (TASK
COMMITTEE ON PREPARATION OF SEDIMENTATION
MANUAL, 1971)

In both cases W/D > 25. Referring to Table IV-36, the suspended load should
be between 30 and 65 percent of the bed material load. Assume it is on the
lower end of the scale, about 40%. Then the suspended load is:

$$g_{ss} = \begin{cases} 0.08 \text{ lb/sec/ft at } q = 8 \text{ cfs/ft} \\ 1.0 \text{ lb/sec/ft at } q = 35 \text{ cfs/ft} \end{cases}$$

or

$$C_{ss} = \begin{cases} 160 \text{ mg/l at } q = 8 \text{ cfs/ft} \\ 440 \text{ mg/l at } q = 35 \text{ cfs/ft} \end{cases}$$

from Equation IV-99. These concentrations indicate that suspended sediment
concentrations are excessively high throughout the range of flows normally
encountered at Taylor's Ferry. Data on suspended sediment concentrations have
been gathered at Taylor's Ferry (U.S. Bureau of Reclamation, 1958). The averages
of 30 measurements taken there are as follows:

Q = 7350 cfs (or q = 21 cfs/ft)

C_{ss} = 132 mg/l

Observed range of suspended sediment concentration: 40-277 mg/l.

    The method of Yang predicts total concentrations of 40 to 80 mg/l, which is
within but toward the lower end of the observated data. The method of DuBoy's
predicts concentration between 160 and 440 mg/l which is toward, and beyond, the
upper end of observation. These results illustrate the possible variability of
predictions between different approaches, and are not necessarily atypical.

———————————————— END OF EXAMPLE IV-17 ————————————————————

4.9 TOXIC SUBSTANCES

4.9.1 Methods of Entry of Toxic Pollutants into Rivers

    Although Chapter 3 discussed both point and nonpoint sources of pollutants,
the major pollutant source categories are summarized in Table IV-38 to indicate
how these scenarios differentially govern a pollutant's fate. For simplicity,
fate is analyzed in terms of volatilization and sorption since these processes
are important for a wide number of toxic organic chemicals. These processes
govern whether a pollutant remains in the water column and whether the pollutant
is transported as solute or sorbate. If the effects of these processes are known,
even if only qualitatively, then the influence of processes such as photolysis and
biodegradation can be better predicted. For example, if a pollutant is sorbed to
suspended and bedded sediments, it is more protected from photolytic reactions than
when it is dissolved in the water column.

    A common mode of pollutant entry is by a continuous discharge, either from
a municipal or industrial source. As mixing of the effluent and river water occurs,

TABLE IV-38

METHODS OF INTRODUCTION OF TOXIC ORGANIC COMPOUNDS INTO RIVERS,
AND FATE IN TERMS OF VOLATILIZATION AND SORPTION

Pathway	Fate
Continuous input	- solute transported and volatilized
	- sorbate transported with suspended solids and with bed load
	- sorbed to immobile sediments
	- buried by sorption and net deposition
Cessation of continuous input	- desorbed from immobile sediments
	- solute transported and volatilized
	- resorbed to suspended sediments
	- contaminated sediments resuspended
	- portion remains buried
Washoff from land application	- transport of a major portion of pollutant may be governed by first large storm event
	- transported as solute and sorbate
	- settles and accumulates on bed
	- buried
	- subsequently resuspended
Accidental releases (e.g. spills)	- If s.g. >1, pollutant settles on streambed
	- Volatilization may be unimportant --reentrained back into stream and sorbed on suspended solids --pollutant can be slowly transported along bottom --diffused into bedded sediments
	- If s.g. <1, pollutant tends to remain on surface and be transported at speed of surface current --volatilization can be important --gradually dissolved and sorbed --dispersion attenuates peak concentrations --wind speed and direction influential
Leaching	- slow movement (years) of solute from dump or disposal site to stream
	- continues for years after cleanup of dump

partitioning begins. The sorbate is transported with the suspended sediments, and can interact with the bed load and immobile bedded sediments. Depending on the rate of exchange of the sorbate with the bedded sediments and on the net sediment deposition rate, some of the sorbate can gradually become buried in the bedded sediments.

If a continuous input ceases, the water column initially tends to clean itself of the pollutant as uncontaminated upstream water replaces contaminated river water downstream from the former source of pollution. However, pollutant from the contaminated bottom sediments can desorb back into the water column at low concentrations and the river bed becomes an internal source of pollutant. The desorption period can last a long period of time, depending on the amount of pollutant contained in the bottom sediments. Section 4.9.3.4 discusses this phenomenon in detail.

Periodic nonpoint sources, such as washoff after an agricultural application, is another pathway of pollutant entry into rivers. The mass of pollutant transported tends to be governed by the timing of the first storm event following application together with the degradation and volatilization processes operative during the interim period.

Accidental releases of pollutants, even through infrequent events, can be important. Exceptionally high concentrations of pollutants can result from spills and the total mass supplied almost instantaneously can be the equivalent of a continuous release lasting for many days. For example, in 1973 a chloroform spill on the Mississippi River resulted in about 800,000 kg (1,750,000 lbs) of chloroform being released over a period of several hours (Thibodeaux, 1977). Based on the background concentration of chloroform in the river (5 ppb), the release was equivalent to a continuous supply of chloroform released at background rates for a period of 300 days.

Many chemicals in their pure or nearly pure form have specific gravities significantly different from unity. Because of this, and their often limited solubility in water, it is a mistake to believe that all spilled pollutants travel with the speed of the river, have infinite dissolution capability, and disperse accordingly. High density pollutants can sink to the river bed and become slowly reentrained back into the water column while simultaneously diffusing and sorbing into the bedded sediments. Depending on the rate of dissolution of the spilled pollutant, as well as the significance of the sorption and diffusion processes, the spilled pollutant may remain in the riverine system for either an extended or brief period of time.

In contrast to high density pollutants, pollutants with specific gravities less than unity tend to at least partially remain on or near the water's surface while undergoing dissolution. For these pollutants, volatilization and photolysis can be extremely important. As the pollutant is dissolved in the water column and moves downstream, dispersion becomes important in attenuating the peak concentration.

Pollutants which leach from a surface or subsurface disposal site may eventually

reach a river. Although the mass input rate may be low, the source can be continuous and last for years, even after cleanup of the site.

The sequence of instream events following the initiation and then the cessation of point sources of toxicants further illustrates the role that sorption plays in governing fate of sorbates. Figure IV-46 illustrates the two situations. Figure IV-46a shows the pollutant distributions below a point source at two distinct times (t_1 and t_2 where $t_2 > t_1$) following initiation of the point source.
As the toxicant is discharged the water column concentration (the sum of the dissolved and sorbed phases) abruptly increases at the mixing location. As the pollutant travels downstream, the sorbate tends to partially desorb onto the formerly uncontaminated bottom sediments. Additionally there may be a net exchange between the bedded sediments and water column sediments, even if there is no net deposition. As a result of these processes, the water column concentration tends to decrease in the downstream direction. It may take a period of time greater than t_1 for the effects of the discharge to reach a distance D^*. Depending on the distance, and on the rate of accumulation of the toxicant in the bottom sediments, as well as on other factors, the time required for the water column concentration to be noticeably elevated at D^* could greatly exceed the travel time of the river over the distance.

After the discharge of the toxicant has continued for a period of time, the net exchange with the bedded sediment may diminish, so that the toxicant concentration becomes constant over some distance both in the water column and in the sediments. This situation is illustrated by the solid curve in Figure IV-46b. Suppose at this time the input of the pollutant ceases. The water column concentration just below the point source tends to abruptly approach zero. As this happens, desorption of the toxicant from the bedded sediment can occur, tending to replenish pollutant levels in the water column, but to a lower level. Gradually, the pollutant can be desorbed from the bedded sediments at a given location so that the bottom sediments are naturally cleansed, from the upstream to the downstream direction. This process can take many years and low levels of pollutant in the water column can be detected throughout this period. More discussion of this phenomenon is provided later in Section 4.9.3 and Example IV-18. Most of the pathways for river contamination presented in Table IV-38 have been programmed on microcomputers (Mills et al., 1985).

4.9.2 Vertical Distribution of Sorbate within Rivers

Even though most of the analytical tools presented later in Section 4.9.3 assume that, for simplicity, suspended solids concentrations are uniformly distributed throughout the water column, in reality this is not true. The vertical distribution of solids depends both on particle and river characteristics. Heavier particles (those with the greater settling velocities) are transported closer to the stream bottom while the lighter particles are more uniformly distributed. This observation is significant because pollutants which sorb to the particles also exhibit a non-
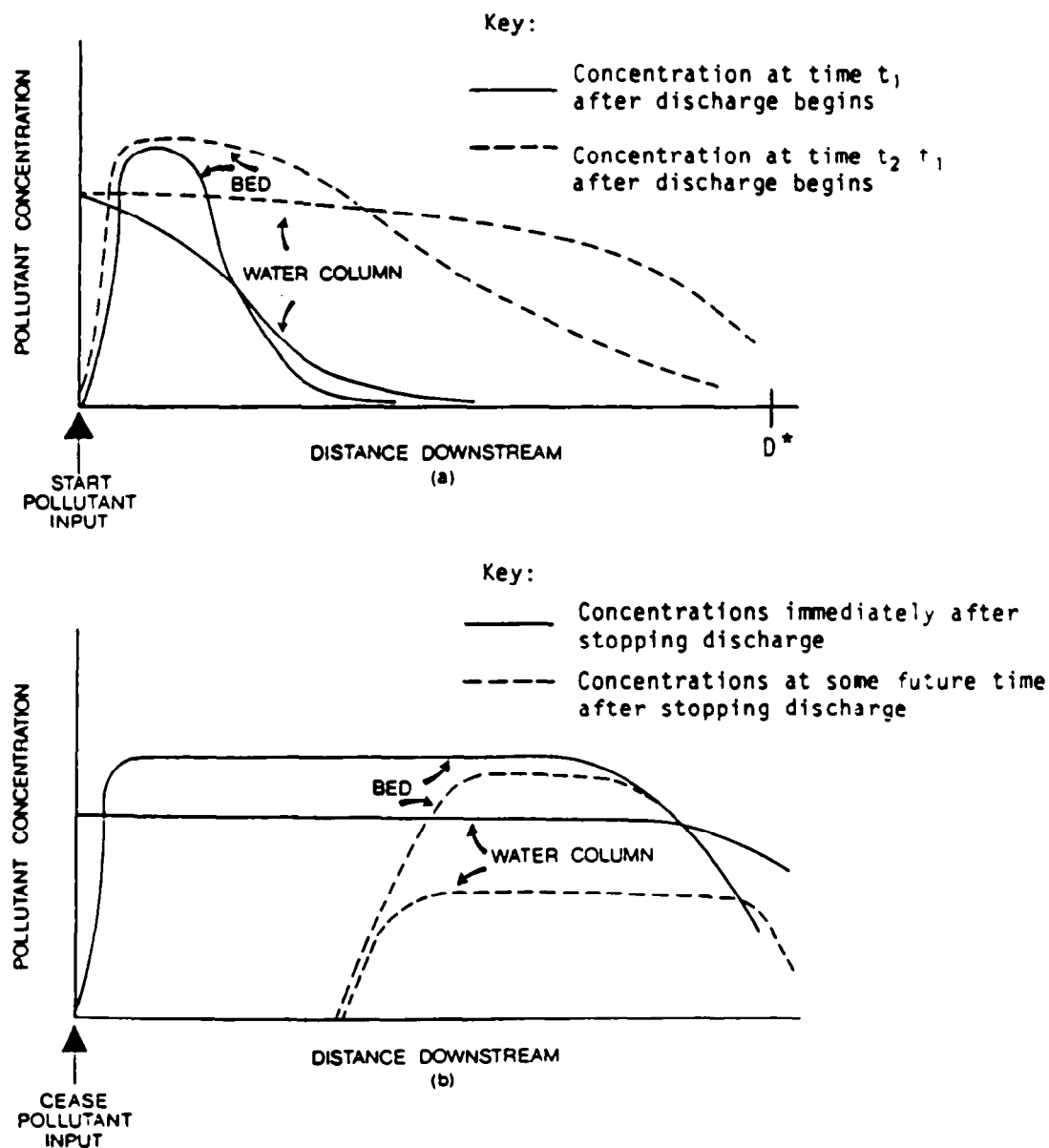
FIGURE IV-46 TOXICANT CONCENTRATIONS FOLLOWING
INITIATION AND CESSATION OF POINT SOURCE.

uniform vertical distribution. Pollutants which do not sorb tend to become uniformly distributed vertically, regardless of the sediment distribution. By understanding this, the user can better interpret instream pollutant data, particularly if the pollutant tends to reside as sorbate. It may be that a single pollutant sample is not sufficient to accurately characterize the pollutant distribution, and in fact could be misleading in terms of the total burden of the pollutant carried within the water column. Depth integrated samples might be necessary to gain an accurate knowledge of the pollutant's distribution.

RELATIVE SEDIMENT CONCENTRATION S/Sa
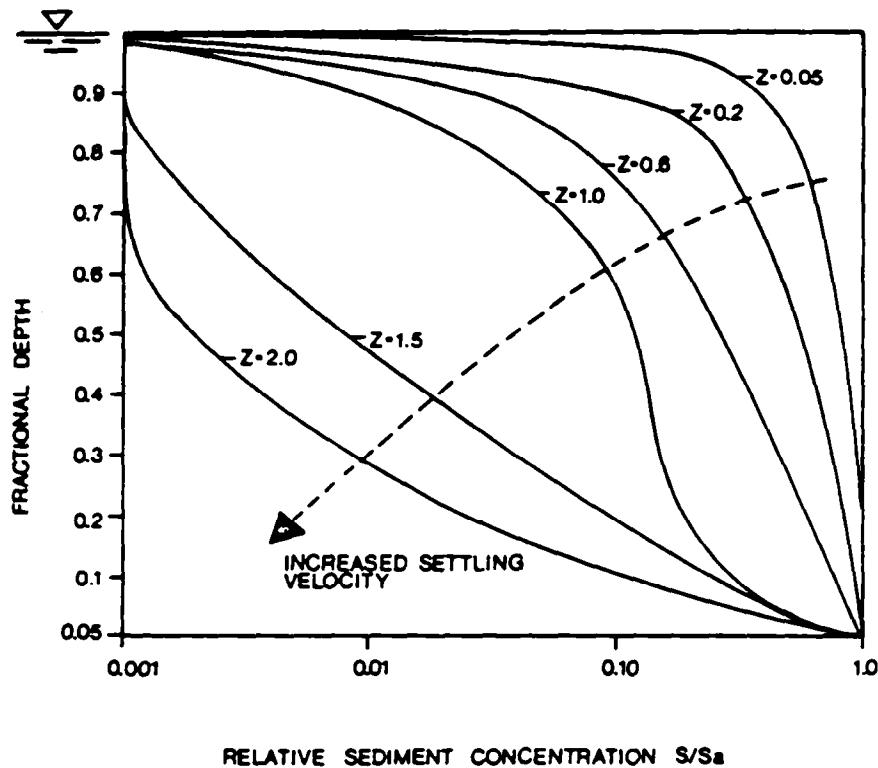
FIGURE IV-47   VERTICAL EQUILIBRIUM DISTRIBUTION OF
SUSPENDED SOLIDS IN A RIVER

Figure IV-47 shows the vertical distribution of suspended solids in an equilibrium condition. The parameter shown in the figure is defined:

$$z = \frac{V_s}{\kappa \, U^*}$$ (IV-103)

where

V_s = settling velocity of suspended solids

κ = von Karman's constant (~0.4)

U^* = shear velocity = $(g \, R_H \, S)^{0.5}$, ft/sec

g = acceleration due to gravity, 32.2 ft/sec^2

R_H = hydraulic radius of river, ft

S = slope, dimensionless.

Very small values of z represent clay-sized particles, while larger values represent first silt, and then sand. Figure IV-47 illustrates that clay particles tend to be uniformly distributed vertically (50 percent in the top half of the water column). About 75 percent of silt and over 95 percent of the sand particles (typically) reside in the bottom half of the water column. This suggests that in rivers where the suspended sediments are silt and sand, the sorbed pollutant distribution will be

vertically skewed. If the suspended material is predominantly clay the sorbed pollutant distribution will be uniform. Since pollutants tend to sorb to sand to a lesser degree than to silt and clay, the vertical distribution of sorbed pollutant will not be as skewed as the suspended sediment distribution.

Figures IV-48 through IV-49 show the fraction of pollutant present as solute (C/C_t) versus relative depth for families of z values and K_pSa values. Sa is the suspended sediment concentration a small distance above the bottom. For K_pSa values less than 0.1, the sorbate concentration is generally negligible compared to the solute concentration regardless of the depth or the nature of the suspended material. For larger K_pSa values, the sorbate level can be important, depending of the nature of the suspended material. For extremely large K Sa values, the sorbate concentration will greatly exceed the solute concentration, at least near the river bed.

Based on the hydraulic characteristics of the river, characteristics of the material being transported in suspension, and the partition coefficient of the pollutant, predictions can be made of the pollutant's distribution in the water column. To use Figures IV-48 and IV-49 requires knowledge of Sa, the suspended solids concentration at a distance n = a above the bottom (where typically a = 0.05, or 5 percent of the river's depth). The equilibrium expression for suspended sediments, which is found in numerous sediment transport texts (e.g. Graf, 1971) can be rearranged to express Sa as:

$$Sa = S(n) \left(\frac{1-n}{n} \frac{a}{1-a} \right)^{-z} \qquad \text{(IV-104)}$$

where

   n = relative depth above bottom.

To use this equation the suspended solids concentration must be known at one depth in the water column. Typically, a depth averaged suspended solids concentration might be readily available. Under these circumstances Sa can be estimated as:

$$Sa = \frac{S \left(1-a \right) \left(\frac{1-a}{a} \right)^{z}}{\int_{a}^{1} \left(\frac{1-n}{n} \right)^{z} dn} \qquad \text{(IV-105)}$$

where

   S = depth average suspended sediment concentration.

The denominator of Equation IV-105 can be integrated numerically by one of many available solution techniques (e.g. see Carnahan et al., 1969). For the case
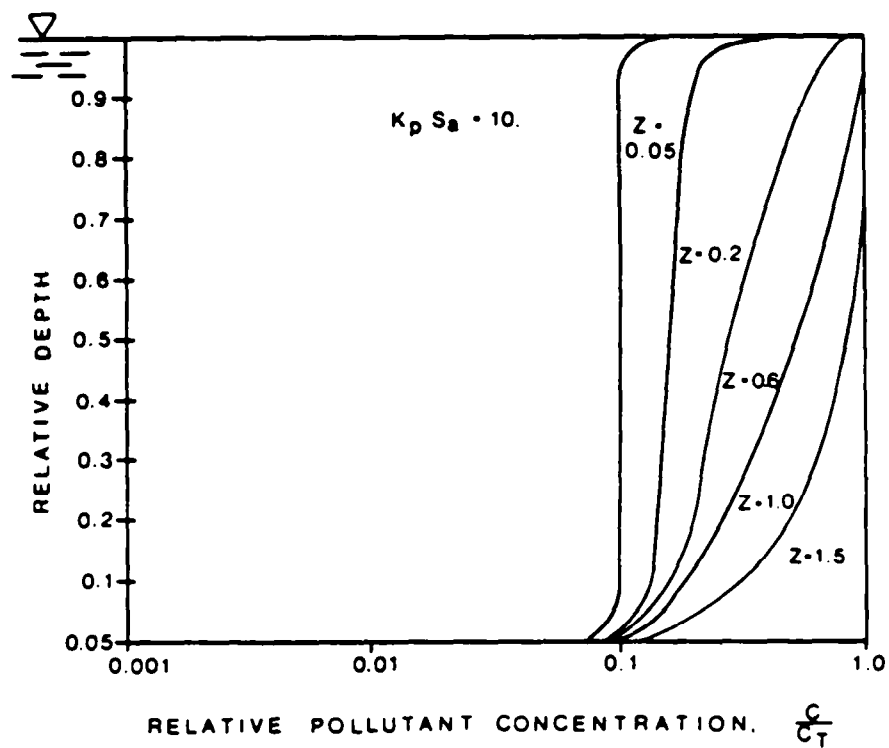
FIGURE IV-48   VERTICAL DISTRIBUTION OF RELATIVE SOLUTE
CONCENTRATION, $K_pS_A = 10$.
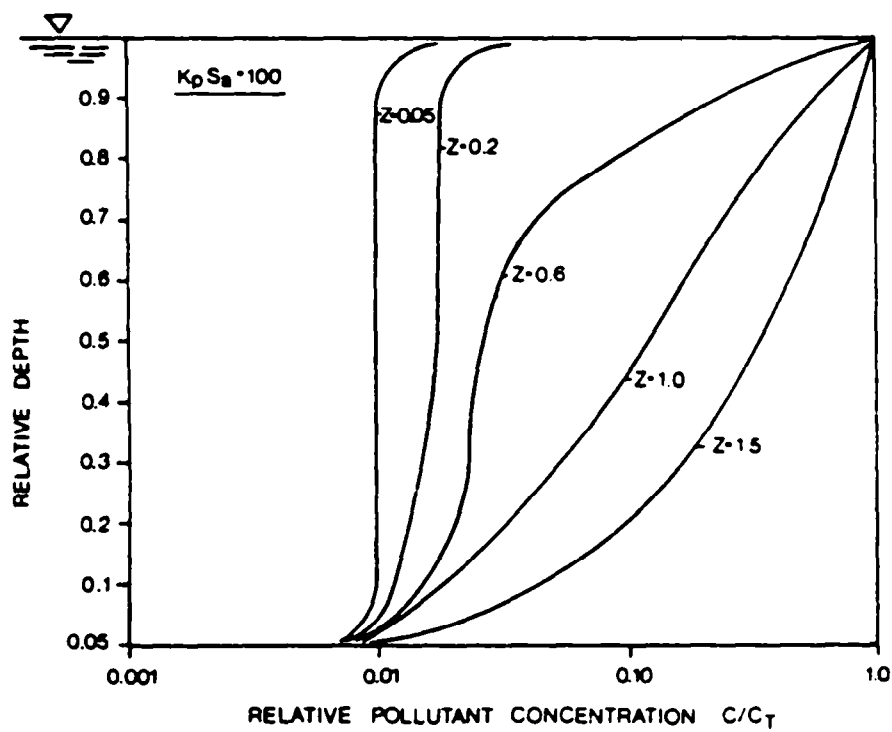
FIGURE IV-49   VERTICAL DISTRIBUTION OF RELATIVE SOLUTE
CONCENTRATION, $K_pS_A = 100$.

when a = 0.05 the relationship between Sa and S is given below:

$$z = 0 \longrightarrow Sa = S$$
$$z = 0.2 \longrightarrow Sa = 1.8\ S$$
$$z = 0.6 \longrightarrow Sa = 4.4\ S$$
$$z = 1.0 \longrightarrow Sa = 8.2\ S \qquad\qquad (IV-106)$$
$$z = 2.0 \longrightarrow Sa = 17\ S$$
$$z = 5.0 \longrightarrow Sa = 20\ S$$

Based on a knowledge of S, Sa can be estimated from Equation IV-106, and in turn can be used in Figures IV-48 and IV-49.

Typically there is a segregation of particle sizes found in suspension compared with these found in the bed load, and in the immobile bed materials. Based on these differences, the following can be hypothesized:

$$X_s > X_{bl} > X_{im}$$

where

X_s = sorbed pollutant concentration on suspended materials, mass pollutant/mass sediment

X_{bl} = sorbed pollutant concentration on bed load, mass pollutant/mass sediment

X_{im} = sorbed pollutant concentration on immovable sediment, mass pollutant/mass sediment.

Investigations carried out by Miles (1976) appear to support this relationship. Miles collected insecticide residues on stream sediments and in the water column. Results of the DDT analysis of Big Creek, Norfolk County, Ontario, 1973 (DDT was banned in 1970) are as follows:

Concentration of DDT on Sediments
(mass of pollutants/mass of sediments)

Suspended sediments	110 ppb =	X_s
Bed load	76 ppb =	X_{bl}
Immovable bed	26 ppb =	X_{im}

Miles (1976) also found that DDT transported in the dissolved phase ranged from 10 to 92 percent of the total transported in the water column. This finding is consistent with the results in Table II-14 which shows that the percent of pollutant transported in the dissolved phase can be high even for pollutants such as DDT as long as the suspended solids concentration is not extremely high.

Contaminant data collected in bedded sediments can be very illuminating. Although in a screening approach it is not anticipated the user will go to the field to collect sediment core samples, some data might be available. Depending

on the quantity of data available the following types of information might be
determinable:

- The spatial extent of contaminated sediments, and pollutant concentrations in the sediments
- The depth of contaminated sediment
- The quantity of toxicant contained in the sediment
- A time history of pollution levels to determine whether they are increasing or decreasing
- The probable sources of the pollutant, based on the location and quantity of contaminated sediments.

Although extensive sampling is required to accurately determine all of the above
items, such programs have been successfully accomplished. For example, an extensive
sediment sampling program was conducted in the Hudson River in New York to determine
the sources of PCBs in the contaminated sediments, and the degree of contamination
(Turk, 1979).

4.9.3 Transport and Transformation Expressions for Toxicants in Rivers

The tools presented in this section can be used to predict instream concentrations of toxicants for a variety of different situations. Specifically, the following
scenarios are addressed:

- Mixing zone analysis
- Continuous point source discharges
- Continuous nonpoint source discharges
- Desorption from bedded sediments
- Spills and instantaneous release of soluble chemicals, and
- Spills of high density chemicals which sink to the river bed.

In contrast to many conventional organic pollutants which degrade into innocuous
substances, many toxicants are transformed to other chemicals which can be as harmful
or more harmful than the original. Consequently, when toxicants are continuously
discharged into a river, in addition to predicting the concentration profile, it is
useful to also determine:

- The pollutant's advection rate past a specified location
- The pollutant's volatilization rate over a specified reach
- The pollutant's rate of transformation to other species over a specified reach.

The toxicant's fate is thus segregated into the processes of advection, volatilization,
and transformation.

In the following three sections on mixing zones, point sources, and nonpoint
sources, the user will find there are different methods of approaching the problems.
One way to simplify the analysis is to first assume toxicants act conservatively.

The user can then perform a first level analysis to find out whether criteria are violated. If they are not, then a detailed analysis is really not required if the objective is to determine criteria compliance. If violations are predicted, a more detailed analysis of these "hot spots" can be performed by considering the various processes affecting the toxicant in the river. This approach requires more work, but by judiciously applying the tools available, the analyses can be expedited.

4.9.3.1 Mixing Zone Expressions

Section IV-4.1.9 presented earlier delineated one- and two-dimensional mixing zone expressions for conventional pollutants. The one-dimensional expressions need to be extended in order to differentiate between solute and sorbate. To do this, the following expressions for pollutant concentration and the suspended solids concentrations are needed:

$$S = \frac{S_u\, Q_u + S_w\, Q_w}{Q_u + Q_w} \qquad\qquad (IV\text{-}107)$$

$$C_{to} = \frac{C_{ut}\, Q_u + C_{wt}\, Q_w}{Q_u + Q_w} \qquad\qquad (IV\text{-}108)$$

where

S_u, C_{ut} = concentration of suspended solids and concentration of sum of solute and sorbate in the river above the location of mixing, respectively

S_w, C_{wt} = concentration of suspended solids and concentration of sum of solute and sorbate in the wastewater, respectively

S, C_{to} = concentration of suspended solids and concentration of sum of solute and sorbate in the river following mixing, respectively

The dissolved phase concentration, C, of the pollutant at the completion of mixing is given by:

$$C = \frac{C_{to}}{1 + k_p\, S} \qquad\qquad (IV\text{-}109)$$

where C_{to} and S are found from the two previous expressions.
The concentration of the solute following mixing depends on characteristics of the waste source, the river's flow rate, and the suspended solids concentration in the river and waste source. The solute concentration might also change after mixing with a tributary of very high suspended solids concentration (high S_w), even if it contains no additional pollutant ($C_{wt} = 0$).

Equation IV-108 is particularly useful because it predicts the total instream

concentration of toxicant following initial mixing. This is often the critical test in establishing whether or not water quality standards are violated by a point source.

In cases where initial mixing is incomplete (that is the waste is initially diluted with a fraction of the total river flow), the two-dimensional mixing equation shown earlier as Equation IV-4 will more accurately predict C_{to}. Then Equation IV-109 can be used to find the solute concentration.

When there are numerous discharges of the same toxicant, analysis becomes more complicated. The most straightforward method of handling this situation is to sequentially apply Equation IV-108 to the series of discharges to find the concentration as a function of distance downstream. If the solute concentration is needed, then sequential application of Equations IV-108 and IV-109 is required.

The analysis of multiple point sources can be simplified in one of two ways. One, the sources can be transformed to an equivalent nonpoint source by assuming that the toxicant input is uniformly distributed between the series of point sources. This approach is discussed in Section 4.9.3.3. Two, a series of closely grouped point sources can be handled as an equivalent point source. The equivalent point source has a flow rate equal to the sum of the flow rates from the individual plants, or:

$$Q_w = \sum_{i=1}^{n} Q_{wi} \qquad (IV-110)$$

where

Q_{wi} = flow rate from ith treatment plant

n = number of treatment plants being grouped.

The total pollutant load can be expressed in one of two ways. If the concentrations in the wastewater are known then the total loading is:

$$C_w Q_w = \sum_{i=1}^{n} C_{wi} Q_{wi} \qquad (IV-111)$$

where

C_{wi} = concentration of toxicant in effluent of ith plant.

If the mass emission rates are known instead then:

$$C_w Q_w = \frac{\sum_{i=1}^{n} M_i}{5.38} \qquad (IV-112)$$

where

M_i = mass emission rate of toxicant from ith plant is lbs/day.

The conversion factor 5.38 converts mass emission rate in lbs/day to flow units in cfs and concentration units in mg/l (ppm).

The grouping procedure described above has been applied by the U.S. Environmental

Protection Agency (1981) to a case study in Indiana to evaluate the economic impact of toxicant standards. Numbers of point sources were grouped together using a procedure called cluster analysis. The cluster analysis added the loadings of major and minor industrial dischargers within a ten-mile radius of each other. Ten clusters were identified and few violations occurred within them once the best available technology was attained.

For certain applications the object of using a mixing zone equation is to directly find the maximum allowable concentration in the discharge so that the receiving water criteria are not violated. Under these circumstances Equation IV-108 can be rewritten as:

$$(C_{wt})_{max} = \frac{C_{tc} (Q_{uc} + Q_w) - C_{ut} Q_{uc}}{Q_w} \qquad (IV-113a)$$

$$= C_{TC} \frac{(Q_{uc} + Q_w)}{Q_w}, \text{ when } C_{ut} = 0 \qquad (IV-113b)$$

where

$(C_{wt})_{max}$ = maximum allowable concentration of the toxicant in the waste discharge so that the water quality criterion is met under critical conditions

C_{tc} = water quality criterion for the toxicant

Q_{uc} = critical river flow rate (e.g., 7Q10).

Equation IV-113b is applicable when the concentration of the toxicant is zero upstream of the discharge point.

4.9.3.2 Point Source Discharges

For point sources of toxicants, the pollutant interactions depicted in Figure IV-50 are simulated. While transformation of toxicants is generally more complex than this, in many instances these interactions are sufficient to analyze the in-stream processes affecting not only point source discharges but also nonpoint source discharges, and instantaneous releases of soluble pollutants. Figure IV-50 reveals that:

- The solute only is assumed to volatilize.
- First order transformation processes degrade only the solute.
- Adsorption and desorption are assumed to occur at rates much faster than other processes.
- No interactions with the bottom sediments occur (this is analyzed in later sections).
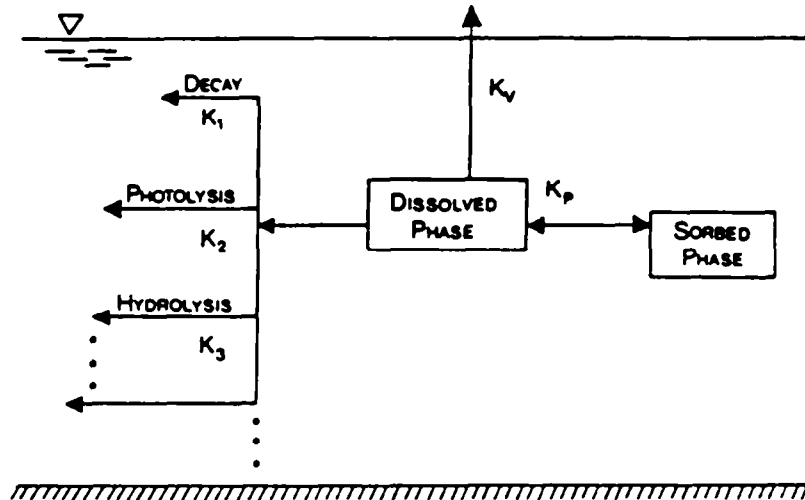
FIGURE IV-50   INSTREAM TRANSFORMATION PROCESSES
ANALYZED FOR TOXICANTS.

Based on these interactions, the concentration profile below a point source of toxicant is expressible as:

$$C = \left\{ C_0 - \frac{k_v'}{k_v' + \sum k_i} \cdot \frac{P}{K_H} \right\} \exp \left\{ - \frac{k_v' + \sum k_i}{U\,(1 + K_p S)} x \right\} + \left(\frac{k_v'}{k_v' + \sum k_i} \right) \frac{P}{K_H} \qquad (IV-114)$$

where

C   = concentration of dissolved phase of the toxicant at a distance x below the point source

C_0 = concentration of the dissolved phase of the toxicant at x = 0 (after the point source discharge has mixed with the river water)

k_v' = k_v/D

D   = water depth

$\sum k_i$ = individual first order decay rates which are transforming the toxicant (other than volatilization)

P   = partial pressure of the toxicant in the atmosphere above the river.

The remaining variables have previously been defined.

Typically the partial pressure is zero, so that Equation IV-114 simplifies to:

$$C = C_0 \exp \left[\frac{-\left(k_v' + \sum k_i \right)}{1 + K_p S} \cdot \frac{x}{U} \right] \qquad (IV-115)$$

-430-

The initial dissolved phase concentration is given by:

$$C_o = \frac{C_{to}}{1 + K_p S}$$

(IV-116)

where

C_{to} was defined by Equation IV-108.
The total pollutant concentration, C_t, at any location is:

$$C_t = C (1 + K_p S)$$

(IV-117)

The sorbed phase concentration expressed as mass per unit volume of water is:

$$C_s = C_t - C$$

(IV-118)

and the sorbed phase concentration expressed as mass per unit mass of sediment is:

$$X = K_p C$$

(IV-119)

The most direct application of Equation IV-114 or IV-115, plus Equations IV-117 through IV-119 is to find the instream concentration as a function of distance below the point source. There are, however, other uses of the expressions. Consider Equation IV-115, for example. The ratio C/C_o can be directly calculated as a function of distance. Thus the fractional dissolved phase concentration can be calculated without ever knowing the initial concentration C_o. This approach has the advantage of requiring less data. Similarly, the fractional concentration can be calculated for any specified distance, such as the end of a reach. Or, the distance x can be found so that the fractional concentration is some specified number, which may relate to an acceptable level of toxicant. The length of river subjected to unacceptable levels can then be found.

The user might additionally want to know the distribution of pollutant fluxes in terms of advection ($\dot{M}_a$), volatilization ($\dot{M}_v$), and transformation ($\dot{M}_t$). Expressions for these are presented for the case of P = 0. These formulae allow the user to predict the fluxes associated with the point source discharge where volatilization is not altered by a background concentration in the atmosphere. Under these conditions:

$$\dot{M} = \dot{M}_a + \dot{M}_v + \dot{M}_t$$

(IV-120)

Equation IV-120 states that the rate of entry of the toxicant into the river ($\dot{M}$) equals the rate of advection of that toxicant past some location x_s, plus the

rate of volatilization across the water surface between the discharge location and some other specified location plus the rate of transformation of the toxicant to other substances within the water column between the same two locations. By knowing expressions for each of $\dot{M}_a$, $\dot{M}_v$, and $\dot{M}_t$ the user knows the major processes controlling the toxicant's fate within any reach of river.

The mass flux advected past a location x_s is given by:

$$\dot{M}_a = (Q_u + Q_w)\, C_s \qquad\qquad (IV-121)$$

where the concentration C_s is evaluated at $x = x_s$. The volatilization mass flux is given by:

$$\dot{M}_v = A_c\, k_v'\, C_o\, \frac{U\,(1 + K_p S)}{k_v' + \sum k_i}\left[1-\exp\left(-\frac{k_v' + \sum k_i}{U\,(1 + K_p S)}\, x_s\right)\right] \qquad (IV-122)$$

where

A_c = cross-sectional area of river

All other terms have previously been defined.

In some cases the user might have an estimate of the average dissolved phase concentration, C, within the reach under consideration. Under these circumstances the volatilization flux is simply:

$$\dot{M}_v = A_s\, k_v\, \bar{C} \qquad\qquad (IV-123)$$

where

A_s = surface area of the reach under investigation.

The transformation mass flux is expressible as:

$$\dot{M}_t = A_c\, \sum k_i\, C_o\, \frac{U\,(1 + K_p S)}{k_v' + \sum k_i}\left[1-\exp\left(-\frac{k_v' + \sum k_i}{U\,(1 + K_p S)}\, x_s\right)\right] \qquad (IV-124)$$

Since the sum of Equations IV-121, IV-122, and IV-124 equals the mass emission rate of the toxicant, Equation IV-120 can be used to double check the fluxes calculated.

4.9.3.3 Nonpoint Source Discharge

This section parallels the previous section on point source discharges by presenting expressions for the steady-state concentration profile, and for mass fluxes. In addition to applying this methodology to a nonpoint source, another and possibly more useful application is to express a series of point sources as an

equivalent nonpoint source. The equivalent nonpoint source discharge rate is simply the sum of the discharge rates of the pollutant from all the point sources. This approach is not as accurate as analyzing each point source individually but is much faster depending on the number of point sources. For example, suppose a river segment has ten separate point sources located within 50 miles of each other. The most rigorous analysis would consist of considering each point source individually, where mixing zone and point source equations are applied sequentially ten times each. This obviously is a great deal of work for a hand calculation approach. By considering these point sources as a single equivalent nonpoint source, a single equation application is sufficient to analyze the problem. Example IV-5 shown earlier in the BOD section illustrates this procedure.

The solute concentration in a river resulting from a steady nonpoint source of toxicant is:

$$C = \frac{-k_4}{k_3} + \left(C_0 + \frac{k_4}{k_3}\right)\left(\frac{Q_0 + mx}{Q_0}\right)^{\frac{-k_3}{k_2}}$$

(IV-125)

where

$$k_2 = \frac{1 + K_p S}{A_c} m$$

$$k_3 = k_2 + k_v' + \sum k_i$$

$$k_4 = \frac{C_{tn}}{A_c} m - \frac{P}{H} k_v$$

C_{tn} = total concentration of toxicant in nonpoint source

$$m = \frac{Q_f - Q_0}{x_1}$$

Q_f = river flow rate at end of nonpoint source

Q_0 = river flow rate at beginning of nonpoint source

x_1 = length of nonpoint source.

Equations IV-117 through IV-119 can be used to find C_t, C_s, and X, respectively.

In a manner similar to point source discharges, Equation IV-120 which expresses the mass balance between toxicant inflow rate to the river and loss rate by advection, and transformation, is valid. The appropriate expressions are (when P = 0):

$$\dot{M}_a = \underbrace{(Q_0 + mx)C}_{\substack{\text{solute} \\ \text{transport}}} + \underbrace{(Q_0 + mx) Ck_p S}_{\substack{\text{sorbate} \\ \text{transport}}} \quad \text{at } x = x_s$$

(IV-126)

for the advective flux. For the volatilization flux:

$$\dot{M}_v = -k'_v \, A_c \, \frac{k_4}{k_3} \, x_s + k'_v \, A_s \left(C_o + \frac{k_4}{k_3} \right) \frac{Q_o}{m} \, \frac{k_2}{k_2-k_3} \left\{ \left(\frac{Q_o + mx_s}{Q_o} \right)^{\frac{-k_3}{k_2}+1} \right\} \quad (IV\text{-}127)$$

For the transformation flux:

$$\dot{M}_t = -\Sigma k_i \, A_c \, \frac{k_4}{k_3} \, x_s + \Sigma k_i A_c \left(C_o + \frac{k_4}{k_3} \right) \frac{Q_o}{m} \, \frac{k_4}{k_2-k_3} \left\{ \left(\frac{Q_o + mx_s}{Q_o} \right)^{\frac{-k_3}{k_2}+1} -1 \right\} \quad (IV\text{-}128)$$

As a first cut analysis, the user might want to assume that the toxicants act conservatively. If criteria are not violated under these circumstances, then criteria will not be violated if decay or transformation processes are included.

4.9.3.4 Desorption of Toxicant from a River Bed

Because many toxicants are transported as sorbate rather than as solute, a significant fraction of the pollutant which enters a riverine system can ultimately be deposited in the bedded sediments. If the toxicant is resistant to degradation processes it can remain in the sediments for extended periods of time. During this time, the toxicant can slowly be desorbed back into the water column or scoured into suspension.

Figure IV-46 shown earlier illustrated an idealization of the process of desorption of a toxicant from bedded sediments. The process can be described as follows. Supposed the average concentration of the pollutant in the bedded sediment is X_o when the analysis begins (called t = 0). The concentration X, at any later time is estimated from mass balance considerations as:

$$X = \begin{cases} X_o \, , \text{ for } x > \dfrac{U \delta t}{M_s K_p} \\ \\ 0 \, , \text{ otherwise} \end{cases} \quad (IV\text{-}129)$$

where

X_o = concentration of pollutant in bed at some time t = 0

M_s = mass of contaminated sediment per unit area of river bed, g/cm^2

U = stream velocity, cm/sec

δ = equivalent depth of water in sediment M_s, cm

K_p = partition coefficient.

Equation IV-129 reveals that desorption can be interpreted as a frontal phenomenon where desorption is completed at one location before progressing downstream. Based on this interpretation, an effective removal velocity of the front is:

$$U_e = \frac{U \delta}{M_s K_p} \quad (IV\text{-}130)$$

The time T_d required to desorb the toxicant over any specified distance is:

$$T_d = x_L / U_e \qquad \text{(IV-131)}$$

where

x_L = length of contaminated river segment.

During the period of desorption the average concentration in the water column is:

$$C = \begin{cases} \dfrac{X_0 \delta}{K_p D} & \text{for } x > U_e t & \text{(IV-132)} \\[3mm] 0 & \text{, otherwise} & \text{(IV-133)} \end{cases}$$

To use Equations IV-129 through IV-133, estimates for X_0, M_s, and δ are required. If both the mass of contaminated sediment per unit area of river bed (M_s) and the mass of toxicant in the sediments are known, then X_0 can be determined. Conversely, if both X_0 and the total mass of toxicant in the sediments are known, then M_s can be calculated.

In lieu of having data on M_s and δ, these quantities can be estimated based on the depth of contaminated sediments by using Table IV-39. In addition to the depth, the percent solids by weight must be estimated. This parameter generally increases with depths and can be chosen as 50 percent, unless better data are available. The data in Table IV-39 were derived from the following two equations:

$$M_s = \frac{D_c}{10 \left(1/S_s + \dfrac{100-P}{P} \right)} \qquad \text{(IV-134)}$$

and

$$\delta = \frac{S_s \times D_c \left(\dfrac{100-P}{P} \right)}{1 + S_s \left(\dfrac{100-P}{P} \right)} \qquad \text{(IV-135)}$$

where

M_s = mass of contaminated sediment, g/m^2
δ = equivalent water depth, mm
S_s = specific gravity of solids
D_c = depth of contamination, mm.

In cases where the depth of contamination exceeds 100 mm the equations can be used in lieu of Table IV-39.

The Hudson River in New York State provides an illustration of an extreme

TABLE IV-39

MASS OF CONTAMINATED SEDIMENTS AND EQUIVALENT WATER
DEPTH AS A FUNCTION OF DEPTH OF CONTAMINATION

Depth (mm)	Percent Solids by Weight	M_s (g/cm^2)	δ(mm)
1	20	0.02	0.9
	50	0.06	0.6
	80	0.11	0.3
5	20	0.11	4.5
	50	0.30	3.0
	80	0.55	1.4
10	20	0.23	9.1
	50	0.60	6.0
	80	1.1	2.7
20	20	0.45	18.
	50	1.2	12.
	80	2.2	5.5
50	20	1.1	45.
	50	3.0	30.
	80	5.5	14.
100	20	2.3	91.
	50	6.0	60.
	80	11.0	27.

case of PCB contamination (Turk, 1980). Between 1951 and 1977 PCBs were discharged from point sources near Fort Edward and Hudson Falls, about 80 km (50 mi) above Albany, New York. Figure IV-51 shows the general vicinity.

During this time period the mass emission rate of PCBs decreased from 15 kg/day (33 lbs/day) to less than 1 g/day (0.002 lbs/day). PCB concentration in the bottom materials range from about 200 μg/g near Fort Edward to about 4 μg/g near Waterford, about 70 km (43 mi) downstream. In 1975 the New York State Department of Environmental Conservation began a study to determine the source of contamination. At that time they estimated that the total mass of PCBs in the bottom sediments was 225,000 kg (500,000 lbs).

It has been found that PCBs are being naturally desorbed from the river bed under moderate and low flow conditions. The estimated transport rates are:

At Glen Falls   = 0.0 kg/day (above discharge)
At Schuylersville = 4.0 kg/day
At Stillwater   = 5.0 kg/day
At Waterford   = 4.0 kg/day (70 km downstream).

It is interesting to note that these transport rates are approximately 30 percent as
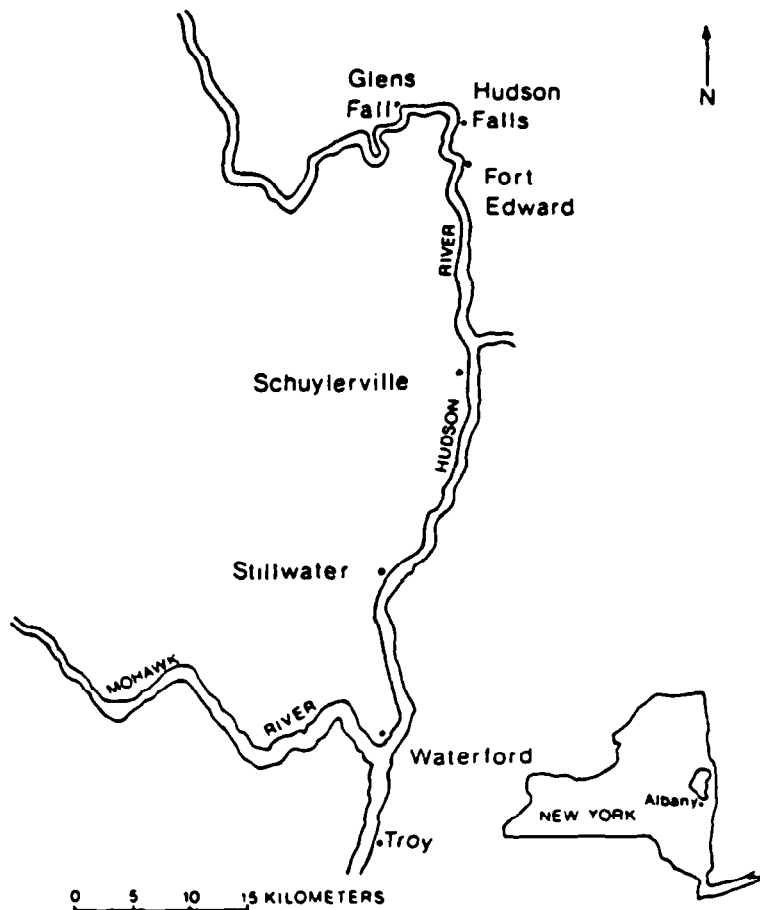
FIGURE IV-51   LOCATION MAP OF HUDSON RIVER, NEW YORK.

high as the original point source mass emission rates. At a desorption rate of about 4 kg/day, the river between Glen Falls and Waterford would be rid of PCBs in about 150 years.

Turk (1980) found that flood events transport large quantities of PCBs, although this transport mechanism is only operative periodically. Turk estimated that due to the combined removal rates of PCBs during high flow periods (by scour) and during low flow periods (by desorption), the residence time of PCBs above Waterford would be about one century.

─────────────── EXAMPLE IV-18 ───────────────

For discharges of 600 m^3/sec or less, it has been found that the Hudson River bed provides 4 kg/day of PCBs to the water column at locations between Schuylersville and Waterford, New York. Determine the PCB concentration in the water column at the following two flow rates:

a. 600 m³/sec

b. 50 m³/sec.

Compare these concentrations to the freshwater criterion of 0.001 µg/l promulgated in the "Red Book".

Since the mass emission rate and river flow rate are known, Equation IV-11 can be rearranged to yield the total instream concentration:

$$C_t = \frac{M}{86.4Q}$$

where

M = mass loading, kg/day

C_t = concentration of pollutant, ppm

Q = flow rate, m³/sec.

For the problem at hand:

M = 4 kg/day

Q = 50 and 600 m³/sec.

For Q = 600 m³/sec:

$$C_T = \frac{4}{86.4 \times 600} = 0.08 \times 10^{-3} \text{ ppm}$$

= 0.08 µg/l, or 80 times the Red Book criterion.

For Q = 50 m³/sec:

$$C_T = \frac{4}{86.4 \times 50} = 0.9 \times 10^{-3} \text{ ppm}$$

= 0.9 µg/l, or 900 times the criterion.

As a second part to the problem estimate the time required to remove the PCBs in the sediment by desorption (ignoring scour), assuming the desorption rate of 4 kg/day is not known. Base the calculations on Table IV-39 or Equations IV-130 and IV-131. Use the following data:

Depth of contaminated sediment = 600 mm

River velocity = 1 fps

Partition coefficient : 10^3 to 10^4

Because the depth of contamination exceeds the maximum value tabulated in Table IV-39, Equations IV-134 and IV-135 are used instead. Assuming S_s = 1.5 and P = 80:

$$M_s = \frac{600}{10\left(\frac{1}{1.5} + \frac{100-80}{80}\right)} = 65 \text{ g/cm}^2$$

$$\delta = \frac{1.5 \times 600 \left(\frac{100-80}{80}\right)}{1 + 1.5 \left(\frac{100-80}{80}\right)} = 160 \text{ mm} = 16 \text{ cm}$$

-438-

The effective transport velocity is:

$$U_e = \frac{U \times 16}{65 \times 10^4} = .25 \times 10^{-4} \, U \quad \text{for } K_p = 10^4$$

and

$$U_e = \frac{U \times 15}{65 \times 10^3} = .25 \times 10^{-3} \, U \quad \text{for } K_p = 10^3$$

The time required for desorption over the 70 km (43 mi) reach is:

$$T = \frac{43 \times 5280}{.25 \times 10^{-4} \times 1} \; \text{Sec} = 290 \; \text{year for } K_p = 10^4$$

and

$$T = 29 \; \text{years for } K_p = 10^3$$

Probably the biggest unknown in this problem is K_p. Based on a range of K_p from 10^3 to 10^4, the time of desorption ranges from 29 to 290 years, within the range predicted from observed desorption rates.

———————— END OF EXAMPLE IV-18 ————————————

4.9.3.5 Instantaneous Releases of Low Density Toxicants

Many toxicants have specific gravities less than or equal to unity. Should a toxicant less dense than water be spilled in its pure form, the toxicant can ride atop the water body for a period of time, while (perhaps) being rapidly volatilized and photolyzed as it becomes entrained and dissolved in the river.

Analysis of releases of low density pollutants is complicated and, in many cases, beyond the scope of hand calculation analyses. Often spills of toxicants occur over a part of the river, so the resultant movement is three-dimensional because the toxicant spreads laterally, longitudinally, and vertically due to turbulence and advection. Buoyant spreading and mixing can further complicate the dispersal process.

Toxicant spills can occur in numerous ways. In one instance the toxicant may be discharged directly onto the surface of the river, and depending on the rate of mixing with ambient water a significant portion could volatilize directly from the pure phase. On the other hand submerged spills may result in the chemical becoming mixed with river water before it reaches the water's surface. Under these circumstances volatilization fluxes will not be as great.

When a chemical is spilled in pure form, the time required for the chemical

It is worthwhile to calculate the volume of water required for a mass M of spilled chemical to be diluted to its solubility limit. This can provide a rough idea as to whether mixing is likely to be "instantaneous" or not. Suppose that a mass M of spilled chemical has a solubility C_s. The volume of water needed to be mixed with the pure chemical so that the solubility limit is achieved is:

$$V_o = \frac{M \times 10^8}{C_s} \qquad \text{(IV-138)}$$

where

M = mass of spill, kg

C_s = solubility, mg/l

V_o = volume of water, m^3

The concentration profile resulting from an instantaneous spill (and assuming concentrations at or below the solubility limit are rapidly attained) is expressed by:

$$C = \frac{M_D}{2A_c \sqrt{\pi D t}} \exp\left[\frac{-(x-ut)^2}{4Dt} - k_e t\right] + \frac{k_v'}{k_v' + \Sigma k_i} \cdot \frac{P}{K_H} \left[1 - \exp(-k_e t)\right] \qquad \text{(IV-139)}$$

where

C = dissolved phase concentration

$$k_e = \frac{k_v' + \sum k_i}{1 + K_p S}$$

$$M_D = \frac{M}{1 + K_p S}$$

M = total mass released

The remaining variables have been previously defined.

In most instances the user would like to predict the maximum concentrations remaining in the river for different elapsed times following the spill, given by the peaks in Figure IV-53. Under such conditions, and assuming $P = 0$, Equation IV-139 simplifies to:

$$C_{max} = \frac{M_D}{2A_c \sqrt{\pi D t}} \exp(-k_e t) \qquad \text{(IV-140)}$$

The various components of the mass balance at time t_s follow (for $P = 0$).

Mass of dissolved pollutants M_D $(t = t_s)$:

$$M_D (t = t_s) = M_D \exp(-k_e t_s) \qquad \text{(IV-141)}$$
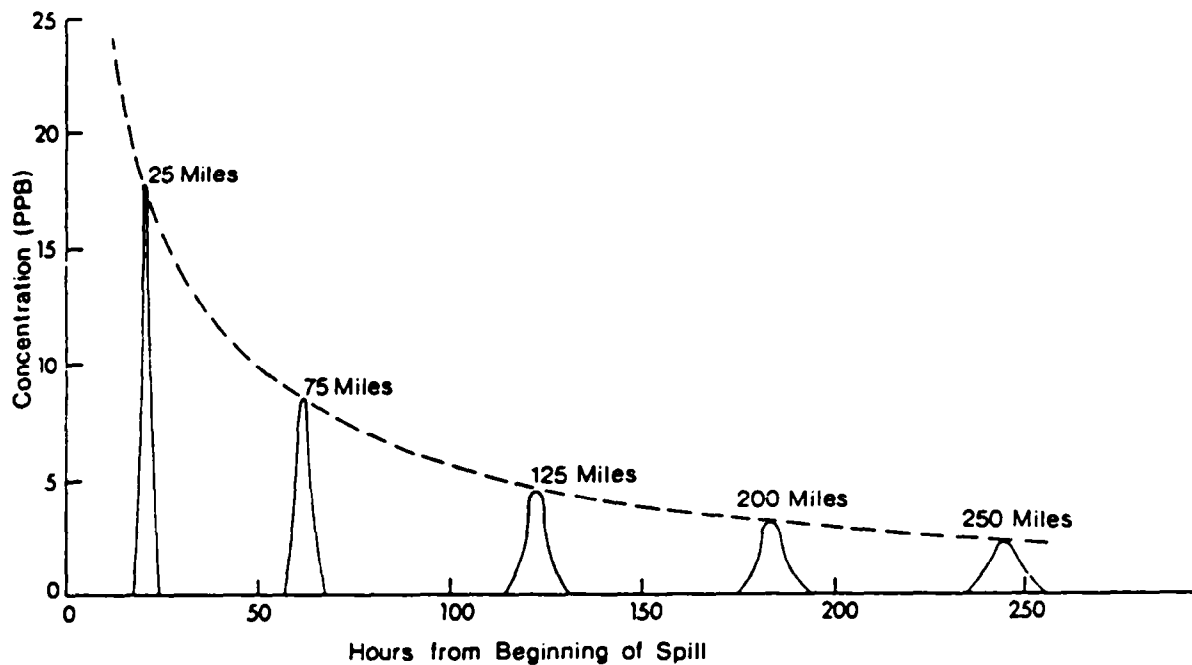
FIGURE IV-53 HYPOTHETICAL DISTRIBUTION OF TOXICANT AT VARIOUS LOCATIONS FOLLOWING A SPILL

Mass of sorbed pollutants M_s $(t = t_s)$:

$$M_s \; K_p S \; M_D \; \exp \; (-k_e t_s) \tag{IV-142}$$

Mass of pollutant which was volatilized M_v $(t = t_s)$:

$$M_v \; (t = t_s) = \frac{M_D \; k'_v}{k_e} \left[1 - \exp(-k_e t_s) \right] \tag{IV-143}$$

Mass of pollutant which has decayed M_{Dk} $(t = t_s)$:

$$M_{Dk} \; (t = t_s) = \frac{M_D \Sigma k_i}{k_e} \left[1 - \exp(-k_e t_s) \right] \tag{IV-144}$$

Equations IV-140 through IV-144 allow the user to assess the fate of the pollutant for any desired time t_s following the spill.

A direct extension of the instantaneous pollutant release in a plane is the volumetric release, where the pollutant is effectively released within some initial

volume of water. For this case, the dissolved phase concentration is:

$$C = \frac{M_D}{2V_0} \left[erf \left(\frac{X - Ut}{\sqrt{4Dt}} \right) - erf \left(\frac{X - L - Ut}{\sqrt{4Dt}} \right) \right] \left(exp(-k_e t) \right) \qquad (IV-145)$$

where

L   = length of zone of initial contamination

erf = the error function

All other variables have been previously defined.

The location of the maximum concentration for any time t_s after release is approximately given by:

$$x = Ut_s + L/2 \qquad (IV-146)$$

4.9.3.6 Spill Analysis of High Density Toxicants

Spills of hazardous chemicals have been of concern for quite a number of years, and interest will increase as the quantity and variety of toxicants transported increase. In past years the primary emphasis has been on analysis and containment of oil spills. This has probably been for a number of reasons:

- Large quantities of oil are transported, and are therefore subject to more frequent spills.

- The environmental consequences of an oil spill can be severe and visually offensive.

- Oil floats, so oil spills are easy to detect and monitor.

In contrast to oil, many hazardous chemicals have specific gravities greater than one, so that in their pure form, they tend to sink in water. Table IV-40 lists some such chemicals. Chlorine, although it may be transported under pressure as a liquid, is a gas under atmospheric conditions. Even so, if a liquid chlorine barge were involved in an accident on a river some of the chlorine could become dissolved in the water since the solubility of chlorine in water is 50,000 mg/l, although most would probably gasify and form a toxic cloud.

The chemicals shown in Table IV-40 are generally either slightly soluble (10 to 10,000 ppm) or soluble (10,000 to 1,000,000 ppm). In any case the solubility levels generally exceed or greatly exceed proposed water quality criteria. Thus if a mass of chemical were spilled into a river, it is to be expected that concentrations near the chemical's solubility limit could be detected in the immediate vicinity of the spill. As the chemical is dissolved and travels downstream, it could eventually become mixed over the channel cross-section and expose all organisms living within the water column (and perhaps those living in the bedded sediments as well) to its effects. With increasing distance the concentrations of the toxicant will decrease to reflect the additional mixing afforded by the flow of the entire river, plus

TABLE IV-40
WATER-SOLUBLE, HIGH DENSITY ($\rho>1$), IMMISCIBLE CHEMICALS

Species	Density in air (g/cm³)	Solubility in water (mg/l)	Interfacial Tension (dynes/cm)[a] Air	Water	Vapor
Acetic acid	1.06	50.000	$68.0_{30°}$	-	$27.8_{20°}$
Acetic anhydride	1.087	500,000	-	-	$32.7_{20°}$
Acetophenone	1.03	5,550	-	-	$39.8_{20°}$
Aniline	1.022	34,000	44.0	-	$42.9_{20°}$
Benzaldehyde	1.04	1,000	40.04	$15.51_{20°}$	-
Benzyl alcohol	1.043	46,000	$39.0_{20°}$	$4.75_{22.5°}$	$39.0_{20°}$
Bromine	2.93	41.700	$41.5_{20°}$	-	$41.5_{20°}$
Carbon disulfide	1.26	2,200	-	$48.36_{20°}$	-
Carbon tetrachloride	1.595	500	-	$45_{20°}$	$26.95_{20°}$
Chlorine (liquid)[b]	3.2	50,000	-	-	$18.4_{20°}$
Chloroform	1.5	5,000	$27.14_{20°}$	$32.8_{20°}$	-
Chloropthalene			-	$40.74_{20°}$	-
Dichloroethane	1.256	9,000	$23.4_{35°}$	-	-
Ethyl bromide	1.431	10,600	-	$31.2_{20°}$	$24.15_{20°}$
Ethylene bromide	2.18	4,300	-	$36.54_{20°}$	$38.37_{20°}$
Furfural	1.159	83,100	$43.5_{20°}$	-	$43.5_{20°}$
Glycerol	1.26		-	$63.4_{18°}$	-
Hydrogen peroxide	1.46	50,000	-	-	$76.1_{18.2°}$
Mercury[c]	13.54	.0005	470	$375_{20°}$	-
Naphthalene	1.15	30	$28.8_{127°}$	-	$28.8_{127°}$
Nitrobenzene	1.205	:900	$43.9_{20°}$	-	$43.9_{20°}$
Phenol	1.071	67,000	$40.9_{20°}$	-	$40.0_{20°}$
Phenylhydrazine	1.097		-	-	$46.1_{20°}$
Phosphorus trichloride	1.5	50,000	-	-	$29.1_{20°}$
Trichloroethane	1.325	10	$22_{144°}$	-	-
N-Propylbromide	1.353	2,500	-	-	$19.65_{20°}$
Quinoline	1.095	60,000	$45.0_{20°}$	-	-
Tetrachloroethane	1.60	3,000	$36.3_{22.5°}$	-	-
Water[b]	1.00	N.A.	$73.05_{18°}$	N.A.	72

a In air, water, and its own vapor. Temperature is °C.

b Under pressure.

c Mercury and water data included for reference.

From: Thibodeaux (1979)

dispersion, degradation, and volatilization processes.

A technique is presented here to estimate the concentration which can exist in the water column and the duration of the elevated levels following a spill. In particular tools are presented to predict:

- The concentration of toxicant in the water column at the downstream end of the spill
- The concentration of the toxicant after it has become completely mixed with the entire river
- The time required to dissolve the spilled toxicant
- The amount of toxicant remaining sorbed to the bottom sediments and in the pore water following dissolution.

It is, of course, more accurate but more costly to measure concentrations directly rather than predicting them. However, since the toxicant is "somewhere" on the river bottom, and might not be immobile, detecting the location of the toxicant will take time. By estimating the dissolution time of the spill, it can be determined if it is feasible to even set up and carry out a sampling program.

The tools delineated above are useful not only to analyze spills which have occurred, but also for answering hypothetical questions which relate to the consequence of spills based on river traffic, sizes of containers, kinds of toxicants being transported, and characteristics of the rivers. Based on this information the user can evaluate possible "spill scenarios" to predict impacts before they occur. Such information would be useful to formulate post-spill responses. In situations where a spill of a toxicant would produce extreme consequences, provisions could be made to mitigate the consequences before they occur.

4.9.3.6.1 Description of Spill Process

Spills which contaminate rivers can be the result of a variety of accidents: leaking barges, broken pipelines, highway accidents, and clandestine dumping. The scope here is limited to those situations where the toxicant has been deposited on the bottom of the river. This situation is most likely to result from an accident on or under the water's surface. Figure IV-54 conceptualizes what might happen when a barge carrying a high density pollutant ruptures.

Depending on the volume of contaminant, the size of the hole, among other factors, the toxicant might issue from the barge as a continuous jet. However, because the volumetric flow rate of the jet is probably small, and perhaps even intermittent, the toxicant probably breaks up into drops of various sizes as it falls through the water column. Some of the finest drops might never reach the stream bed, but rather be transported in suspension within the water column, and gradually dissolve. The majority of the toxicant may settle on the river bed and form drops, globs, or pools (using the terminology of Thibodeaux, 1979). The drop
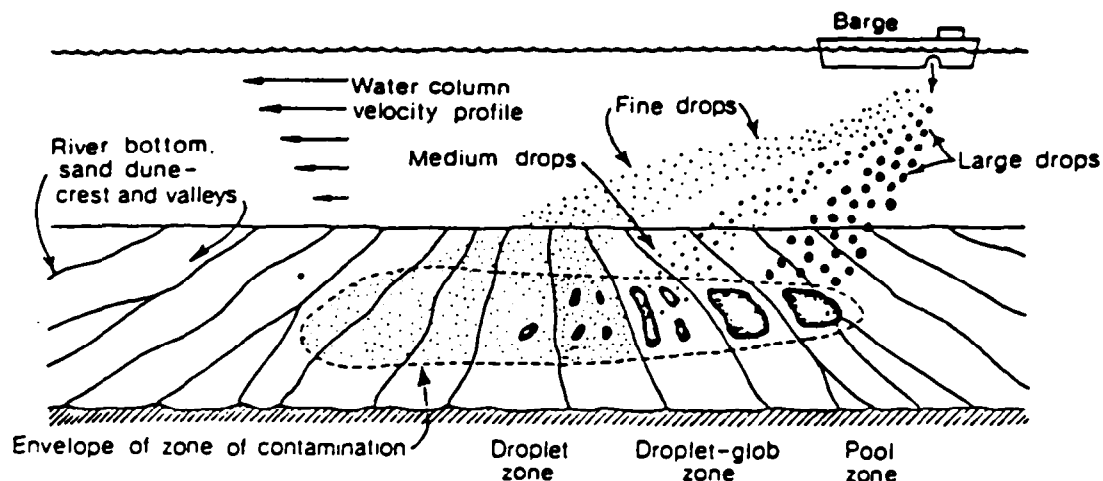
FIGURE IV-54   ILLUSTRATION OF HYPOTHETICAL SPILL INCIDENT
(FROM THIBODEAUX, 1979).

size depends on the intrafacial tension and density differences between the toxicant and the water (Hu and Kintner, 1955). Pools tend to form in the valleys of sand waves, and occur when large drops or globs coalese. Thibodeaux (1980) provides techniques to estimate the residence time of drops, globs, and pools. For the simplified analyses here the spill is assumed to be in the shape of a continuous pool.

4.9.3.6.2 Fate of Pollutant Following Settling

Once the toxicant has settled on the river bed its fate is governed by numerous processes. Depending on the texture of the bottom materials (e.g. sands, cobbles, boulders), the density of the toxicant, and its interfacial tension, the toxicant could settle in deep depressions, and dissolution would be slowed.

Many pollutants have large partition coefficients so that sorption to bottom sediments is significant. The characteristics of the sediments affect the partition coefficient, but in many cases sorption can compete with dissolution as a major process controlling the pollutant's fate. Although transformation processes other than sorption and dissolution are operative the moment the toxicant enters the water, they are not considered here.

In September 1974 an electrical transformer being loaded onto a barge fell into the Duwamish Waterway in the State of Washington (Thibodeaux, 1980). 250 gallons of Aroclor 1242, a PCB mixture of specific gravity 1.4, were spilled into the river. Divers observed that pools of free PCB on the bottom moved back and forth with the tide. Pools of PCBs were removed from the bottom using suction dredges, and a second stage operation involved a high solids dredge. Probably due to its low solubility (0.2 ppb) and high sorption characteristics, much of the PCB was recovered (from 210 to 240 gallons).

4.9.3.6.3 Predictive Tools

It is hypothesized that a toxicant spill contaminates an area of width W_s and length L_s, where the length is measured in the flow direction. The toxicant which reaches the river bed is assumed to be highly concentrated, and its dissolution is controlled by a thin layer immediately above where molecular diffusion limits the vertical flux of the pollutant. Above this layer the toxicant is rapidly entrained into the river. There are several expressions available to determine the thickness of the diffusion layer (e.g. Novotny, 1969 and Mills, 1976). The expression developed by Mills will be used here, because the required information is easier to attain while the two approaches appear to give comparable results. The expression is:

$$\delta_d = \frac{11.6 \cdot 1.49 \, \nu \, R_h^{1/6}}{\sqrt{g} \, Un} \qquad \text{(IV-147)}$$

where

$\quad \delta_d \quad$ = thickness of diffusive sublayer

$\quad \nu \quad$ = dynamic viscosity of water

$\quad R_h \quad$ = hydraulic radius of the river

$\quad U \quad$ = river velocity

$\quad n \quad$ = Manning's coefficient.

Just downstream from the spill zone, but before complete mixing with the river, the concentration of the toxicant in the water column is:

$$C_L = (C_0 - C_s) \exp \left(-\frac{D_{cw} L_s}{\delta_d H U} \right) + C_s \qquad \text{(IV-148)}$$

where

$\quad C_0 \quad$ = background concentration of chemical

$\quad C_s \quad$ = solubility of chemical in water

$\quad D_{cw} \quad$ = diffusion coefficient of chemical in water

$\quad H \quad$ = water depth

$\quad U \quad$ = river velocity.

The concentration at the location of complete mixing is:

$$C_{WM} = C_L \cdot \frac{W_s}{W} + C_0 \left(1 - \frac{W_s}{W} \right) \qquad \text{(IV-149)}$$

where

$\quad W_s \quad$ = spill width

$\quad W \quad$ = river width.

The time T_d required to dissolve the chemical is:

$$T_d = \frac{M_D}{C_L \cdot U \cdot H \cdot W_s}$$

(IV-150)

where

M_D = total amount of pollutant which is dissolved (an amount less than or equal to the amount spilled).

As the spilled toxicant dissolves in the flowing river water, it concurrently diffuses into the immobile bedded sediments, where a portion is sorbed onto the sediments. Consequently, some residual toxicant will remain in the bottom sediments following the initial dissolution phase. The residual will then slowly diffuse and desorb back out into the river, although diffusion deeper into the sediments can also occur because of the concentration gradient. The time required for the residual toxicant to naturally desorb and diffuse back into the water column can greatly exceed the original period of dissolution.

The quantity of toxicant which resides in the sediments following the initial dissolution period can be predicted as follows. It is assumed that the dissolution and downward diffusion/sorption proceed independently until all the spilled toxicant has been removed. The time t can be found such that this statement is true. From a practical standpoint, the user can simply determine the time required for complete dissolution, and then find the total mass which would have diffused/sorbed into the bottom sediments during this period. Since this approach accounts for more toxicant than was originally present, the time period should be decreased by the fractional amount of toxicant created. If the amount of excess toxicant is no more than 15 percent of the total amount spilled, then a time adjustment is not required.

Based on the processes of sorption and diffusion the vertical profile of dissolved chemical in the river bed at time t following the appearance of the toxicant on the bottom is given by:

$$\frac{C - C_b}{C_s - C_b} = 1 - \text{erf} \left(\frac{z}{\sqrt{4 D_p t}} \right)$$

(IV-151)

where

C = concentration of dissolved chemical in the pore water, in units of mass of dissolved chemical per unit volume of pore water

C_b = background concentration of chemical in pore water

C_s = solubility of chemical in water

z = vertical distance, measured downward from the sediment-water interface

$$D_p = D_e \left/ \left(1 + \rho_s K_p \frac{1-n}{n} \right) \right.$$

D_e = effective molcular diffusion coefficient

ρ_s = density of sediments

K_p = partition coefficient

n = porosity of porous medium.

From Equation IV-151, the total mass of pollutant found in the sediments at time t is:

$$M_T = \int \left(C + C_s\right) n dV \qquad \text{(IV-152a)}$$

$$= A_c n \int \left(C + C_s\right) dZ \qquad \text{(IV-152b)}$$

where

A_c = spill area

C_s = concentration of pollutant sorbed to sediments, per unit volume of pore water.

C_s can be related to C by:

$$C_s = C \rho_s K_p \left(\frac{1-n}{n}\right) \qquad \text{(IV-153)}$$

Combining Equations IV-151, IV-152 and IV-153 the total mass in the sediment is:

$$M_T = 0.563_n C_s \left(1 + \rho_s k_p \; \frac{1-n}{n}\right) A_c \sqrt{4D_p t} \qquad \text{(IV-154)}$$

———————————————— EXAMPLE IV-19 ————————————————

The following is an excerpt from __Chemical Engineering__ Volume 80, September 3, 1973, as reported in Thibodeaux (1979).

"Approximately 1.75×10^6 lbs of chloroform were released
from a barge that sank near Baton Rouge, Louisiana, and the
chemical began flowing down the Mississippi River toward the
Gulf of Mexico. Although state health officials did not push
the panic button, noting that they did not anticipate too much
trouble from the accident, the U.S. Coast Guard warned downriver
communities to keep a close surveillance on their water supply
systems, particularly if intakes were close to the river bottom
(chloroform is heavier than water)."

Based on the low flow conditions and the time history of the chloroform concentra-

tion much of the chloroform (of specific gravity 1.5) was initially deposited on the river bed. Determine the fate of the chloroform during the first few days following the spill. The following processes are considered:

- Dissolution into the main body of the water
- Diffusion and sorption into the bottom sediments
- Volatilization into the atmosphere
- Sorption to suspended sediments.

Since chloroform is highly volatile and does not have a strong tendency to sorb to solids, volatilization is an important process controlling its fate, while sorption is not. The following analysis substantiates this statement.

The data pertinent to the spill are (Thibodeaux, 1979; Neely et al., 1976):

River flow rate = 7590 m^3/sec (268,000 cfs)

Width of river = 1220 m = 4000 ft

River velocity = 56.3 cm/sec = 1.85 ft/sec

Water depth = 11 m = 36.3 ft

Diffusion coefficient of chloroform in water = 1×10^{-5} cm^2/sec

Length of spill zone = 180 m = 590 ft

Background chloroform concentration = 5 ppb.

Using a Manning's n of 0.03, the diffusion layer thickness is:

$$\delta = \frac{11.6 \times 1.49 \times .915 \times 10^{-5}}{\sqrt{32.2} \times 1.85 \times 0.03} \times (36)^{1/6} = 9 \times 10^{-4} \text{ ft} = 2.8 \times 10^{-2} \text{ cm}$$

The average concentration of chloroform in the water just below the spill zone during the period of dissolution is:

$$C_L = (5 \times 10^{-3} - 8200) \exp\left(\frac{-1. \times 10^{-5} \times 180}{2.8 \times 10^{-2} \times 11. \times 56.3}\right) + 8200$$

$$= 850 \text{ ppb}$$

In order to estimate the time required to dissolve the chloroform the average width of the spill zone is required. The width is estimated to be 256 ft (78 m) (Thibodeaux, 1981).

Based on these data the dissolution time is:

$$T_d = \frac{0.9 \times 1.75 \times 10^6}{5.38 \times .850 \times 1.85 \times 156 \times 36.3} = 20 \text{ days}$$

The factor 0.9 is used in the above expression because about 10 percent of the spill dissolved before ever reaching the bottom (Neely et al., 1976).

The amount of chloroform which diffused and sorbed into the sediments

during this time period (20 days) will be estimated. The porosity of the sandy bottom is approximately 0.35, and the partition coefficient is assumed to be 1.0. This is a realistic value based on K_{ow} = 93 (see Table II-5). The total mass contained in the sediments after 20 days is:

$$M_{Total} = .35 \ (180 \times 78) \ \left(1+2.65 \times 1 \times \frac{.65}{.35}\right) 8200 \sqrt{\frac{4.10^{-5} \times 20 \times 86400}{1 \times 2.65 \times 1 \times \frac{.65}{.35}}}$$

$$\times \ 10^{-2-3} \times (5-4.437) \ \cong 6000 \ kg$$

6000 kg is less than 2 percent of the total mass which reaches the bottom (715,000 kg). Based on this result, it is not likely that the dissolution period is markedly affected by diffusion of the chloroform into the bottom sediments. Because of the vertical concentration gradient that has been established in the sediment profile, some of the chloroform will temporarily continue to diffuse downward after the dissolution period. Hence concentrations in the water column due to desorption of the chloroform and upward diffusion back into the water column are not likely to be high compared to those observed during the initial dissolution period.

Following the chloroform spill, chloroform concentrations were measured at several locations in the Mississippi River below the spill. Figure IV-55a shows the time history of the chloroform concentration at a location 16.3 miles below the spill for the first 60 hours following the spill. A more compressed time scale is shown in Figure IV-55b and illustrates how the concentrations varied for 20 days following the spill. The peak concentration passes very rapidly (on the order of 1 day) and the maximum observed concentration is about 365 ppb. At this location, the chloroform is approximately well-mixed with the river at this point (Neely et al., 1976).

Based on Figure IV-55b the total amount of chloroform passing the location can be estimated as follows:

$$Mass = \int CQdt = Q \int Cdt$$

The right-most integral is simply the area under the concentration-time curve in Figure IV-55b. Without showing the calculations, the total mass of chloroform (above background) which passes the location 16.3 miles below the spill is about 300,000 kg. Since the total amount of chloroform spilled was about 800,000 kg, more than half of the chloroform was unaccounted for. It is unlikely, as earlier calculations showed, that diffusion and sorption into the bottom sediment was significant. Volatilization could be important and will be discussed shortly.
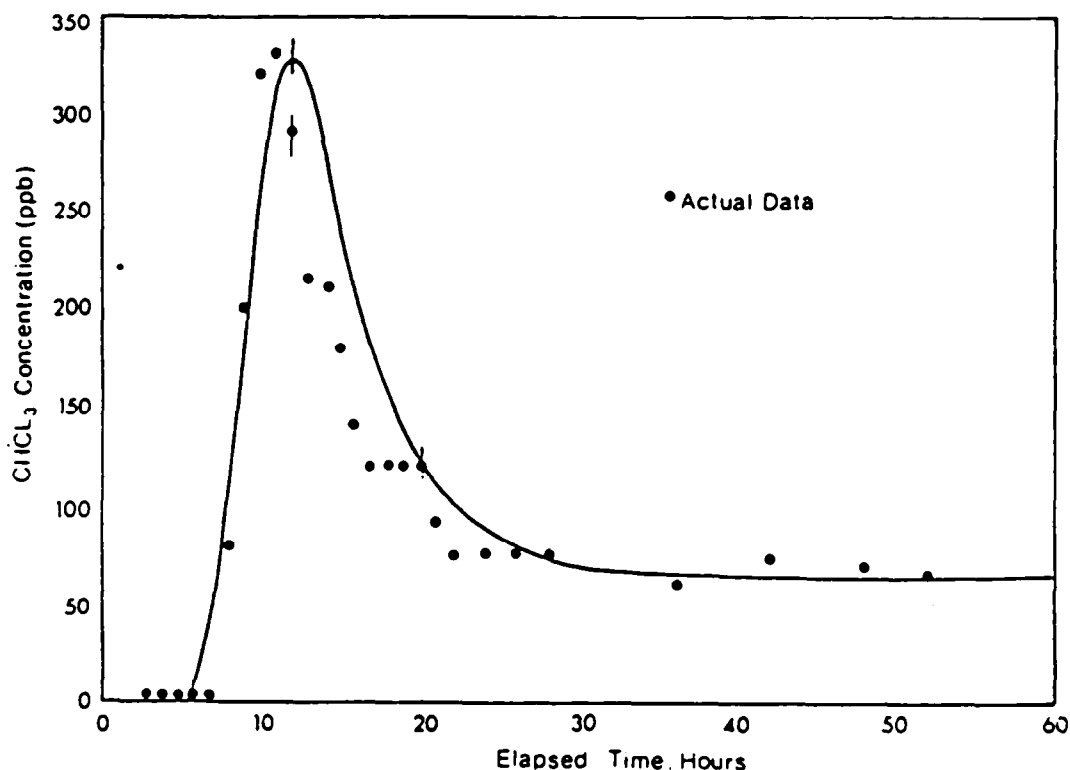
FIGURE IV-55A   CHLOROFORM CONCENTRATION IN WATER COLUMN
FOR FIRST 60 HOURS FOLLOWING A SPILL
16.3 MILES UPSTREAM.

The observed results shown in Figure IV-55a are compared against those predicted in this example. A concentration of 850 ppb was predicted just below the spill site; the maximum shown in Figure IV-55a is 365 ppb. It is expected, for several reasons, that the concentrations 16.3 miles below the spill site will be less than at the spill site. First it is probable that additional dilution occurred as the chloroform was transported to the sampling site. An estimate of the dilution can be attained by multiplying the river width by the spill width, or:

$$\frac{4000}{260} = 15$$

The well-mixed concentration becomes:

$$\frac{850}{15} = 60 \text{ ppb}$$

Comparing this to Figure IV-55a, it is noted that this value approximates the average concentration following an elapsed time of about 20 hours, but misses the peak during the first 20 hours. There may be a number of factors responsible for
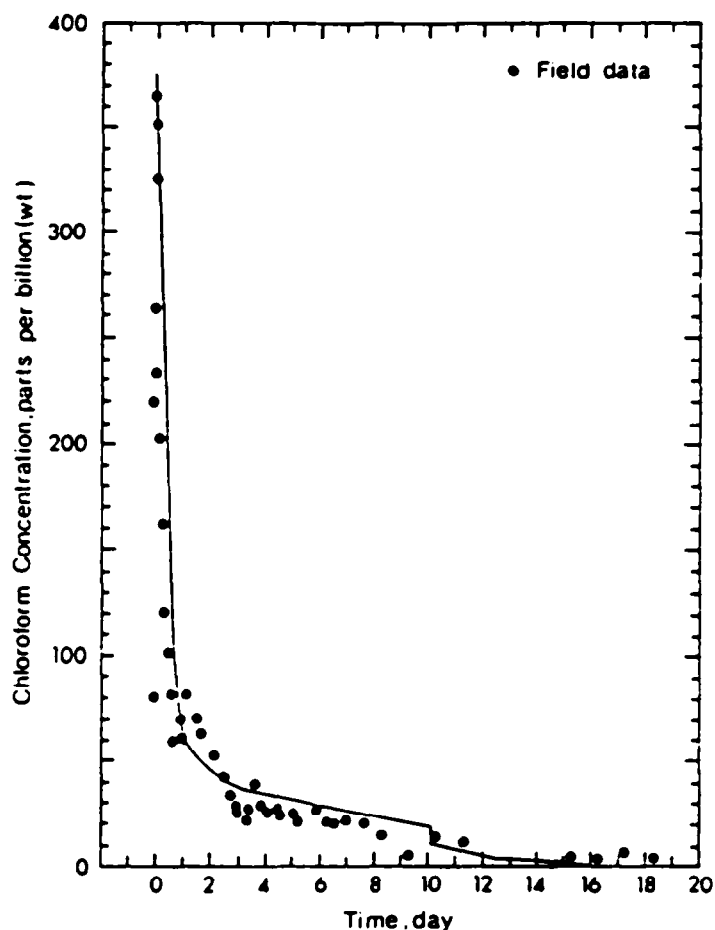
FIGURE IV-55B   CHLOROFORM CONCENTRATION IN THE
                MISSISSIPPI RIVER AT A LOCATION 16.3
                MILES BELOW THE AUGUST 19, 1973 SPILL.

this behavior, and one of the most important will be examined here. During the
spill of chloroform, it was estimated that about 10 percent, or 80,000 kg were
transported downstream directly without ever reaching the river bottom. The
travel time to the sampling site is:

$$\frac{16.3 \text{ mi}}{1.26 \text{ mph}} = 13 \text{ hours}$$

Figure IV-55a shows that this coincides with the arrival of the peak at mile
16.3. The peak concentration can be estimated using Equation IV-140 presented
earlier. The diffusion coefficient is approximately 210 m^2/sec (McQuivey
et al., 1976) for the lower Mississippi River. The predicted peak in concentration
at mile 16.3 is:

$$C = \frac{80000 \times 10^3}{2 \times 4000 \times 36.3 \times (.3048)^2 \sqrt{\pi \cdot 210 \cdot 3600 \cdot 13}} = 520 \text{ ppb}$$

This concentration is somewhat higher than the maximum 365 ppb observed, but this is to be expected since Equation IV-140 assumes the mass is input instantaneously, while in reality about 8 hours elapsed. Further if the concentration due to the dissolved portion of the spill is calculated at 20 hours, a concentration of 15 ppb is obtained. This illustrates that the mass due to initial dissolution has almost passed the sampling location, and the remaining contribution to the elevated concentrations measured is due largely to dissolution of chloroform which has settled on the river bottom. It appears that there are two basic phenomena which account for the measured concentration-time profile: an initial period of dissolution of chloroform (less than 1 day) before it settles to the bottom, and a subsequent period (10 to 15 days) of dissolution of settled chloroform.

The absence of an adequate mass balance between the amount of chloroform which entered the river as a result of the spill and the amount which passed a location 16.3 mi below the spill has not been addressed. Volatilization losses could be one reason for the imbalance.

Equation IV-123 can be used to estimate the volatilization losses. Since the chloroform was initially deposited on the bottom of the river, during a portion of the travel distance it was not in contact with the atmosphere, and so volatilization could not occur. The approximate travel time for vertical mixing to occur is (Fischer et al., 1979):

$$t = \frac{0.4\ H^2}{\varepsilon_z}$$

where

H = water depth

ε_z = vertical diffusivity.

Choosing an ε_z value of 50 cm^2/sec, based on Fischer et al. (1979) and a depth of 11 m, the travel time required to effect vertical mixing is:

$$t = \frac{0.4\ (1100)^2}{50 \cdot 3600}\ \text{hr} = 2.7\ \text{hrs}$$

Based on a velocity of 1.85 ft/sec, the travel distance is about 3.3 miles. Hence the pollutant is in contact with the atmosphere for about 13 miles.

Since only the dissolved phase of chloroform volatilizes, the fraction of the total chloroform as solute will be estimated using Equation IV-109:

$$C = \frac{C_t}{1 + k_p \cdot S}$$

The partition coefficient K_p was estimated as 1.0. The sediment concentration is about 400 ppm. Hence:

$$\frac{C}{C_t} = \frac{1}{1 + 1 \times 400 \div 10^{-6}} \approx 1.0$$

Thus, essentially all the chloroform is dissolved and is available for volatilization.

Henry's Law constant for chloroform can be found based on the data in Table II-5:

Vapor pressure = 150 Torr

Solubility in water = 8200 ppm

Molecular weight = 118.

Henry's Law constant is:

$$\frac{150 \times 118}{760 \times 8200} = 3 \times 10^{-3} \frac{atm \cdot m^3}{mole}$$

From Table II-15 a typical volatilization rate is about 17 cm/hr.

The average chloroform concentrations for the 13 miles above the data collection point are:

200 ppb for 1 day

40 ppb for the next 9 days

10 ppb for the next 9 days.

The total amount of chloroform volatilized is (using Equation IV-109):

$$\Sigma \, k_v \, C_i \, A_c \, \Delta t$$

$$= 0.17 \times 24 \times 1200 \times 21 \times 10^3 (200 + 40 \times 9 + 10 \times 9 - 5 \times 19) \times 10^3$$

$$= 5.8 \times 10^7 \, g = 58000 \, kg$$

Hence, all of the unaccounted for chloroform (about 480,000 kg) could not have volatilized within 13 miles.

Over 50 percent of the chloroform still remains unaccounted for. It is possible that other transformation processes were operative. The environmental fate of chloroform in terms of photolysis, hydrolysis, oxidation, and biological degradation was reviewed in Callahan et al., 1979. It was concluded that these processes are of minor importance compared to volatilization and so are probably not significant here.

It is possible that the samples of chloroform shown in Figure IV-55b were not cross-sectional averages. The chloroform concentration could have been weighted toward the stream bottom or toward one side. A dye study performed by McQuivey (1976) on the lower Mississippi River showed that 50 miles were required before complete mixing was attained, while the sampling was conducted 16.3 miles below the spill. Even though chloroform does not sorb strongly, there is a possibility that the suspended solids and bed load concentration near the bottom of the river were high enough to cause substantial sorption. Based on the evidence there is a distinct possibility that some of the "missing" chloroform was actually advected past the sampling locations without being detected.

—————————— END OF EXAMPLE IV-19 ——————————

4.10 METALS

4.10.1 Introduction

4.10.1.1 Background

In addition to organic chemicals, metals comprise a second major category of toxic contaminants which are discharged into rivers. Metals differ from toxic organics in a number of ways, and these differences influence the approach used to predict their fate. One difference is that metals are naturally occurring elements and their fate can be detailed individually since the number of different elements is relatively small. In contrast, an individualized approach is not always feasible for the thousands of organic toxicants. However, basic properties of many organic chemicals have been tabulated or are derivable which can be used to predict their fate.

Two, organic chemicals are occasionally spilled into rivers because many of the chemicals are transported in large volumes. Metals, on the other hand, most often enter rivers from continuous sources. Consequently, methods to handle spills, while being an integral part of the screening procedures presented for organic toxicants in the previous section, are not emphasized here.

Three, metals are naturally occurring and are cycled throughout the environment by biogeochemical processes. Consequently it is _not_ appropriate to arbitrarily ignore background concentrations of metals, an approach reasonable for synthetic organic toxicants. Background sources of metals can produce concentrations which, in certain instances, approach water quality standards.

Four, the fate of many metals is predominantly controlled by transport processes since they generally do not degrade, volatilize, or photolyze as do many organic toxicants (although there are exceptions). However, metals do speciate into many different forms in the aquatic environment, and the species may differ in toxicity and behavior.

4.10.1.2 Organization

Screening methods presented in Section 4.10.3 can be used to predict the fate of metals. These tools assume that metals are distributed between two basic phases: dissolved and adsorbed. Linear partitioning is used to represent equilibrium adsorption and thus to quantitatively relate the two phases.

In Section 4.10.4, a detailed analysis of the speciation of arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc (As, Cd, Cr, Cu, Pb, Hg, Ni, Ag, and Zn, respectively) is presented. The major processes affecting speciation are delineated, and the equilibrium model MINEQL is used to predict the speciation of the above solutes for 14 different rivers and an acidified lake in the United States.

Simulated metal concentrations vary from background to well above the 1984 U.S. EPA water quality criteria.

While the tools presented in Section 4.10.3 can be used independently of metal species distribution predicted by MINEQL, the two approaches can be coupled together to estimate species concentrations at different locations throughout a river. The steps required to accomplish this are described at the end of Section 4.10.4.

Because of the potential importance of background contributions of metals, methods are presented in Section 4.10.2 to address this problem. Since background sources can be significant, this contribution should not be arbitrarily dismissed.

Numerous case studies of metals in rivers in the eastern and western United States are also reviewed. The reviews may help the user to understand how metals respond to different aquatic conditions and to establish concentration ranges which have been documented in past studies.

Finally, in Section 4.10.5, guidance is provided for a limited field sampling program and river/stream reconnaissance. A primary reason for suggesting a low-level data collection program is a concession to the difficulty of predicting metal concentrations in rivers. Although users are not required to perform a field study before doing the screening analyses, in some instances they may decide a limited field study is appropriate.

The data requirements for the screening methods are summarized in Table IV-80 of Section 4.10.5. Because degradation or removal rates are not required for the screening analyses, the data requirements are somewhat more modest than for organic toxicants. The more important data are flow rates, loading rates, background levels, and partition coefficients. Section 4.10.5 provides more discussion on the relative importance of the data requirements. A summary of the screening methods for metals is shown in Figure IV-56. An application and summary of the methods has recently been published (Mills and Mok, 1985). Also, many of the algorithms presented in Section 4.10 have been programmed for microcomputers (Mills, et al., 1985).

4.10.2 Water Quality Criteria, Background Concentrations, and Case Studies

4.10.2.1 Water Quality Criteria

Table IV-41 summarizes the most current U.S. EPA criteria (Federal Register July 29, 1985 and November 28, 1980) for the protection of freshwater aquatic life for arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc. The 1984 criteria pertain to arsenic, cadmium, chromium, copper, lead, and mercury. The 1980 criteria pertain to nickel, silver, and zinc. Many of the criteria depend on water hardness. Examples are shown in the table for hardnesses of 50, 100, and 200 mg/l as $CaCO_3$. At the bottom of the table, expressions relating hardness to the water quality criteria are shown. Note that the water quality criteria are expressed as total dissolved metal.
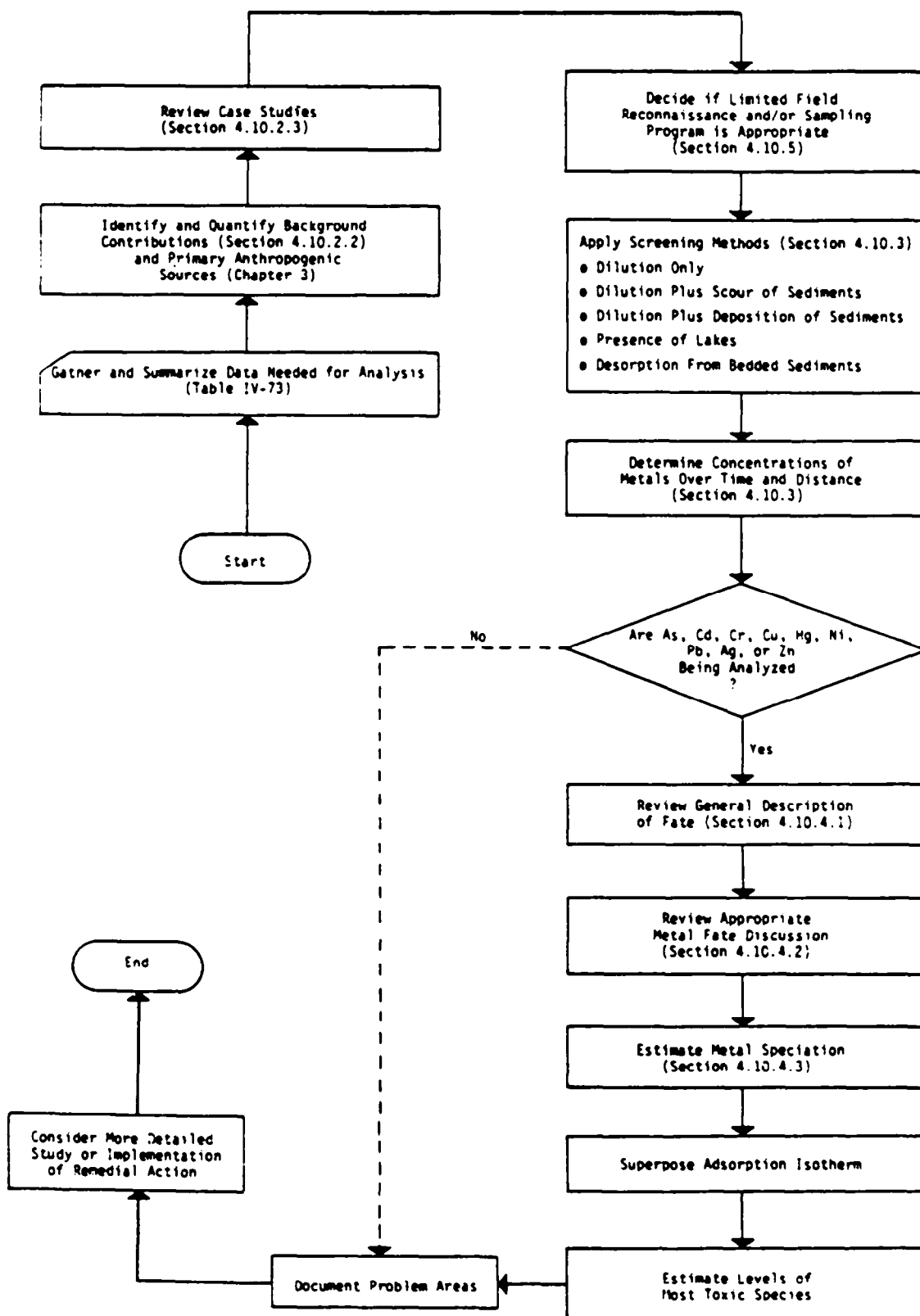
FIGURE IV-56   SUMMARY OF SCREENING PROCEDURES FOR METALS IN RIVERS

TABLE IV-41

WATER QUALITY CRITERIA FOR SELECTED PRIORITY METALS FOR
PROTECTION OF FRESHWATER AQUATIC LIFE
(1980 and 1985 U.S. EPA Criteria)

Total Dissolved Metal[a]	4 day Average Concentration Not to Be Exceeded More Than Once Every 3 Years[b,c]	1 hour Average Concentration Not to Be Exceeded More Than Once Every 3 Years[b,c]
Arsenic (trivalent inorganic)	190	360
Cadmium	0.66, 1.1, 2[c]	1.8, 3.9, 8.6[c]
Chromium (hexavalent)	11	16
Chromium (trivalent)	120, 210, 370[c]	980, 1700, 3100[c]
Copper	6.5, 12, 21[c]	9.2, 18, 34[c]
Lead	1.3, 3.2, 7.7[c]	34, 83, 200[c]
Mercury	0.012	2.4
Nickel	56, 96, 160[c] (30 day average)	1100, 1800, 3100[c] (instantaneous maximum)
Silver	-	1.2, 4.1, 13[c] (instantaneous maximum)
Zinc	47 (30 day average)	180, 320, 570[c] (instantaneous maximum)

[a]The total dissolved metal is defined to be "acid soluble". No approved methods are presently available. The total recoverable method is recommended.

[b]The water quality criteria (g/l) are related to water hardness (mg/l as $CaCO_3$) as:

Arsenic: independent of hardness

Cadmium = $\exp (0.7852 (\ln (hardness)) -3.49)$, 4-day average
$\exp (1.128 (\ln (hardness)) -3.828)$, 1-hour average

Chromium (VI): independent of hardness

Chromium (III) = $\exp (0.819 (\ln (hardness)) + 1.56)$, maximum, 4-day average
$\exp (0.819 (\ln (hardness)) + 3.688)$, 1-hour average

Copper = $\exp (0.8548 (\ln (hardness)) -1.465)$, 4-day average
$\exp (0.9422 (\ln (hardness)) -1.464)$, 1-hour average

Lead = $\exp (1.266 (\ln (hardness)) -4.661)$, 4-day average
$\exp (1.266 (\ln (hardness)) -1.416)$, 1-hour average

Mercury: independent of hardness

Nickel = $\exp (0.76 (\ln (hardness)) +1.06)$, 30-day average
$\exp (0.76 (\ln (hardness)) +4.02)$, maximum at any time

Silver = $\exp (1.72 (\ln (hardness)) -6.52)$, maximum at any time

Zinc = $\exp (0.83 (\ln (hardness)) +1.95)$, maximum at any time

[c]The three water quality criteria are examples for total hardness levels of 50, 100, and 200 mg/l as $CaCO_3$.

4.10.2.2 Background Levels of Metals

4.10.2.2.1 Introduction

In contrast to most organic toxicants which are not initially present in the environment, metals occur naturally and cycle by biogeochemical processes throughout the environment. Consequently, of the metals that may be present in a stream or river, a small fraction, a moderate fraction, or nearly all might be from natural sources.

When trace metal concentrations in streams are analyzed to see whether water quality standards are violated, and whether wasteload allocation schemes are required, a knowledge of background sources should be included as a part of the analysis. Background sources can be defined to include both natural sources and sources produced by man which are transported across watershed boundaries (e.g. dry deposition of metal-enriched ash). Background sources can also be thought of as sources which are not readily controllable, and thus contributions from these sources are likely to be present regardless of the remedial action chosen.

In this section, coverage of background sources is limited to weathering from rocks and riparian soils. Typical values of metal concentrations are provided. However, metals are not uniformly distributed throughout the environment but can be locally enriched in natural deposits. Should a river intersect a mineral deposit, the levels of metals in the stream from this source can be high. Contributions of background sources can be quantified by sampling upstream of the locations of major anthropogenic influence.

4.10.2.2.2 Stream Contributions From Rocks and Soils

Tables IV-42 and IV-43 summarize data which show typical concentrations of metals and inorganics in soils and rocks. The soil samples from New Jersey and New York in Table IV-42 are generally similar to average concentrations in the earth's crust. However, deviations can occur locally, so these numbers should be used with caution. Soil Conservation Service soil surveys might provide data on levels of metals in local soils. Chapter 3 also provides additional data.

Concentrations of metals in streams from the background sources can be estimated from the following formula:

$$C_b = X \cdot S \cdot 10^{-3} \qquad \text{(IV-155)}$$

where

    X = metals concentration in soils, $\mu g/g$

    S = background instream suspended solids concentration, mg/l

    C_b = total metal concentration in the stream due to the soil and rock particles in suspension and may include a dissolved component, $\mu g/l$.

As an example, suppose a stream has a background suspended solids level of 40 mg/l. Based on a typical zinc concentration of 90 $\mu g/g$ in soils,

TABLE IV-42

TYPICAL CONCENTRATIONS OF METALS IN SEVERAL SOILS
AND IN THE EARTH'S CRUST
(Values in $\mu g/g$)

Metal	Soils in New Jersey[a]	Soils in Upstate New York[b]	Average in Earth's Crust[c]
Ag	--	--	0.5
As	--	--	5.0
Cd	--	0.2	0.15
Cr	9.3	--	10.-100.
Cu	40.5	21.6	4.-55.
Hg	--	--	0.005.-1.0
Ni	11.9	--	80.
Pb	86.8	7.9	15.
Zn	96.3	79.9	50.

[a]Kubota et al. (1974).

[b]Wilber and Hunter (1979).

[c]Weast (1977).

$$C_b = 40 \cdot 80 \cdot 10^{-3} = 3 \ \mu g/l \text{ of zinc}$$

This is less than 10 percent of the U.S. EPA criteria level of 47 $\mu g/l$ (Table IV-41). However, for some of the other metals (e.g. copper), typical contributions from background sources can approach the 30-day criteria.

For a number of the metals (Cr, Cu, Ni, Pb, and Zn), background levels of about 1 $\mu g/l$ are common. For Ag, Cd, and Hg, background levels are probably closer to 0.1 $\mu g/l$, or even less.

4.10.2.3 Case Studies of Metals in Rivers

4.10.2.3.1 Introduction

This section provides a sampling of case studies of metals in rivers. Case studies help to reveal important master variables which control the fate of metals.

TABLE IV-43

AVERAGE CONCENTRATION OF METALS IN VARIOUS TYPES OF ROCK AND DEEP OCEAN SEDIMENTS
(Values in μg/g)

	Plutonic				
			Granitic		
	Ultramafic	Basaltic	Plagioclase	Orthoclase	Syenite
Chromium	1.6×10^3	170	22	4.1	30
Manganese	1.62×10^3	1.5×10^3	540	370	850
Iron	9.4×10^4	8.65×10^4	2.64×10^4	1.42×10^4	3.67×10^4
Cobalt	150	48	7	1.0	1
Nickel	2.0×10^3	130	15	4.5	4
Copper	10	87	30	10	5
Zinc	50	105	60	39	132

	Sedimentary Rock			Deep Ocean Sediments	
	Shale	Sandstone	Carbonate	Carbonate	Clay
Chromium	90	35	11	11	90
Manganese	850	100	1.1×10^3	1.0×10^3	6.7×10^3
Iron	4.72×10^4	9.8×10^3	3.8×10^3	9.0×10^3	6.5×10^4
Cobalt	19	0.3	0.1	7	74
Nickel	68	2.0	20	30	225
Copper	45	1	4	30	250
Zinc	95	16	20	35	165

From: Rubin, 1976.

Since there are potentially _many_ processes which influence the behavior of metals in aquatic systems (see Section 4.10.4.1), elimination of processes of secondary importance is beneficial in screening analyses.

Some of the questions which users are likely to pose during a fate analysis are:

- Is downstream transport of metals important? That is, do metals move downstream in the water column significant distances below their points of entry or are they rapidly deposited and/or adsorbed in the bedded sediments so that water column concentrations are rapidly depleted?

- Are the metals in the water column present in adsorbed or dissolved form? Dissolved species are likely to be more toxic and can be transported further than the particulate form of the metal.

- What is the relationship between water column concentrations and concentrations in the bedded sediments? Metal concentrations in bedded sediments are often found to far exceed those in the water column.

- What metals are typically present in rivers in the highest concentrations?

- What is the effect of a reservoir (or large backwater region) on the metal concentrations further downstream?

- Is metal desorption from bottom sediments likely to occur as a result of decreased water column concentrations? Desorption is a natural cleansing mechanism, but may also take a significant period of time (e.g. 1 to 5 years for several stream miles). During the period of desorption, a low level of metal is maintained in the water column.

A review of case studies often provides insights into resolving these questions, and others which arise during the course of a study. Methods to address each of these questions are presented in Section 4.10.3, and general qualitative answers to these questions are provided in Section 4.10.3.3.

Before discussing individual case studies, the U.S. Geological Survey's NASQAN network is briefly mentioned. Through the USGS's National Stream Quality Accounting Network (NASQAN), water quality samples are collected at approximately 345 stations throughout the United States (Briggs and Ficke, 1977). Among the quality parameters measured are arsenic, cadmium, chromium, copper, lead, mercury, selenium, and zinc. The data contained in Briggs and Ficke (1977) are summarized in Tables IV-44 and IV-45.

Note that the upper limits of the measured concentrations for cadmium, chromium, copper, lead, and zinc are, at times, close to U.S. EPA criteria for instantaneous maximum levels (see Table IV-41). The upper levels measured for mercury occasionally exceed the suggested criteria of 4.1 μg/l (instantaneous maximum). These results suggest that cadmium, chromium, copper, lead, zinc, and mercury often require careful investigation on a site-by-site basis.

TABLE IV-44

RANGES OF CONCENTRATIONS OF DISSOLVED MINOR ELEMENTS MEASURED AT NASQAN STATIONS DURING THE 1975 WATER YEAR,
SUMMARIZED BY WATER RESOURCES REGIONS (Briggs and Ficke, 1977)[a]

Region Number and Name	Range of Concentrations (µg/l)							
	Arsenic (As)	Cadmium (Cd)	Chromium (Cr)	Copper (Cu)	Lead (Pb)	Mercury (Hg)	Selenium (Se)	Zinc (Zn)
01 New England	0.0-3[b]	0.0-10	0.0-20	0.0-20	0.0-45	0.5	0.0-1	0.0-40
02 Mid-Atlantic	.0-3	.0-5	.0-70	.0-30	.0-42	.0-1.3	.0-2[b]	.0-130
03 South Atlantic-Gulf	.0-3	.0-7	.0-11	.0-18	.0-73	.0-2.0	.0-1	.0-100
04 Great Lakes	.0-5	.0-5	.0-20	.0-24	.0-35	.0-1.1	.0-3	.0-80
05 Ohio	.0-5	.0-23[b]	.0-10[b]	.0-100	.0-34	.0-0.5	.0-2	.0-260
06 Tennessee	.0-2	.0-2	.0-1	1-8	.0-9	.0-0.3	.0	.0-40
07 Upper Mississippi	.0-5	.0-5	.0-10	.0-20	.0-38	.0-1.2	.0-3	.0-190
08 Lower Mississippi	.0-4	.0-190	.0-10	.0-25	.0-10	.0-0.5	.0-2	.0-90
09 Souris-Red-Rainy	.0-7	.0-2	.0-10	.0-13	.0-6	.0-0.2	.0-2	.0-30
10 Missouri Basin	.0-65	.0-8	.0-40	.0-320	.0-16	.0-9.0	.0-6[b]	.0-360
11 Arkansas-White-Red	.0-10	.0-8	.0-20	.0-80	.0-50	.0-8.2[b]	.0-25	.0-460
12 Texas-Gulf	.0-17	.0-1	.0-30	.0-8	.0-34	.0-0.3	.0-7	.0-210
13 Rio Grande	.0-13	.0-1	.0-20	.0-12	.0-20	.0-1.0	.0-2	.0-60
14 Upper Colorado	.0-18	.0-2	.0-40	1-46	.0-23	.0-0.6	.0-16	.0-70
15 Lower Colorado	.0-20	.0-3	.0-20	.0-35	.0-12	.0-0.4	.0-13	.0-70
16 Great Basin	.0-48	.0-1	.0-20	.0-11	.0-6	.0-1.8	.0-4	.0-40
17 Pacific Northwest	.0-11	.0-10	.0-40[b]	.0-30	.0-43	.0-0.3	.0-1	.0-300
18 California	.0-32	.0-3	.0-40	.0-80	.0-48	.0-1.6	.0-4	.0-150
19 Alaska	.0-4	.0-1	.0-30	1-10	.0-10	.0-1.8	.0-1	.0-80
20 Hawaii	.0-8	.0-1	.0-10	.0-5	.0-11	.0-0.2	.0-1[b]	.0-20
21 Caribbean	.0-1	.0-5	.0-1	.0-34[b]	.0-17[b]	.0-0.3	.0	.0-40

[a] Figure IV-90 shows the locations of these regions.

[b] The maximum concentration shown exceeds the maximum total metal concentration reported in Table IV-45.
No explanation is provided in Briggs and Ficke.

TABLE IV-45

RANGES OF TOTAL CONCENTRATIONS OF MINOR ELEMENTS MEASURED AT NASQAN STATIONS DURING THE 1975 WATER YEAR, SUMMARIZED BY WATER RESOURCES REGIONS (Briggs and Ficke, 1977)[a]

Region Number and Name	Range of Concentrations ($\mu g/l$)							
	Arsenic (As)	Cadmium (Cd)	Chromium (Cr)	Copper (Cu)	Lead (Pb)	Mercury (Hg)	Selenium (Se)	Zinc (Zn)
01 New England	0.0-2[b]	0.0-19	0.0-70	0.0-30	0.0-100	0.0-1.1	0.0-2	0.0-150
02 Mid-Atlantic	.0-9	.0-1	.0-70	.0-30	.0-57	.1-1.3	.0-1[b]	.0-190
03 South Atlantic-Gulf	.0-50	.0-50	.0-50	.0-40	.0-100	.0-2.2	.0-3	.0-440
04 Great Lakes	.0-11	.0-20	.0-20	.0-170	.0-100	.0-1.1	.0-3	4-320
05 Ohio	.0-6	.0-22[b]	.0-20[b]	.0-110	.0-250	.0-1.2	.0-3	.0-600
06 Tennessee	.0-5	.0-13	.0-10	3-40	2-130	.0-0.9	.0-2	10-80
07 Upper Mississippi	.0-31	.0-20	.0-40	.0-460	1-200	.0-2.1	.0-3	10-380
08 Lower Mississippi	.0-14	.0-840	.0-160	.0-120	.0-200	.0-0.5	.0-4	.0-230
09 Souris-Red-Rainy	.0-10	<10-20	.0-20	<10-60	<100-200	.0-0.6	.0-2	6-110
10 Missouri Basin	.0-2300	.0-40	.0-250	.0-610	1-600	.0-11	.0-5[b]	.0-1900
11 Arkansas-White-Red	.0-240	.0-40	.0-290	2-550	.0-400	.0-1[b]	.0-34	.0-870
12 Texas-Gulf	.0-200	<10-50	.0-120	<10-180	<100-200	.0-1.2	.0-8	.0-710
13 Rio Grande	.0-140	.0-30	.0-150	<10-210	<100-500	.0-1.7	.0-7	.0-920
14 Upper Colorado	.0-56	<10-20	.0-140	<10-1400	<100-200	.0-0.6	.0-21	20-690
15 Lower Colorado	1-110	<10-20	.0-90	<10-480	<100-300	.0-0.8	.0-14	.0-470
16 Great Basin	.0-50	.0-40	.0-20	.0-270	<100-300	.0-2.6	.0-4	.0-580
17 Pacific Northwest	.0-20	.0-20	.0-10[b]	.0-2300	<100	.0-1.5	.0-4	.0-360
18 California	.0-220	.0-30	.0-1100	.0-4500	<100-300	.0-1.1	.0-4	.0-1600
19 Alaska	.0-11	<10	.0-20	10-140	<100	.0-2.2	.0-1	10-90
20 Hawaii	.0-10	<10	.0-60	.0-1000	<100-200	.0-0.9	.0-2[b]	10-110
21 Caribbean	.0-2	.0-20	10	.0-29[b]	.0-15[b]	.0-0.3	.0	.0-170

[a] Figure IV-90 shows the locations of these regions.

[b] The maximum concentration shown is less than the maximum dissolved concentration reported in Table IV-44. No explanation is provided in Briggs and Ficke.

4.10.2.3.2 Case Studies

The following case studies illustrate a range of metal concentrations which are present in rivers and streams in the United States. The case studies are summarized in Table IV-46. A number of different source types are represented.

4.10.2.3.2.1 Flint River, Michigan

The Flint River study in Michigan (Delos et al., 1983) provides a detailed account of the fate of zinc, cadmium, and copper in the river. Results of the study are used in Section 4.10.3 to compare against predictions made by the analytical screening procedures in this document.

During the Flint River study, zinc, cadmium, and copper were analyzed in a 60 km (37 mile) stretch of the river. Data were collected in August 1981, December 1981, and March 1982. The watershed is both agricultural and urban. Two wastewater treatment plants provide the main sources of metals within the study reach (in addition to the flux of metal across the upstream boundary).

Table IV-47 summarizes the reported average metal concentrations and average suspended solids levels. The metal concentrations shown in the table are the range of averages at the locations sampled (typically 5 to 9 stations in the 60 km reach). Zinc and cadmium levels are generally below the criteria levels of 47 μg/l and 2.0 μg/l, respectively, and copper is near its criterion level.

In most cases, the levels of metals in the water column do not decrease substantially with distance downstream. Figure IV-57 illustrates the total and dissolved copper levels during the August 1981 survey. Wastewater discharges are present at km 41 and km 71. Only minor sources are present between these locations.

4.10.2.3.2.2 Chattanooga Creek, Tennessee

Chattanooga Creek is tributary to the Tennessee River and is 42 km (20 miles) in length. The basin is significantly industrialized and contains 18 permitted industrial sources, as well as agricultural and domestic discharges. Past studies indicate that the creek is degraded by both conventional and toxic pollutants. The September 1980 study of Milligan et al. (1981) report that the creek is contaminated with organic and inorganic toxicants. Their findings related to metals are summarized here.

Figure IV-58 shows the 12 sampling locations selected in the lower 15 km of the creek. The priority metals detected in the water column and in the sediments are summarized in Table IV-48. The metal concentrations are generally indicative of contaminated conditions. Mercury levels in the water column (0.3 to 0.9 μg/l) are above the 1984 U.S. EPA criteria for the protection of aquatic life (0.2 μg/l for chronic toxicity). Chromium and zinc levels are near their criteria limits. Levels in the water column appear to be fairly constant over distance. As noted by Milligan

Table IV-46

SUMMARY OF CASE STUDIES

Location	Source of Metal	Metals	Concentrations Measured in Water?	Bed?	EPA Chronic Criteria Exceeded?	Downstream Transport Important?
Flint River, MI	wastewater	Zn, Cd, Cu	Yes	No	No	Yes
Chattanooga Creek, TN	industrial	Cr, Hg, Zn, As,	Yes	Yes	Hg, Zn	Yes
North Fork Holston River, VA	chloralkali plant	Hg	Yes	Yes	Hg	Yes
Slate River, CO	mine drainage	As, Cd, Cr, Cu, Pb, Ni, Ag, Zn	Yes*	No	As,* Cd,* Cu*	Yes
Saddle River, NJ	urban	Pb, Zn, Cu, Ni,	No	Yes	--	not documented
Cayuga Watershed, NY	rural	Pb, Cd, Zn, Cu	Yes	No	No	not documented

*Acute criteria exceeded.

TABLE IV-47

SUMMARY OF METAL AND SUSPENDED SOLIDS CONCENTRATIONS IN FLINT RIVER, MICHIGAN

Study Period	Suspended Solids (mg/l)	Zinc (µg/l)			Cadmium (µg/l)			Copper (µg/l)		
		Total	Particulate	Dissolved	Total	Particulate	Dissolved	Total	Particulate	Dissolved
August 1981	4.-13.	8.-24.	6.-20.	4.-12.	0.05-0.16	0.04-0.1	0.02-0.12	2.5-8.	1.-4.	2.-4.
December 1981 (Run 1)	8.-15.	5.-14.	2.-11.	4.-14.	0.05-0.15	0.02-0.08	0.00-0.15	2.-5.	1.-2.	2.-4.
December 1981 (Run 2)	6.-22.	6.-30.	2.-22.	2.-8.	0.02-0.13	0.01-0.08	0.00-0.08	2.-15.	1.-7.	1.-3.
March 1982	16.-24.	7.-17.	4.-8.	4.-6.	0.02-0.06	0.01-0.02	0.00-0.02	2.2-5.2	0.5-1.5	2.-2.5
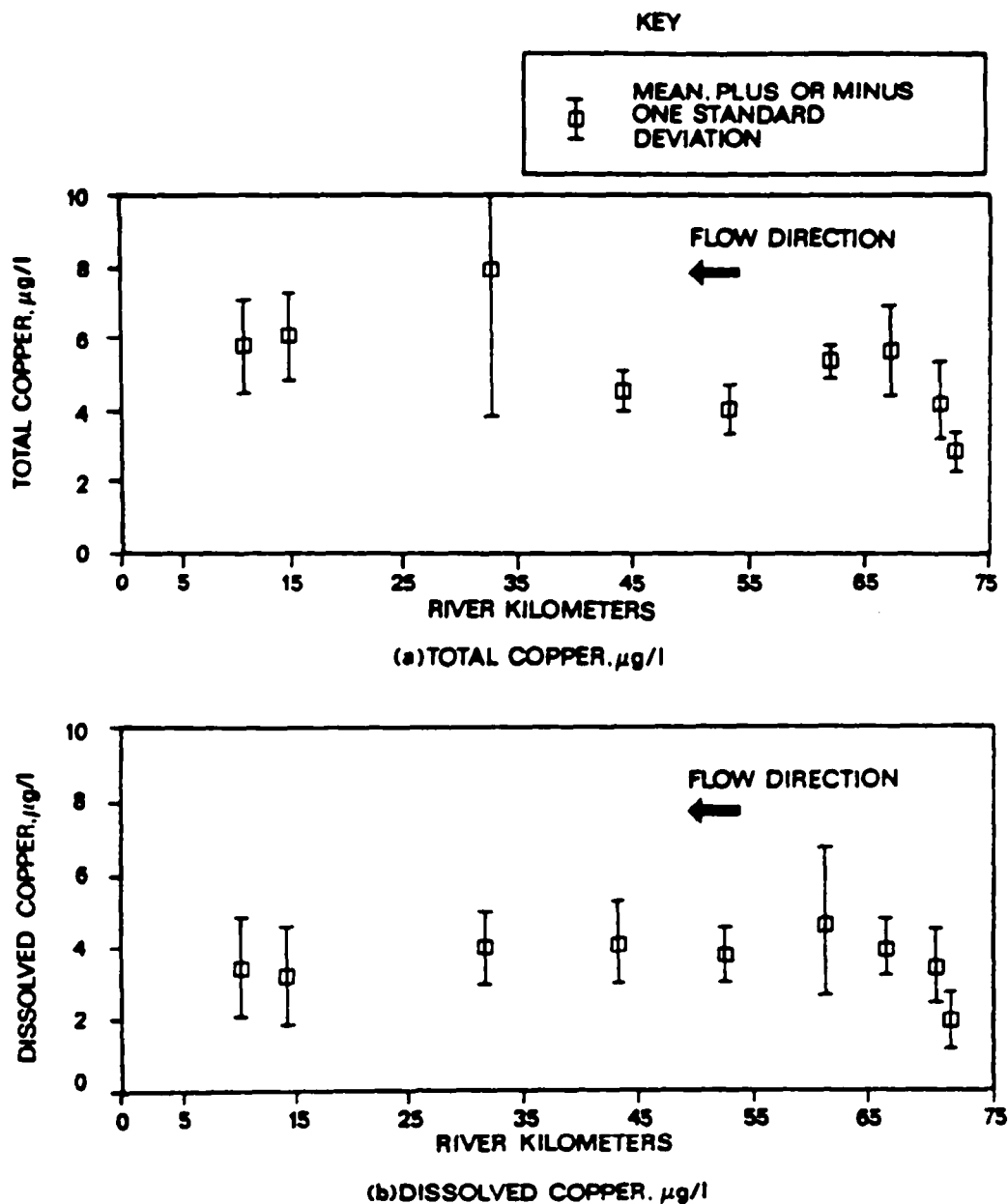
FIGURE IV-57   MEASURED TOTAL AND DISSOLVED COPPER CONCENTRATIONS
IN FLINT RIVER, MICHIGAN, DURING AUGUST 1981 SURVEY.

et al. (1981), the levels of metals in the sediments are from 2 to 50 times nigner
than levels measured in the Tennessee River sediments, which suggest that the source
of metal contamination in Chattanooga Creek is local.

4.10.2.3.2.3 North Fork Holston River, Virginia

Wastes from an inactive chloralkali plant closed in 1972 and located on the
North Fork Holston River continue to contaminate both the water column and bottom

-470-
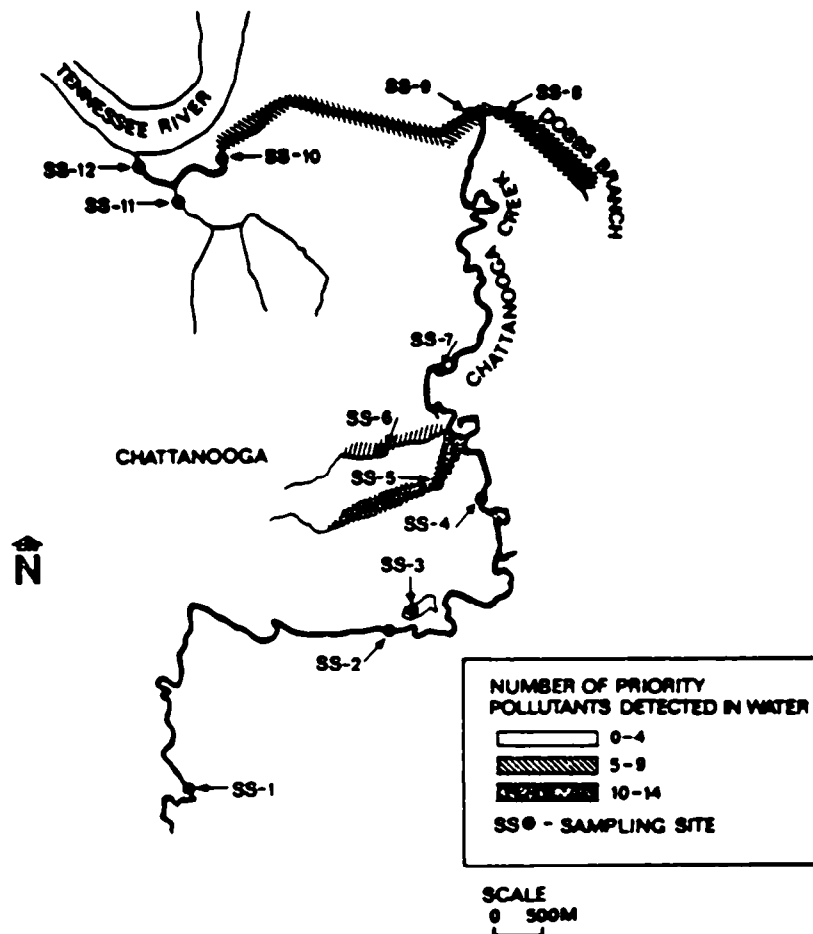
FIGURE IV-58   EXTENT OF PRIORITY POLLUTANT CONTAMINATION IN CHATTANOOGA
                CREEK WATERS.

sediments of the river (Turner and Lindberg, 1978). The river is a fast-flowing mountain stream with a coarse, rocky substrate in many areas, but with silt and clay substrates in backwater regions.

Two large settling ponds at the plant site drain into the river and provide the source of contamination. Upstream of the ponds the levels of mercury are low. Below the plant, the levels increase significantly, as shown in Table IV-49. Upstream of the plant, the mercury in the water column averages 0.008 μg/l, while downstream, the average is 0.15 μg/l, a 20-fold increase. Approximately a third of the mercury below the discharge is in dissolved form.

Plots of total mercury in the water column versus distance below the waste discharge were developed by Turner and Lindberg for low and high flow rates. They are shown in Figure IV-59. They plotted predicted levels of mercury versus distance, assuming that the mercury behaves conservatively in the water column. At high flow, the mercury appears to be conservative while at low flow rates, some loss of mercury

TABLE IV-48

INORGANIC PRIORITY POLLUTANTS DETECTED IN CHATTANOOGA CREEK, SEPTEMBER 1980

	Station Number and Chattanooga Creek Mile												
	1	2	3	4	5	6	7A	7B	8	9	10	11	12
Compound	9.1	6.6	Pond (6.3)	5.2	Unnamed Tributary (4.5)	(4.5)	(4.15)	(4.15)	Dobbs Brook (2.2)	2.1	0.6	Unnamed Tributary (0.3)	0.1
Water Column Samples (µg/l)													
Chromium, total	-	-	-	142.	-	-	-	-	-	-	-	-	-
Mercury, total	0.3	0.3	0.3	0.3	0.8	0.9	0.5	0.4	0.9	0.9	0.4	0.5	0.3
Zinc, total	19.	31.	29.	22.	55.	140.	24.	23.	52.	30.	38.	40.	43.
Sediment Samples (µg/g)													
Arsenic, total	0.2	4.1	3.0	13	13.0	8.5	2.0	2.4	2.	4.	1.7	1.2	1.2
Beryllium, total	0.295	0.56	0.48	0.5	0.6	0.7	0.7	0.7	0.5	0.5	0.3	0.4	0.8
Cadmium, total	--	-	-	1.7	1.7	-	-	-	1.2	0.4	1.9	4.0	2.4
Chromium, total	21.	20.	33.	98.	110.	76.	24.0	37.	35.	59.	25.0	12.0	26.0
Copper, total	2.4	8.6	6.7	140.	27.4	11.7	7.4	8.2	32.9	28.6	33.0	48.0	33.0
Lead, total	7.04	26.	21.	66.	37.	38.	10.	16.	232.	106.	140.	250.	150.
Mercury, total	0.85	0.98	0.49	240.	64.4	3.5	0.01	0.9	1.8	2.3	0.24	1.8	0.88
Nickel, total	10.3	23.	12.	18.	7.0	11.0	10.	11.	16.	21.	13.0	20.1	14.5
Selenium, total	-	-	-	-	-	2.5	-	-	-	-	-	-	-
Silver, total	-	-	-	1.0	0.6	-	-	-	0.6	0.4	1.7	1.6	1.7
Zinc, total	25.	45.	29.	230.	83.0	62.	37.	46.	234.	154.	380.	1,100.	340.

TABLE IV-49

MERCURY CONCENTRATIONS IN WATER, SUSPENDED MATTER, AND BED SEDIMENTS
IMMEDIATELY UPSTREAM AND DOWNSTREAM OF FORMER CHLORALKALI PLANT
ON NORTH FORK HOLSTON RIVER

	Water Column (μg/l)		Suspended Particulate Hg	Bottom Sediment Hg[a]
Statistic	Total Hg	Dissolved Hg	(μg/g)	(μg/g)
Upstream				
Mean	0.008	0.001	0.41	0.13
Standard Deviation	0.004	--	0.17	0.03
Number Samples	10.	9.	7.	7.
Downstream				
Mean	0.15	0.05	7.6	19.3
Standard Deviation	0.05	0.02	3.8	1.2
Number Samples	11.	11.	10.	3.

[a]Silt-clay fraction only.

from the water column is evident. In both cases, however, mercury is transported far downstream (120 km) in significant concentrations.

Further down the river, at km 155 (not shown in the figure), is a large impoundment - Cherokee Lake. Much of the suspended sediments settle in this lake and take the adsorbed mercury with them. Mercury in the surficial sediments ranges from about 0.47 μg/g to 2.4 μg/g. These levels are expected based on the levels of mercury found in the suspended matter in the North Fork Holston River (Table IV-49).

4.10.2.3.2.4 Slate River, Colorado

Slate River, Colorado, is one of a number of rivers and creeks (see Table IV-50) investigated in a cooperative effort by U.S. EPA's Environmental Monitoring Systems Laboratory, Las Vegas, Nevada. The purpose of the investigations was to study degradation and recovery of biological communities in streams where the toxic metal concentrations exceed the U.S. EPA's 1980 recommended acute criteria for aquatic life. The Slate River study is summarized here as an example (Janik et al., 1982).

Figure IV-60 shows the station locations on the Slate River and its tributary, Coal Creek, where drainage from the Keystone Mine enters the creek. Locations

Graph (a) HIGH FLOW: TOTAL Hg (μg/l) vs RIVER KILOMETERS, Q = 28.7 m³/sec, showing OBSERVED and PREDICTED (Dilution Model) curves.

Graph (b) LOW FLOW: TOTAL Hg (μg/l) vs RIVER KILOMETERS, Q = 1.56 m³/sec, showing PREDICTED (Dilution Model) and OBSERVED curves.
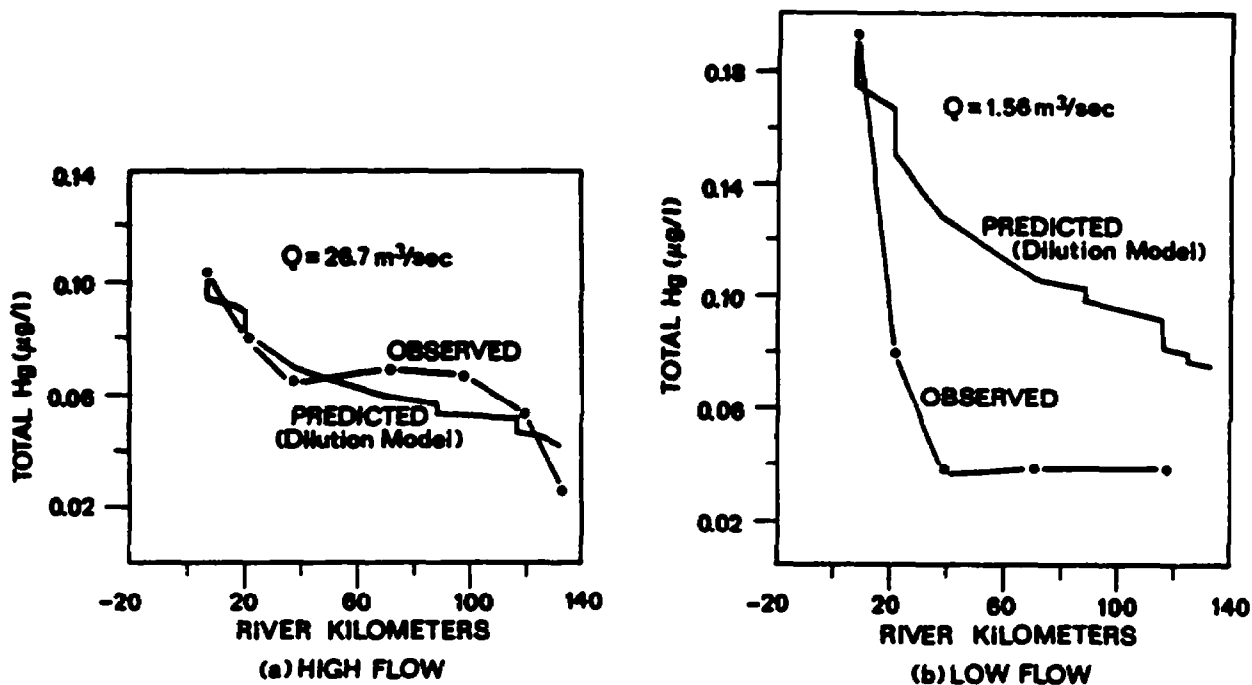
REFERENCE: TURNER AND LINDBERG, 1978.

FIGURE IV-59 COMPARISON OF OBSERVED AND PREDICTED MERCURY CONCENTRATION CALCULATED FROM A DILUTION MODEL FOR THE NORTH FORK HOLSTON RIVER.

sampled on the Slate River include a control station (034), two stations in the impact zone downstream of Coal Creek (035, 036) and two stations in the recovery zone (037, 038).

Table IV-51 shows average concentrations at each station and the water quality criteria. The criteria are exceeded for arsenic, cadmium, copper, silver, and zinc. There is generally some decrease in the level of total metals from the impact zone to the recovery zone, although statistical tests reported by Janik, et al., indicate that analytical variation or field replicate variation may be an important reason for the difference. Even so, water quality criteria are exceeded in the recovery zone as well as in the impact zone.

Janik et al. (1982) also indicate that a large percentage (generally 75 to 100 percent) of the metals are transported in the dissolved fraction. While suspended solid levels are not reported, these results do, in a general sense, appear to be contradictory to the findings of other investigations.

TABLE IV-50

STREAMS SELECTED FOR 1980 U.S. EPA FIELD SURVEYS AND METALS ANTICIPATED TO BE PRESENT IN EXCESS OF U.S. EPA RECOMMENDED AQUATIC LIFE CRITERIA

Major Pollution Source

Stream	Metal(s)
Mining	
Prickly Pear Creek, Montana	Copper, Zinc, Cadmium
Silver Bow Creek, Montana	Copper, Cadmium, Zinc
Slate River, Colorado	Copper, Zinc, Silver, Cadmium
Tar Creek, Oklahoma	Zinc, Cadmium, Silver, Lead
Red River, New Mexico	Copper, Cadmium
Industrial	
Leon Creek, Texas	Chromium, Nickel
Little Mississinewa River, Indiana	Lead, Chromium
Public-Owned Treatment works (POTW)	
Bird Creek, Oklahoma	Arsenic, Selenium
Cedar Creek, Georgia	Chromium, Silver
Maple Creek, South Carolina	Chromium
Irwin Creek, North Carolina	Chromium, Zinc, Nickel, Lead
Blackstone River, Massachusetts	Cadmium, Lead
Mill River, Ohio	Nickel
Cayadutta Creek, New York	Chromium, Cadmium
White River, Indiana	Copper

References: Janik et al. (1982).

4.10.2.3.2.5 Saddle River, New Jersey

The Saddle River near Lodi, New Jersey was investigated to determine the impact of urbanization on the levels of heavy metals in the bottom sediments of the river (Wilber and Hunter, 1979). The study area encompasses a distance of about 13 km (8 mi). The lower 8 km (5 mi) are dominated by nonpoint sources of runoff from the city of Lodi. Industries and municipalities do not discharge directly into this section of the river. Further upstream, however, two wastewater treatment plants discharge their effluent.

The average heavy metal concentrations in the sediments of the river are shown in Table IV-52. Ninety-six sediment samples from 18 cores were taken. The priority metals analyzed are lead, zinc, copper, nickel, chromium, and cadmium. The tabulations indicate a general enrichment of each of the priority metals in the lower
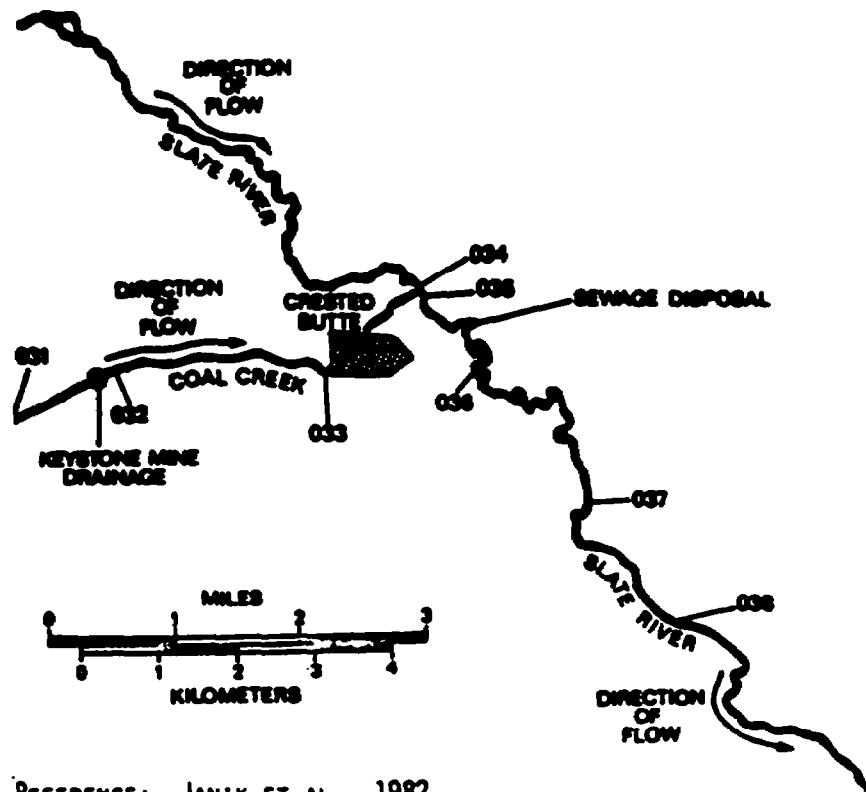
REFERENCE: JANIK ET AL., 1982.

FIGURE IV-60   STATION LOCATIONS ON COAL CREEK AND SLATE RIVER, COLORADO.

urbanized Saddle River. Average enrichment factors (concentrations in the lower river divided by concentrations in the upper river) are 6.7 for Pb, 3.5 for Zn, 3.1 for copper, 2.8 for nickel, 5.1 for chromium, and 5.2 for cadmium. The results appear to indicate that the urban nonpoint sources have increased concentrations of metals in the river's sediments.

The heavy metal concentrations were subdivided by bedded sediment particle size. The results are shown in Table IV-53 for sizes ranging from coarse sand to clay. Generally the concentrations increase with decreasing particle size. However, on a total mass basis, most of the metals are associated with the larger particles because the silt-clay fraction comprises only 1 percent of the solids by weight.

4.10.2.3.2.6 Cayuga Lake Basin, New York

The water of 12 streams tributary to Cayuga Lake, New York were sampled for the priority metals lead, cadmium, zinc, and copper (Kubota et al., 1974). A number of the streams flow predominantly through rural countryside and others flow through the City of Ithaca. Sample collection focused on periods of high and low streamflow from March through August 1970.

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TABLE IV-51

COMPARISON OF MEAN TOTAL CONCENTRATIONS OF SELECTED METALS (μg/l) IN THE SLATE RIVER VERSUS U.S. EPA CALCULATED ACUTE WATER QUALITY CRITERIA FOR AQUATIC LIFE

	Stations				
	Control	Impact		Recovery	
	034	035	036	037	038
Hardness (mg/l)	55.	61.	68.	71.	75.
Total Arsenic (Detection Limit = 110.0)					
Actual ($\bar{X}$)	658.9	1069.7	936.5	776.6	617.6
1980 Criterion	440.	440.	440.	440.	440.
Total Cadmium (Detection Limit = 7.5)					
Actual ($\bar{X}$)	ND*	13.2	10.2	8.1	9.6
1980 Criterion	2.	2.	2.	2.	2.
Total Chromium (Detection Limit = 5.0)					
Actual ($\bar{X}$)	9.2	9.8	7.7	7.6	12.4
1980 Criterion**	21.	21.	21.	21.	21.
Total Copper (Detection Limit = 11.0)					
Actual ($\bar{X}$)	11.0	38.8	24.0	16.6	15.6
1980 Criterion	13.	14.	15.	16.	17.
Total Lead (Detection Limit = 120.0)					
Actual ($\bar{X}$)	ND	ND	ND	ND	ND
1980 Criterion	83.	95.	107.	113.	122.
Total Nickel (Detection Limit = 9.0)					
Actual ($\bar{X}$)	46.5	95.4	72.9	43.8	45.2
1980 Criterion	1174.	1270.	1374.	1418.	1485.
Total Silver (Detection Limit = 12.0)					
Actual ($\bar{X}$)	12.4	17.7	ND	ND	ND
1980 Criterion	1.	2.	2.	2.	2.
Total Zinc (Detection Limit = 9.0)					
Actual ($\bar{X}$)	55.8	1068.3	1005.2	744.5	430.4
1980 Criterion	196.	214.	233.	241.	254.

*ND = Nondetectable.

**Criteria are for hexavalent chromium.

TABLE IV-52

METAL CONCENTRATIONS IN BOTTOM SEDIMENTS OF SADDLE RIVER, NEW JERSEY, AND IN ADJACENT SOILS

River Mile	Metal Concentration (μg/g)							
	Pb	Zn	Cu	Ni	Cr	Cd	Mn	Fe
Upper Saddle River								
16.6	38.6	84.2	28.9	6.5	6.5	0.4	197.4	8439
8.2	12.6	66.4	20.5	6.4	3.6	0.4	111.0	5956
Lower Saddle River								
5.6	163.5	247.6	60.3	17.5	24.6	1.7	200.2	12872
1.3	152.4	275.1	61.5	15.2	17.8	1.6	185.2	11092
0.5	200.0	269.8	104.8	22.3	34.9	2.9	164.0	14565
Adjacent Soils in Watershed								
N/A	86.8	96.3	40.5	11.9	9.3	not measured	145.0	12300

Data of Wilber and Hunter (1979).

Table IV-54 summarizes the levels of dissolved and particulate lead in the water column. The concentrations of soluble lead in the rural streams do not differ appreciably from concentrations in the streams flowing through urbanized areas. Particulate and dissolved levels of cadmium, zinc, and copper also do not reflect an impact from urbanization (Tables IV-55 and IV-56). The observed levels of trace elements in these streams appear to reflect predominantly natural background sources.

4.10.2.3.2.7 Additional Studies

Numerous other studies of metals in rivers can be found throughout the literature. Of the various priority metals, mercury appears to be the most widely studied. Some of the remaining literature on metals in rivers is briefly summarized here.

Mercury distribution in the Ottawa River, Canada, has been studied and reported by a number of researchers, including Ramamoorthy and Rust, 1976; Kudo et al., 1977;

TABLE IV-53

AVERAGE HEAVY METAL CONCENTRATIONS BY PARTICLE SIZE FOR SEDIMENTS OF THE SADDLE RIVER, NEW JERSEY
(μg/g)

Particle Size (μ)	River Mile	Pb	Zn	Cu	Ni	Cr	Cd
420-1000	16.6	15	22	11	4	5	ND[*]
(coarse sand)	8.2	9	42	7	4	3	0.2
	5.6	310	388	206	20	29	2.0
	0.5	482	413	252	28	46	4.0
250-420	16.6	23	30	11	4	5	ND
(medium sand)	8.2	13	28	8	4	3	0.3
	5.6	16	63	10	6	5	0.5
	0.5	90	119	44	12	15	1.0
125-250	16.6	45	48	14	4	6	0.1
(fine sand)	8.2	18	34	12	5	5	0.5
	5.6	11	35	6	4	4	0.3
	0.5	91	135	29	11	12	0.9
63-125	16.6	126	125	81	14	18	1.4
(very fine sand)	8.2	349	440	3180	169	34	3.4
	5.6	113	155	31	11	15	1.3
	0.5	173	251	44	21	27	1.3
5.8-63	16.6	360	420	735	60	41	5.2
(silt)	8.2	1127	3298	1222	202	127	14.5
	5.6	259	389	151	23	33	7.9
	0.5	582	661	258	46	143	6.9
0.15-5.8	16.6	860	917	1017	72	201	7.2
(fine to coarse clay)	8.2	3073	3365	12221	559	321	27.9
	5.6	816	1320	417	99	126	30.6
	0.5	1940	2348	1042	189	563	26.9
0.01-0.15	16.6	1894	2159	2272	ND	530	37.9
(very fine clay)	8.2	13372	21279	84302	2907	1337	290.7
	5.6	1476	4715	1145	488	610	120.0
	0.5	2747	4680	1364	444	852	94.0

[*]ND = Nondetectable

Kudo et al., 1975; and in the Proceedings of the International Conference on Transport of Persistent Chemicals in Aquatic Ecosystems, 1974. Much of the research on mercury in rivers deals with adsorption and desorption between the bedded sediments and the water column.

Jenne (1972) summarizes concentrations of mercury in rivers throughout the United States. The U.S. Geological Survey provides a compilation of papers on

TABLE IV-54

LEAD CONCENTRATIONS IN STREAMS TRIBUTARY TO CAYUGA LAKE, NEW YORK

	Soluble µg/l			Particulate Fraction, µg/l		
Sample Source	No. Samples With Detectable Amounts[a]	Mean[b]	Maximum	No. Samples With Detectable Amounts	Mean	Maximum
Primarily rural						
Canoga	4/8	1.17	2.67	5/8	1.37	2.06
Great Gully	6/8	0.62	1.33	8/8	1.38	6.17
Little Creek	4/7	0.57	1.00	6/7	0.66	1.85
Sheldrake	5/8	0.42	0.67	7/8	1.39	2.62
Taughannock	5/8	0.74	1.00	8/8	1.57	4.01
Salmon	5/9	2.99	16.1	8/9	0.91	2.62
Inlet	8/9	0.66	1.33	8/9	1.89	6.17
Buttermilk	3/8	0.40	0.67	6/8	1.45	3.09
Urbanized						
Trumansburg[c]	4/8	1.11	1.67	7/8	3.94	7.41
Six Mile	6/9	0.73	1.33	8/9	3.14	8.23
Cascadilla	5/9	0.50	1.00	9/9	3.88	6.99
Fall Creek	7/9	0.93	2.67	7/9	2.91	8.33

Source: Kubota et al., 1974.

[a]Samples with detectable amounts/total number of samples.

[b]Means are given for detectable amounts.

[c]Sampling site located below sewage treatment plant.

mercury (1970) and lead (1976) in the environment. The U.S. Geological Survey (1970) also has summarized data on selected trace elements (arsenic, cadmium, hexavalent chromium, lead, zinc, and mercury) in surface waters in the United States.

Finally, the U.S. Environmental Protection Agency has published a series of documents that review the environmental effects of pollutants. Among the pollutants reviewed are chromium (Towill et al., 1978), lead (Bell et al., 1978), and cadmium (Hammons et al., 1978).

4.10.3 Analytical Models for Fate Prediction of Metals in Rivers

4.10.3.1 Introduction

Figure IV-61 illustrates a number of important processes which influence the fate of metals in rivers. Consider an example where effluent from the pond in the

TABLE IV-55

SUMMARY OF CADMIUM, ZINC, AND COPPER IN PARTICULATES CARRIED BY TRIBUTARY STREAMS OF CAYUGA LAKE

Stream	Cadmium, $\mu g/l$		Zinc, $\mu g/l$		Copper, $\mu g/l$	
	No. Samples With Detectable Amounts[a]	Mean[b]	No. Samples With Detectable Amounts	Mean	No. Samples with Detectable Amount	Mean
Primarily rural						
Canoga	5/8	0.09	8/8	6.40	8/8	1.69
Great Gully	6/8	0.06	8/8	10.28	8/8	1.35
Little Creek	1/7	≤0.05	6/7	2.91	7/7	1.72
Sheldrake	7/8	0.09	8/8	5.48	8/8	1.11
Taughannock	7/8	0.11	8/8	6.95	8/8	1.46
Salmon	6/9	0.10	9/9	3.94	9/9	1.37
Inlet	4/9	0.13	8/9	10.71	9/9	3.37
Buttermilk	5/8	0.10	7/8	8.96	8/8	1.64
Urbanized						
Trumansburg[c]	5/8	0.09	8/8	9.45	8/8	1.30
Six Mile	4/9	0.21	8/8	10.05	9/9	5.92
Cascadilla	6/9	0.10	8/8	14.67	9/9	2.43
Fall Creek	5/9	0.44	8/9	14.29	9/9	2.89

Source: Kubota et al., 1974.

[a]Samples with detectable amounts/total number of samples.

[b]Means are given for detectable amounts.

[c]Sampling site located below sewage treatment plant.

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figure overflows into the river. The main objective of predictive analyses for metals is normally to find their concentration distributions with distance, and possibly with time (i.e., to find C_1, C_2, C_3, and C_4 as depicted in the figure). Once metals enter a river, they begin to adsorb to particles suspended in the water column and to particles in the river bed. Eventually, the bed can become contaminated with metals at depths below the sediment-water interface ranging from a few millimeters to many centimeters. If the flow rate in the river were to increase enough, the shear force exerted by the moving water on the bed would be sufficient to scour metal-contaminated solids back into the water column. In zones where velocity is significantly diminished, as in a reservoir, the metal-contaminated sediments can settle out of the water column, and establish a metal-contaminated

TABLE IV-56

SUMMARY OF SOLUBLE CADMIUM, ZINC, AND COPPER IN TRIBUTARY STREAMS OF CAYUGA LAKE

Stream	Cadmium, μg/l		Zinc, μg/l		Copper, μg/l	
	No. Samples with Detectable Amounts[a]	Mean[b]	No. Samples with Detectable Amounts	Mean	No. Samples with Detectable Amounts	Mean
Primarily rural						
Canoga	6/8	0.25	8/8	7.97	8/8	0.79
Great Gully	5/8	0.07	8/8	1.88	8/8	0.40
Little Creek	3/7	0.20	7/7	2.24	7/7	0.32
Sheldrake	6/8	0.10	8/8	1.61	8/8	0.53
Taughannock	4/8	0.28	8/8	1.17	8/8	0.53
Salmon	8/9	0.10	9/9	2.27	9/9	0.51
Inlet	6/9	0.28	9/9	2.71	9/9	0.39
Buttermilk	7/8	1.10	8/8	0.83	8/8	0.54
Urbanized						
Trumansburg[c]	6/8	0.07	8/8	3.20	8/8	0.77
Six Mile	6/9	0.25	9/9	1.57	8/9	0.88
Cascadilla	2/9	0.29	9/9	1.40	9/9	1.70
Fall Creek	7/9	0.17	9/9	3.51	8/9	0.75

Source: Kubota et al., 1974.

[a]Samples with detectable amounts/total number of samples.

[b]Means are given for detectable amounts.

[c]Sampling site located below sewage treatment plant.

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layer on the bottom. In the thin layer of contaminated sediments along the bottom, metal concentrations can be hundreds to thousands of times higher on a unit-volume basis than in water column.

Tributaries provide dilution water which can rather abruptly decrease metal concentrations. Also partitioning between the dissolved and sorbed phases can be shifted if the suspended solid concentrations or other water quality parameters are altered.

Suppose that the pond overflow in Figure IV-61 is eliminated after a period of discharge of many years. During the period of the discharge the bottom sediment on the river has probably accumulated metals. Once the metal concentrations in the water column are lowered due to elimination of the pond overflow, the metal in the bed tends to desorb back into the water column, a process which may continue (depend-
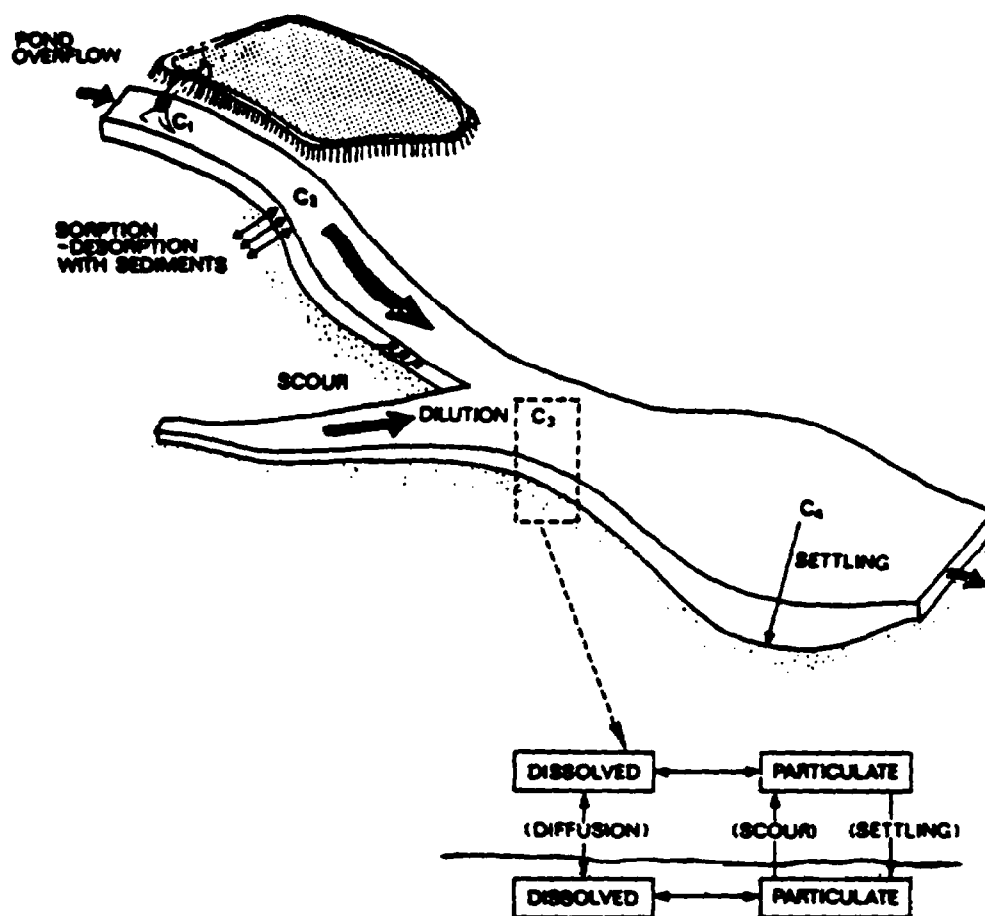
FIGURE IV-61   PHYSICAL PROCESSES INFLUENCING THE FATE OF METALS IN RIVERS

ing on the rate of desorption) for years. Thus, the recovery period of the metal-
contaminated river may take considerably longer than anticipated from the point
source elimination.

The tools presented in this section can be used to address the cases described
above and are limited to steady-state analyses, with the exception of the method
which predicts adsorption and desorption of metals on bottom sediments. The methods
treat metals as pollutants with two phases: an adsorbed phase and a dissolved phase.
Each approach is summarized below.

● **Dilution Approach.** The change in metal concentration in a river is
assumed due to loading from point and nonpoint sources, and dilution
with background water.

● **Dilution Plus Scour or Deposition of Metal-Contaminated Sediments.**
Exchange of metal-contaminated sediments between the water column and
river bed can alter the concentration in the water column.

- **Influence of Small Lakes.** Small lakes or backwater regions are often present on river systems, and potentially could be a sink of adsorbed metals which settle along with suspended solids in these quiescent regions.

- **Desorption from (or Adsorption to) Bedded Sediments.** Dissolved metal in the water column can be adsorbed to bedded sediments if a nonequilibrium condition exists between the bed and the water column. Similarly, desorption of particulate metal from bedded sediments may occur if metal concentrations are reduced in the water column (for example, by waste load allocation).

- **Concentration Factors in Bedded Sediments.** Concentrations of metals in many bedded sediments are often significantly higher than levels in the water column.

While some of the equations presented in the following sections may appear complicated, the equations are no more sophisticated than the more familiar BOD-DO analyses presented earlier in the chapter. Even the data requirements are generally less comprehensive than for dissolved oxygen analyses. However, since the methods are less familiar, they may require some study before they are fully understood.

4.10.3.2 Dilution Approach

Using the dilution approach, total metal concentration (particulate plus dissolved) is simulated as a conservative pollutant. The dissolved component is estimated from the total concentration using linear partitioning:

$$C = \frac{C_T}{1 + K_p S \cdot 10^{-6}}$$

(IV-156)

where

C = dissolved phase metal concentration, $\mu g/l$

C_T = total metal concentration, $\mu g/l$

S = suspended solids concentration, mg/l

K_p = partition coefficient, cm^3/gm (or l/kg).

Partition coefficients are summarized later in Section 4.10.4.1.

Under the appropriate conditions the dilution approach appears to be useful for predicting metal concentrations throughout a river. Before the method is discussed, the major assumptions inherent in the procedure are reviewed. Decay or other loss processes (e.g., volatilization) are not considered. For metals this is generally a good assumption for the range of environmental conditions likely to be encountered in rivers. Even though the species distribution can change with distance (in response to a pH change, for example), total metal typically is not degraded. A second important assumption made in the dilution approach is that the metal in the water column does not interact with the river bed, either in the particulate form or in the

dissolved form. This situation is generally true when:

- The suspended solids in the river remain fairly constant with distance. If scour or deposition is significant then a net influx or loss of solids and metals may occur.
- The sources of metals to the river are fairly constant over time. If major changes in the discharge of metals occur, this can create a driving force for adsorption to (or desorption from) the bed, which then acts as an internal source or sink.

Field data of suspended solids can be reviewed to determine whether significant losses or gains of solids occur within the study reach. Alternatively, a predictive method, such as Figure IV-62, can be used. Based on the mean river velocity, the figure shows when deposition, transport, and erosion of solid particles is likely to occur. Note that the velocity when erosion occurs is significantly higher than the sedimentation velocity, except for particle sizes larger than sand (which are not of concern for metals adsorption). This means that as the stream velocity first drops below the velocity required to erode a certain size particle, the particle is _not_ deposited, but continues to be transported unless the velocity further decreases below the sedimentation velocity.

As the figure shows, sedimentation of clays and small silts is not likely to occur in free flowing rivers, but can occur in relatively small reservoirs on the river with detention times exceeding a few days. Under such conditions the net velocity can be on the order of 0.1 cm/sec, or less, and the effects of settling of particulates may be important.

While sedimentation of clays and small silts is not likely in most free flowing rivers, scour of these same sized particles is more probable. Clay is likely to be scoured at velocities near 3 fps (100 cm/sec), and silts between 1 and 3 fps (30 to 100 cm/sec), depending on their size. Consequently, during high flow conditions when the water is moving rapidly, bottom scour of silts and clays, and perhaps of sand is possible. If the scoured sediments are contaminated with metals then the total metal being transported will increase over distance (assuming for the moment that further dilution is negligible). Based on Figure IV-62, a fairly large envelope of stream velocities exists such that the clay and silt fractions of solids (those which adsorb most of the metals) are transported in suspension with the stream water.

Dilution models are useful for both point and nonpoint sources. While dilution models have been presented elsewhere in this document they are summarized here for ease of reference. For point sources, the concentration in a stream following mixing, C_{Tf} is:

$$C_{Tf} = \frac{C_{Tu} Q_u + C_{Tw} Q_w}{Q_u + Q_w}$$

(IV-157a)
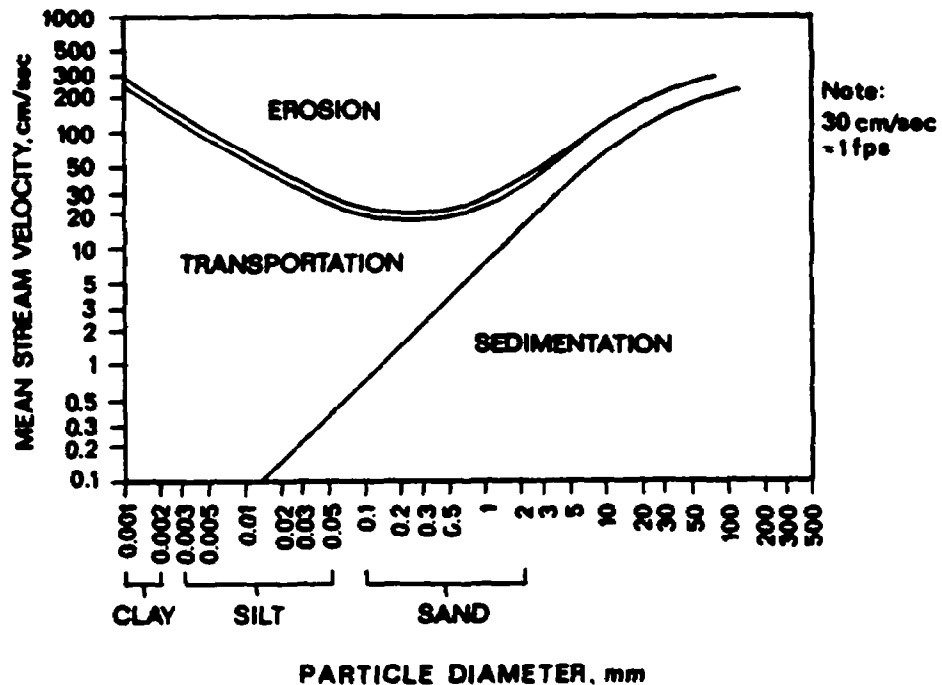
FIGURE IV-62   RELATIONSHIP BETWEEN STREAM VELOCITY, PARTICLE SIZE, AND
THE REGIMES OF SEDIMENT EROSION, TRANSPORT, AND
DEPOSITION (FROM GRAF, 1971).

where

C_{Tu} = concentration of total metal in the river above the point source, $\mu g/l$

Q_u = flow rate in the river above the point source, m^3/s or cfs

C_{Tw} = concentration of total metal in the point source, $\mu g/l$

Q_w = flow rate of the point source, m^3/s or cfs.

According to the dilution model, the metal's concentration does not change with distance downstream unless there are additional inflows as loadings of metals.

When C_{Tu} is negligible, Equation IV-157a can be rewritten as:

$$C_{Tf} = \frac{C_{Tw}}{\frac{Q_u + Q_w}{Q_w}} = \frac{C_{Tw}}{D} \qquad (IV-157b)$$

where

D = dilution attained after mixing.

The nonpoint source representation can be written in one of two forms:

$$C_T = \frac{A_o}{A(x)} (C_{T_o} - C_{Tb}) + C_{Tb} \qquad\qquad (IV-158)$$

or

$$C_T = \frac{Q_o}{Q(x)} (C_{T_o} - C_{Tb}) + C_{Tb} \qquad\qquad (IV-159)$$

where

A_o = drainage basin area at location where $C_T = C_{T_o}$, m^2

$A(x)$ = drainage basin area at a distance x further downstream, m^2

C_{Tb} = average total metal concentration in nonpoint source (background concentration), $\mu g/l$

Q_o = river flow rate at location where $C_T = C_{T_o}$, m^3/s or cfs

$Q(x)$ = flow rate at a distance x further downstream, m^3/s or cfs.

In some instances these equations can be quite useful. One particularly useful feature of these equations (beyond their applicability to nonpoint sources) is that they can be applied to a series of point sources by treating the point sources as one or more equivalent nonpoint sources. For example, if a particular river has 30 small sources entering along a stretch of river, it may be more convenient for screening purposes to treat the series as an equivalent nonpoint source. Using this approach there is no need to apply the point source equation 30 times; rather the nonpoint source equation can be used once. For more details of this procedure, see Example IV-5.

The approach of treating metals as conservative pollutants is one which some investigators have considered before. Turner and Lindberg (1978) investigated the mercury distribution in the North Fork Holston River downstream from an inactive chloralkali plant (mercury cell process). Mercury was still being leached into the river at a steady rate years after the plant had closed. Turner and Lindberg plotted total mercury versus distance during both high flow and low flow conditions, and then compared the observed concentrations against predicted concentrations, assuming the mercury levels are influenced only by dilution processes. Figure IV-59 shown earlier summarizes their results. During high flow mercury acts conservatively, while during low flow mercury levels are overestimated by a factor of two to three. In both cases, however, the importance of downstream transport is apparent: much of the mercury remains in the water column either in adsorbed or dissolved form, and is advected downstream. Thus, even for a metal which adsorbs as strongly as mercury, a dilution model is able, at least under certain conditions, to provide reasonable estimates of instream concentrations of total metal.

The Flint River study described earlier (Section 4.10.2.3.2.1) provides an
opportunity to test the dilution approach under a variety of hydrologic conditions.
To implement the dilution approach, the data required are river and wastewater
flow rates, and associated metal concentrations. The data used are summarized in
Table IV-57. Two wastewater treatment plants are the largest sources of metals in
the study reach. Together with the upstream contributions from the river, these
three sources are assumed to comprise the total metal input to the system (the
minor sources shown in Table IV-57 are neglected).

The Flint Wastewater Treatment Plant discharges at km 70.7, which is about 1.2
km below the boundary at Mill Street. After mixing, the levels of total zinc,
cadmium, and copper in the river are:

Zinc:

$$Zn_T = \frac{2.66 \times 7.7 + 1.68 \times 55}{2.66 + 1.68} = 26 \ \mu g/1$$

Cadmium:

$$Cd_T = \frac{2.66 \times 0.067 + 1.68 \times 0.16}{2.66 + 1.68} = 0.10 \ \mu g/1$$

Copper:

$$Cu_T = \frac{2.66 \times 2.9 + 1.68 \times 8.3}{2.66 \div 1.68} = 5.0 \ \mu g/1$$

By ignoring the minor sources, these instream concentrations can be assumed
to remain constant down to the Ragnone WWTP at km 41.1. After mixing with the
effluent from the Ragnone WWTP, the instream concentrations for the metals become:

Zinc:

$$Zn_T = \frac{26 \times 4.34 + 0.69 \times 84}{4.34 + 0.69} = 34 \ \mu g/1$$

Cadmium:

$$Cd_T = \frac{0.10 \times 4.34 + 0.69 \times 0.54}{4.34 + 0.69} = 0.16 \ \mu g/1$$

TABLE IV-57

**BOUNDARY CONDITIONS AND POINT SOURCES TO FLINT RIVER
FOR AUGUST 4-7, 1981**

Source	Discharge Flow (m^3s)	Discharge Concentration		Total Zinc (μg/ℓ)	Total Cadmium (μg/ℓ)	Total Copper (μg/ℓ)
		Suspended Solids				
		(mg/ℓ)	(kg/d)			
Upstream Boundary Mill Road (km 71.9)	2.66	13.5	3100.	7.7	0.067	2.9
Flint WWTP (km 70.7)	1.68	4.1	600.	55.	0.16	8.3
Flint Fly Ash Ponds (km 70.0)	0.04	39.5	150.	63.	1.32	80.
Brent Run (km 41.6)	0.15	5.9	77.	3.8	0.11	3.8
Ragnone WWTP (km 41.1)	0.69	58.7	3500.	84.	0.54	28.5
Pine Run (km 29.7)	0.06	7.0	33.7	5.0	0.04	3.8
Silver Creek (km 25.2)	0.085	6.8	50.0	5.0	0.04	3.8

Modified from: Delos et al. (1983)

Copper:

$$Cu_T = \frac{5.0 \times 4.34 + 0.69 \times 29.5}{4.34 + 0.69} = 8.2 \; \mu g/l$$

Neglecting the minor sources below the Ragnone WWTP, the profiles of total zinc, cadmium, and copper are shown in Figure IV-63. Also shown in the figure are observed data (mean and one standard deviation) and predictions from the MICHRIV model as reported by Delos et al. (1983). MICHRIV is a computer model which analyzes metals in greater detail than the screening procedures, and therefore requires more data.

The dilution model generally predicts values within 25 to 50 percent of the means of the observed values, and also within 25 to 50 percent of the MICHRIV
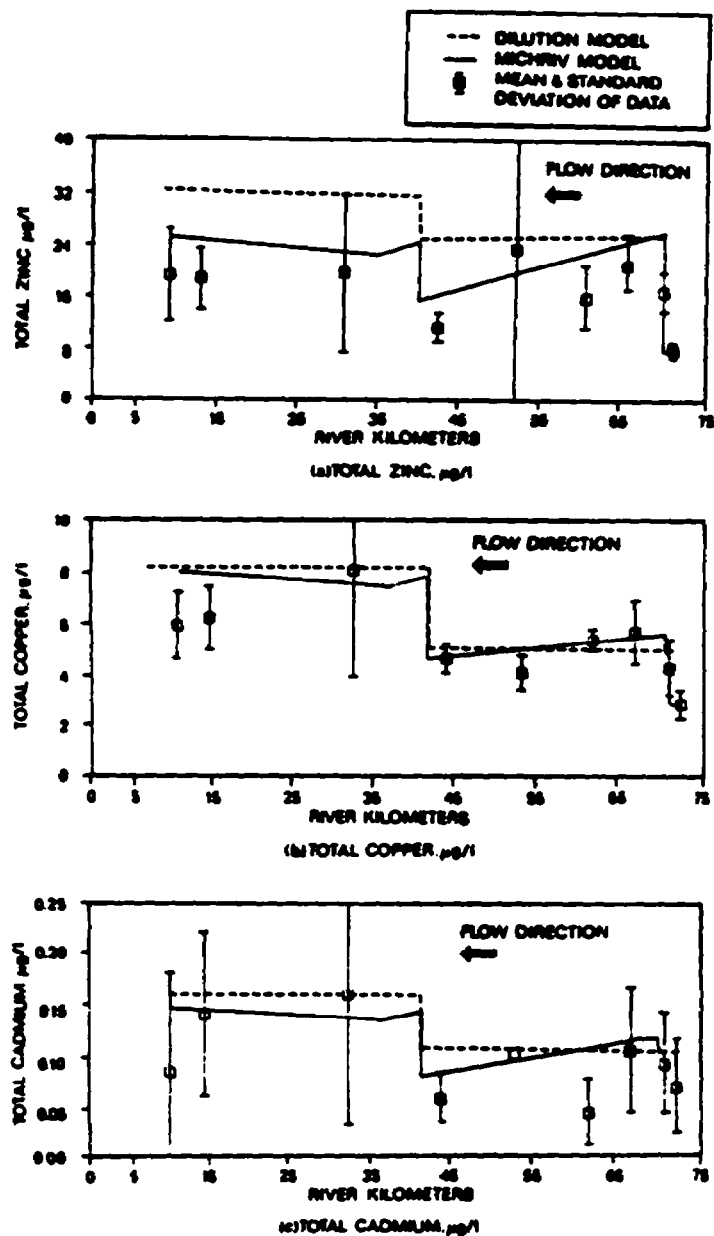
FIGURE IV-63   COMPARISON OF PREDICTED AND OBSERVED
TOTAL METAL CONCENTRATIONS IN FLINT RIVER,
MICHIGAN (AUGUST 1981). (AVERAGE FLOW =
2.66 M³/SEC (94 CFS) AT KM 71.9)

model predictions. Figure IV-64 shows that the dilution model also is applicable
under other flow regimes in the Flint River: December when the flow rate was
about 26.4 m³/sec (930 cfs), and March when the flow rate was 93.4 m³/sec (3300cfs).
For both the December and March surveys, there do not appear to be significant
differences between predictions from the dilution model and from the MICHRIV model.

KEY

--- DILUTION MODEL
— MICHRIV MODEL
● MEAN & STANDARD
  DEVIATION OF DATA
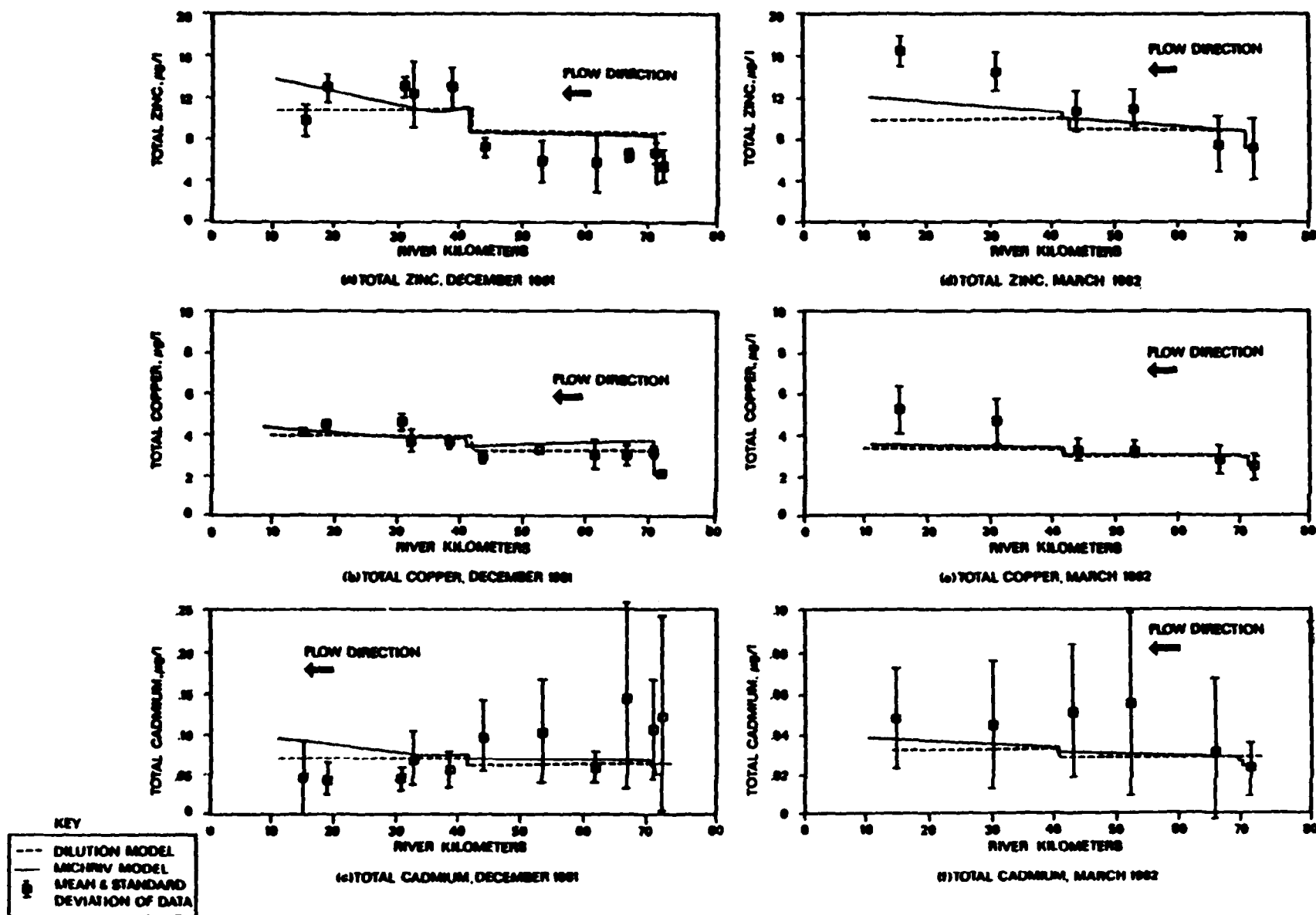
FIGURE IV-64   TOTAL ZINC, COPPER, AND CADMIUM IN THE FLINT RIVER

While dilution modeling can produce quite acceptable results under a variety of conditions, the user should have access to tools which can be used when processes in addition to dilution are important. The following section addresses some of these situations.

4.10.3.3 Settling and Resuspension of Adsorbed Metals in Rivers

This section begins with a brief discussion of the recently completed MICHRIV model (Delos et al., 1983). This model's framework is shown in Figure IV-65. The most interesting feature of the model is that it attempts to handle the exchange of contaminants between the water column and the bed. Resuspension and deposition of contaminated sediments redistributes adsorbed contaminants to and from the bed. Also, diffusion can be a driving force for dissolved phase interaction between the sediment and water column. For purposes of illustration, the MICHRIV model is simplified here, but the essence of the model (exchange of metal between the water column and bed) is retained.

The model is simplified based on these two assumptions:

- $K_{d1} = K_{d2} = 0$; that is, there is no degradation or decay of metals, and

- $K_{p1} = K_{p2}$; that is, the partition coefficient in the bedded sediments and in the water column are the same.

The first assumption is quite reasonable since most metals do not decay or otherwise degrade (an exception is elemental mercury which can volatilize).

Regarding the second assumption, there is reason to suspect that the solids partition coefficients for suspended and bedded sediments can differ since the characteristics of solids in the bed can differ from those suspended in the water column. However, because of the range of uncertainty inherent in partition coefficient prediction, there is no reason to consider differences between K_{p1} and K_{p2} for these screening analyses.

Using these two assumptions, the model formulations from Delos et al. (1983) are simplified as follows. The simplification procedure is shown in detail so the user can clearly see how the two assumptions are used. The final results of these simplifications are shown later as Equations IV-172 through IV-175, and show how the metal concentrations in the water column and bed are related.

From Delos et al. the relationship between the total concentration of metal in the water column (C_{T1}) and in the bed (C_{T2}) is:

$$\frac{C_{T2}}{C_{T1}} = \frac{w_s f_{p1} + K_L f_{d1}}{(w_{rs} + w_d) f_{p2} + K_L f_{d2} + K_{d2} f_{d2} H_2} \qquad \text{(IV-160)}$$
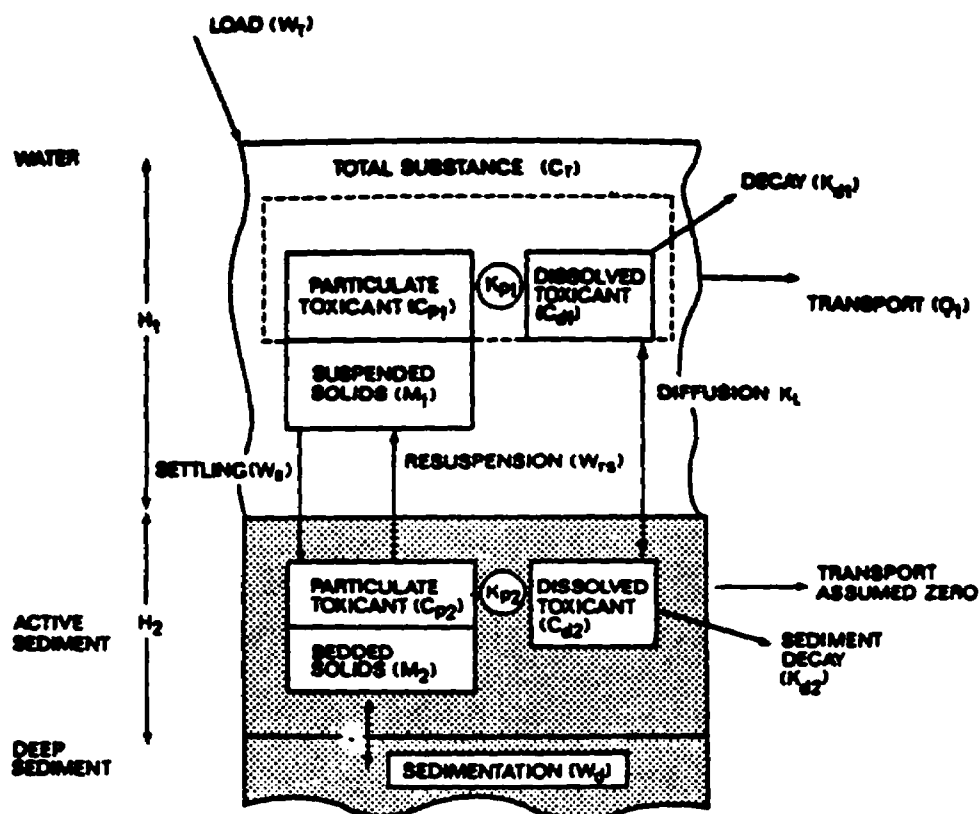
FIGURE IV-65   FRAMEWORK FOR RIVER MODEL MICHRIV (REDRAWN
FROM DELOS ET AL., 1983)

where

f_{p1}, f_{p2} = particulate fraction of metal in water column and in bed,
respectively

f_{d1}, f_{d2} = dissolved fraction of metal in water column and in bed,
respectively

w_s = settling velocity, m/day

w_{rs} = resuspension velocity, m/day

K_L = diffusion coefficient, m/day

K_{d2} = decay rate in sediment, 1/day

H_2 = depth of active sediment, m

m_1,m_2 = solids concentration in water column and in bed, respectively,
kg/l.

From Equation IV-160:

$$\frac{C_{d2}}{C_{d1}} = \frac{f_{d2}}{f_{d1}} \frac{C_{T2}}{C_{T1}} = \frac{[f_{d2}\, w_s\, f_{p1} + K_L\, f_{d1}]}{f_{d1}\, [(w_{rs} + w_d)f_{p2} + K_L f_{d2} + K_{d2}f_{d2}\, H_2]}$$

-493-

$$= \frac{w_s \frac{f_{p1}}{f_{d1}} + K_L}{w_s \frac{m_1}{m_2} \frac{f_{p2}}{f_{d2}} + K_L + K_{d2}H_2} \qquad \text{(IV-161)}$$

since

$$\frac{m_1}{m_2} w_s = (w_{rs} + w_d)$$

Now

$$f_{p2} = \frac{m_2 K_{p2}}{1 + m_2 K_{p2}} \qquad \text{(IV-162)}$$

and

$$f_{d2} = 1/(1 + m_2 K_{p2})$$

so

$$\frac{f_{p2}}{m_2} = \frac{K_{p2}}{1 + m_2 K_{p2}} = K_{p2} f_{d2} \qquad \text{(IV-163)}$$

or

$$\frac{f_{p2}}{f_{d2} m_2} = K_{p2} \qquad \text{(IV-164)}$$

Similarly

$$\frac{f_{p1}}{m_1} = K_{p1} f_{d1} \qquad \text{(IV-165)}$$

or

$$\frac{f_{p1}}{f_{d1}} = K_{p1} m_1 \qquad \text{(IV-166)}$$

Substituting Equations IV-164 and IV-166 into Equation IV-161 produces:

$$\frac{C_{d2}}{C_{d1}} = \frac{w_s\, m_1\, K_{p1} + K_L}{w_s\, m_1\, K_{p2} + K_L + K_{d2}\, H_2}$$ (IV-167)

Since K_{d2} is assumed to equal zero for metals:

$$\frac{C_{d2}}{C_{d1}} = \frac{w_s\, m_1\, K_{p1} + K_L}{w_s\, m_1\, K_{p2} + K_L} \quad .$$ (IV-168)

With the further assumption that $K_{p1} = K_{p2}$

$$\frac{C_{d2}}{C_{d1}} = \frac{w_s\, m_1\, K_{p1} + K_L}{w_s\, m_1\, K_{p1} + K_L} = 1$$ (IV-169a)

or

$$C_{d2} = C_{d1} \quad .$$ (IV-169b)

Thus, the dissolved phase concentration of the metal in the bed and in the water column are equal to each other for the conditions specified above. This result is often an implicit assumption made in water quality analyses when the effects of the bed are ignored.

Since $C_{d1} = C_{d2}$, the net diffusive flux transfer between the bed and water column is zero, so that there is no need to include the K term in the following analyses.

In Delos et al. (1983) the total water column concentration is given by:

$$C_{T1}(x) = C_{T1}(0)\, exp\, (-k_T\, x/u)$$ (IV-170)

where

      x = distance downstream, m

      u = stream velocity, m/day

      k_T = effective first order decay term, 1/day.

Delos et al. show that the first order decay term is:

$$k_T = K_{d1} f_{d1} + \frac{w_s f_{p1}}{H_1} + \frac{K_L f_{d1}}{H_1} - \frac{m_2 H_2 f_{p1}}{m_1 H_1 f_{p2}} \frac{1}{H_2} \frac{r_2}{r_1} (w_{rs} f_{p2} + K_L f_{d2})$$ (IV-171a)

where

$$\frac{r_2}{r_1} = \frac{(w_{rs} + w_s)f_{p2} + K_L(K_{p2}/K_{p1})f_{d2}}{(w_{rs} + w_s)f_{p2} + K_L f_{d2} + K_{d2}f_{d2}H_2}$$

Using the assumptions made before ($K_{p1} = K_{p2}$ and $K_{d1} = K_{d2} = 0$), $r_2/r_1 = 1$. Thus k_t simplifies to:

$$k_T = \frac{w_s f_{p1}}{H_1} - \frac{m_2 f_{p1} w_{rs}}{m_1 H_1} = \frac{f_{p1}}{H_1}\left[w_s - \frac{m_2}{m_1} w_{rs}\right]. \qquad \text{(IV-171b)}$$

To summarize, under the simplifications made here, the MICHRIV model equations become:

$$C_{T1}(x) = C_{T1}(0) \exp\left[-\frac{f_{p1}}{H_1}\left(w_s - \frac{m_2}{m_1} w_{rs}\right)\frac{x}{u}\right] \qquad \text{(IV-172)}$$

$$C_{d1}(x) = \frac{C_{T1}(x)}{1 + K_{p1} m_1} \qquad \text{(IV-173)}$$

$$C_{d2} = C_{d1} \qquad \text{(IV-169b)}$$

$$\frac{C_{p1}}{m_1} = \frac{C_{p2}}{m_2} \qquad \text{(IV-174a)}$$

or

$$X_1 = X_2 \qquad \text{(IV-174b)}$$

$$C_{T2} = C_{T1}\frac{f_{d1}}{f_{d2}} = C_{T1}\frac{1 + K_p m_2}{1 + K_p m_1} \qquad \text{(IV-175)}$$

and

$$m_2 = \rho_s(1-n). \qquad \text{(IV-176)}$$

where

X_1, X_2 = mass of pollutant adsorbed per mass of sediment in the water column and in the bed, respectively, $\mu g/g$

ρ_s = density of solids in sediment, gm/cm^3 (e.g. for sand 2.54 gm/cm)

n = porosity of sediment (volume fraction occupied by water).

The most notable results obtained in the above analyses are that the dissolved metal concentration in the water column and in the bedded sediments are the same (Equation IV-169b), and so are the particulate metal concentrations, expressed per unit weight of sediment (Equation IV-174b). However, on a unit volume basis, the total metal concentration in the sediment far exceeds the concentration in the water column (Equation IV-175).

Typically, first order decay rates are positive numbers, which indicate that pollutants decrease in concentration with distance. However, the k_T term in Equation IV-171b can either be positive or negative. For example, if significant scour of particulate metal from the bottom is occurring, then $k_T < 0$ and the total metal concentration can increase downstream.

While it is possible that metal concentrations can increase in the water column due to scour (e.g., see Figure IV-64 which shows total zinc and copper in the Flint River during March 1982), at steady-state conditions this should not happen when the only source of loading is a single source located at $x = 0$. Rather than use Equation IV-172 to simulate the effects of scour on water column concentration, one of two other alternatives has been selected. One approach is to retain the unsteady-state nature of the transient scour situation. While this introduces more complexity, it shows that elevated metal concentrations in the water column caused by scour are due to a previous discharge or hydrologic condition when metals had contaminated the bed, and not due to the current steady discharge conditions.

The two unsteady equations relating the total metal concentrations in the bed and in the water column are (using the previous notation):

$$\frac{\partial C_{T2}}{\partial t} = \frac{w_s \, f_{p1} \, C_{T1}}{H_2} - \frac{w_{rs} \, f_{p2} \, C_{T2}}{H_2} + \frac{K_L \, f_{d1} \, C_{T1}}{H_2} - \frac{K_L \, f_{d2} \, C_{T2}}{H_2} \qquad (IV-177)$$

and

$$\frac{\partial C_{T1}}{\partial t} + u \frac{\partial C_{T1}}{\partial x} = \frac{-w_s \, f_{p1} \, C_{T1}}{H_1} + \frac{w_{rs} \, f_{p2} C_{T2}}{H_1} - \frac{K_L \, f_{d1} \, C_{T1}}{H_1} + \frac{K_L \, f_{d2} \, C_{T2}}{H_1} \qquad (IV-178)$$

While these equations can be solved exactly and used to predict the total instream metal concentration due to a scour condition, they are not practical for screening analyses. The primary emphasis here is to predict longitudinal pollutant distribution when scour is much more important than deposition or diffusion. The approach is to specify (rather than calculate) the concentration in the bed and to assume it remains constant over the period of analysis. Thus the screening tools which are presented on the following pages are fundamentally different from the previous MICHRIV equations, such as Equation IV-172. Table IV-58 summarizes the screening equations and defines the variables used in each equation.

$$C_{T1}(x) = \frac{w_{rs} \; f_{p2} \; C_{21}}{H_1 \; u} x + C_{T1}(0) \qquad \text{(IV-179)}$$

where

C_{21} = concentration of total metal in the bedded sediments, $\mu g/l$ (a direct measurement of this value is preferable)

$C_{T1}(0)$ = concentration of total metal in the water column at an upstream boundary, $\mu g/l$.

While Equation IV-179 represents steady-state conditions, it is valid only as long as the sediments being scoured have a total metal concentration of C_{21}. Once the contaminated sediments have been scoured, then the instream metal concentration is expected to return to $C_{T1}(0)$. The period of validity, T, of the equation can be approximated by:

$$T = \frac{H_2}{w_{rs}} \qquad \text{(IV-180)}$$

where

H_2 = depth of contaminated sediment, m

w_{rs} = resuspension velocity, m/day

Typically, Equation IV-179 is expected to be used during high flow conditions, perhaps for a seasonal analysis. For an application of this type, the period of validity of the equation should be on the order of one to two months. Using representative data (H_2 = 5 cm and w_{rs} = 2×10^{-4} m/day) for an example,

$$T = \frac{5 \times 10^{-2} \text{m}}{2 \times 10^{-4} \text{m/day}} = 250 \text{ days.}$$

For the example conditions, Equation IV-179 is applicable for seasonal analysis.

When settling of solids is insignificant, the resuspension velocity, w_{rs}, can be estimated as:

$$w_{rs} = \frac{uH_1 \Delta SS}{m_2 \Delta x \cdot 10^6} \qquad \text{(IV-181)}$$

TABLE IV-58

SUMMARY OF SCREENING PROCEDURES FOR METALS IN RIVERS AND LAKES

Equation	Use	Data Requirements		Comments
		Dilution Analysis		
IV-157a	This equation is used to calculate the concentration of total metal in a river after a point source discharge mixes with river water.	Q_u	= flow rate in river above point source	This equation is most applicable when exchange of suspended solids and metals with bed is negligible. See Figure IV-62: when mean water velocity is in "transportation" regime, this condition is approximately true. Also, the equation can be used as a first approximation regardless of exchange with bed.
		Q_w	= flow rate of point source	
		C_{Tw}	= concentration of total metal in point source	
		C_{Tu}	= concentration of total metal in river above the point source	
IV-156	Once the total concentration versus distance is found from Equation IV-157a, the amount dissolved can be calculated using this equation.	S	= suspended solids concentration	This equation is used to find total dissolved metal at locations in a river once total metal concentration at these same locations has been calculated.
		K_p	= partition coefficient	
		C_T	= total metal concentration	
		Dilution and Scour of Metal-Contaminated Sediments		
IV-179	This equation is used to predict the total metal concentration in a river when metal-contaminated sediments are resuspended into the water column.	C_{21}	= concentration of total metal in bedded sediments	The equation does not keep track of the depth of contaminated sediments. It assumes this depth is not exceeded during the period of scour. Equation IV-180 can be used to estimate the period of validity of the equation. Figure IV-66 illustrates the importance of scour.
		$C_{T1}(0)$	= concentration of total metal in the water column at an upstream boundary	
		H_1	= water depth	
		u	= stream velocity	
		f_{P2}	= fraction of metal in bed which is in particulate form (≈ 1)	
		w_{rs}	= resuspension velocity (see Equation IV-181)	

TABLE IV-58 (continued)

Equation	Use	Data Requirements		Comments
		Dilution and Scour of Metal-Contaminated Sediments (continued)		
IV-182	This equation is used to calculate the total metal concentration in a river when metal-contaminated sediments are resuspended into the water column. This is an alternate form of Equation IV-179. See Comments.	ΔSS	• change in suspended concentration over the distance where the total metal concentration is to be calculated	This equation can be used in lieu of Equation IV-179 when the concentration of total metal in the bed, C_{2i}, is unknown.
		K_p	• partition coefficient	
		S_p	• average suspended solids concentration during the previous steady hydrologic period	
		C_{T1p}	• concentration of total metal in water column during the previous steady hydrologic period	
		Dilution and Deposition of Metal-Contaminated Sediments		
IV-185d	This equation is used to predict the concentration of total metal in a river when metal-contaminated solids are settling.	C_{T0}	• concentration of total metal at an upstream boundary	Figure IV-67 illustrates the importance of deposition.
		K_p	• partition coefficient	
		$SS(0)$	• suspended solids concentration at upstream boundary	
		H_1	• depth of water	
		u	• velocity of water	
		w_s	• settling velocity (see Equation IV-184)	
IV-186a	This equation is a simplification of Equation IV-185d. See Comments.	C_{T0}	- see above	This equation is used when the metal is highly adsorbed to the suspended solids (i.e., when $K_p \cdot SS \cdot 10^{-6} \gg 1$).
		$SS(0)$	- see above	
		$SS(x)$	• suspended solids concentration at a distance x below upstream boundary, where total metal concentration is to be calculated	

TABLE IV-58 (continued)

Equation	Use	Data Requirements	Comments

Equation	Use	Data Requirements	Comments
IV-186b	This equation is also a simplification of Equation IV-185d. See Comments.	c_{To} - see above K_p - see above $SS(0)$ - see above w_s - see above H_1 - see above u - see above	This equation is applicable when the amount of metal which is adsorbed is small. When this is true, settling is relatively unimportant, as Equation IV-186c shows, and the metal tends to act conservatively in the water column.

Settling of Metals in Lakes

Equation	Use	Data Requirements	Comments
IV-188c	This equation predicts the concentration of total metal leaving a lake, based on the suspended solids concentrations entering and leaving the lake.	c_T^i = concentration of total metal coming into the lake s^i, s^0 = concentration of suspended solids entering and leaving the lake, respectively (See Equation IV-187). K_p = partition coefficient	This equation considers a median-size suspended solid, and does not differentiate by size fraction.
IV-189	This equation shows that the dissolved phase metal concentration is not affected by the settling adsorbed metal.		
IV-195b	This equation predicts the concentration of total metal leaving a lake, based on concentrations of suspended solids by size fraction.	c_T^i - see above s_j^i, s_j^0 = concentration of suspended solids in class j entering and leaving the lake, respectively (see Equation-190) K_{pj} = partition coefficient of metals associated with sediment size j	Size fractions of sand, silts, and clays entering a lake are required. Settling velocity of solids in each group are predicted using Equation IV-191.

TABLE IV-58 (continued)

Equation	Use	Data Requirements	Comments

Equation	Use	Data Requirements	Comments
IV-197	This equation is the same as Equation IV-195b, except the partition coefficients are related to specific surface area.	Same as Equation IV-195b, except specific surface areas (SA's) are required	Typical values of specific surface areas for this equation are 10 m^2/g for sand, 60 m^2/g for silt, and 200 m^2/g for clay.

Adsorption and Desorption of the Metal Between Water Column and Bed

| IV-199 | This equation is used to predict water column concentration of metal due to adsorption or desorption with bed. | C_o = initial total metal concentration in water column (at t=0)
 C_b = upstream boundary concentration (at x=0)
 M_s = mass of contaminated sediments per unit area (see Table IV-38)
 H = water depth <br> u = stream velocity
 K_p = partition coefficient
 D_H = vertical diffusion coefficient
 θ = void fraction of underlying sediment
 ρ_b = bulk density | This equation differs from all of the above in that it is an unsteady-state equation (i.e., time variability is considered). This equation is intended to provide only a crude approximation of the importance of adsorption or desorption from the bed, because some of the required data will likely be difficult to estimate. Equation IV-200 is a simplification of Equation IV-199 when the mixed layer is small. Equation IV-201 is also a simplification useful when the boundary concentration is negligible. |

The term $\Delta SS/\Delta x$ is the change in suspended solids concentration over distance $\Delta x[mg/(1 \cdot m)]$

If C_{21} in Equation IV-179 is not available, Equation IV-179 can be expressed in the alternate form as:

$$C_{T1}(x) = \frac{\Delta SS \ K_p \cdot 10^{-6}}{1 + K_p \ S_p \cdot 10^{-6}} C_{T1p} + C_{T1}(0) \qquad (IV-182)$$

where

C_{T1p} = concentration of total metal in the water column during the <u>previous</u> steady period (previous to the period of sustained scour)

S_p = suspended solids concentration during <u>previous</u> steady period, mg/1.

The purpose of using the previous steady-state period (a non-scour period) is that the concentration in the bedded sediments during the scour period is to a large degree dictated by the previous conditions.

Equation IV-182 shows that the product

$$\frac{\Delta SS \ K_p \cdot 10^{-6}}{1 + K_p \ S_p \cdot 10^{-6}}$$

is a helpful indicator of the importance of scour. If

$$\frac{\Delta SS \ K_p \cdot 10^{-6}}{1 + K_p \ S_p \cdot 10^{-6}} > 1,$$

then the total metal concentration during the scour period (at a distance downstream where the suspended solids have increased by ΔSS) will exceed the total metal concentration during the previous steady-state period. If this fraction is less than unity then the background concentration ($C_{T1}(0)$) is important in determining whether scour produces higher concentrations than the previous period.

· — · — · — · — · — · — · — · EXAMPLE IV-21 — · — · — · — · — · — · — · — · — · — ·

The Flint River study provides a source of data to simulate a scour condition. Figure IV-66a shows the suspended solids concentration in the river during the March 1982 survey and indicates a net scour condition exists. The resuspension velocity is:

$$w_{rs} = \frac{1 \cdot 2 \cdot (25 - 12)}{0.2 \cdot 30 \cdot 10^3 \cdot 10^6} \ 86400 = 1.4 \cdot 10^{-4} \ m/day$$
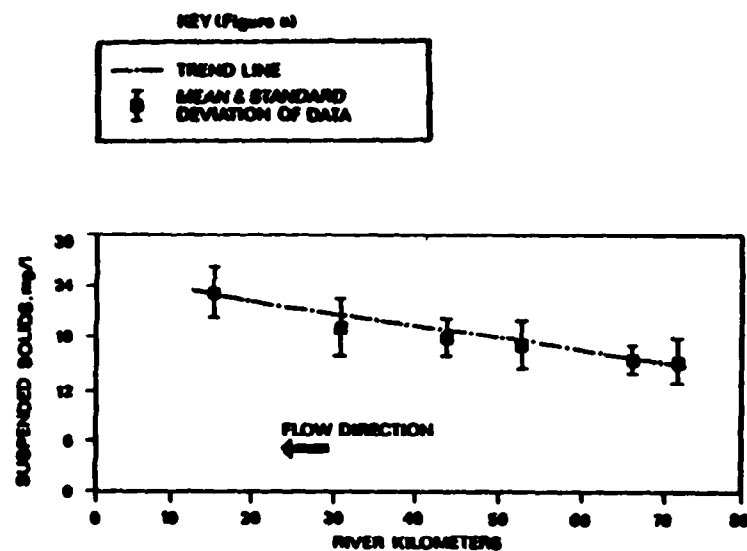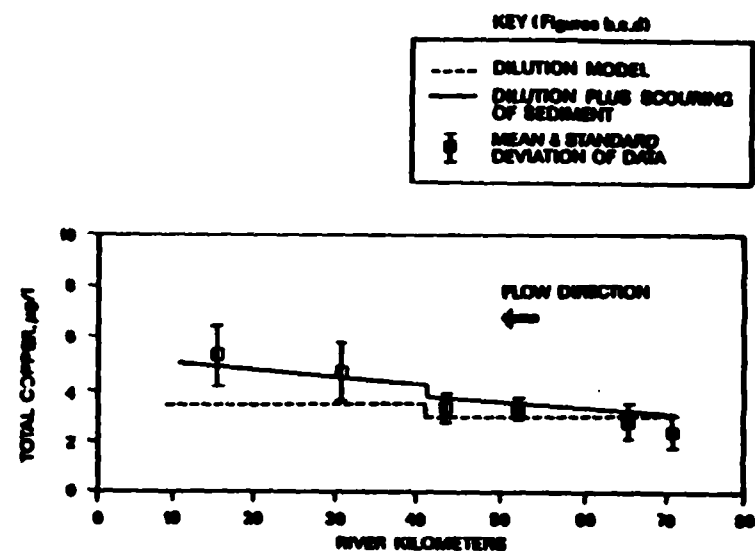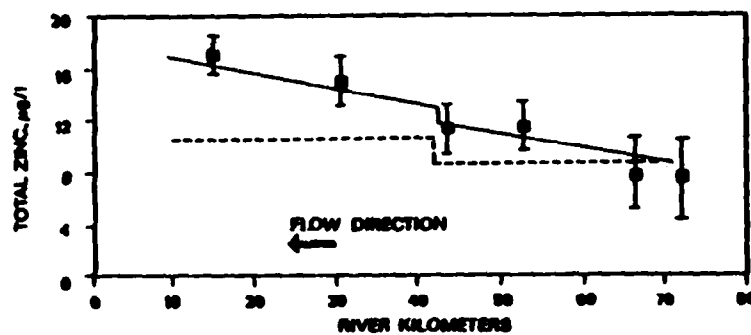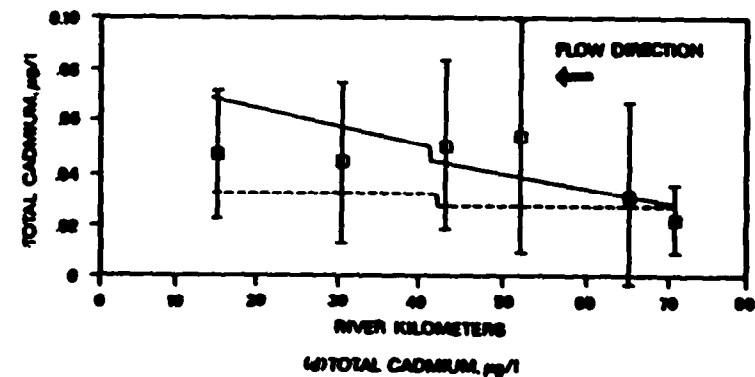
FIGURE IV-66   SUSPENDED SOLIDS AND TOTAL METAL CONCENTRATIONS IN THE
FLINT RIVER, MICHIGAN (MARCH 1982).

The data for velocity (1 m/sec), depth (2 m) and bedded sediment concentration (0.2 kg/l) are from Delos et al. (1983). Note that Figure IV-62 shown earlier suggests that scour may be important at a stream velocity of 1 m/sec.

The fraction f_{p2} is probably very close to unity for each of the three metals zinc, copper, and cadmium. To use Equation IV-179, the concentration in the bed, C_{2i}, and the upstream concentrations $C_{T1}(0)$ are needed. The $C_{T1}(0)$ values are the same as those calculated in preparing the dilution analyses for Figures IV-64(d) through (f).

The C_{2i} values can be estimated looking at the historical data for the previous steady period (December), and by calculation based on total metal concentration as found by the dilution model (Figure IV-64a, b, and c). For the present analysis, C_{2i} is based on the particulate levels in the water column (during December 1981):

$$C_{2i} \approx C_{p2} = \frac{m_2}{m_1} C_{p1}$$

The levels are shown below:

	$C_{pi}, \mu g/l$	$C_{p2}, \mu g/l$
Zinc	6.	12 x 10
Copper	1.	2 x 10
Cadmium	0.03	0.06 x 10

These numbers are based on $m_1 = 0.00001$ kg/l (for December 1981) and $m_2 = 0.2$ kg/l. Substituting the required information into Equation IV-179, the results are shown plotted in Figure IV-66b, c, and d. Equation IV-156 is applied twice, since there are two point sources in the reach.

The increase in concentration due to scour over the 70 km region for each metal is:

	ΔC_1, $\mu g/l$, due to scour over 70 km
Zinc	6.8
Copper	1.1
Cadmium	0.04

For example, the incremental zinc concentration is:

$$\frac{w_{rs} \, f_{p2} \, C_{2i}}{H_1 u} x = \frac{1.4 \cdot 10^{-4} \cdot 1 \cdot 12 \cdot 10^{+4}}{2 \cdot 1 \cdot 86400} \cdot 70 \cdot 10^3 = 6.8 \, \mu g/l$$

— END OF EXAMPLE IV-21 —

During periods when settling rather than scour is the predominant mechanism affecting suspended solid concentrations in t' water column, the suspended solids concentrations, SS(x), change over distance:

$$SS(x) = SS(0) \exp\left(\frac{-w_s x}{H_1 u}\right) \tag{IV-183}$$

The effective settling velocity can be found directly from this equation:

$$w_s = \frac{-H_1 u}{x} \ln\left[\frac{SS(x)}{SS(0)}\right] \tag{IV-184}$$

When metal-contaminated solids settle out of the water column, the process can be modeled by the following ordinary differential equation:

$$u \frac{dC_T}{dx} = \frac{-w_s C_s}{H_1} \tag{IV-185a}$$

where C_s is the particulate metal concentration, $\mu g/l$. C_s can be related to C_T by

$$\frac{C_s}{C_T} = \frac{K_p SS \cdot 10^{-6}}{(1 + K_p SS \cdot 10^{-6})} \tag{IV-185b}$$

Upon substitution of C_s from Equation IV-185b and SS from Equation IV-183 into Equation IV-185a, and by specifying the boundary condition for C_T as:

$$C_T = C_{T_0} \text{ at } x = 0 \tag{IV-185c}$$

it is possible to solve Equation IV-185a as a function of distance to get:

$$C_T = C_{T_0} \exp\left[\ln\left(K_p SS(0) \cdot 10^{-6} + e^{\frac{w_s x}{H_1 u}}\right) - \ln\left(K_p SS(0) \cdot 10^{-6} + 1\right) - \frac{w_s}{H_1 u} x\right] \tag{IV-135d}$$

When the metal is highly sorbed to the sediment (i.e., $K_p SS \cdot 10^{-6} \gg 1$), this equation simplifies to:

$$C_T = C_{T_0} \exp\left(\frac{-w_s}{H_1 u} x\right) = \frac{C_{T_0}}{SS(0)} SS(x) \tag{IV-186a}$$

If settling were to continue indefinitely downstream, then the metal would eventually be depleted from the water column. The above equation also shows that the decrease in metal concentration is directly proportional to decrease in solids concentration. By monitoring solids the decrease in metals can be directly estimated as long as $K_p SS \cdot 10^{-6} >> 1$.

If the fraction of metal which is adsorbed is small, Equation IV-185 simplifies to

$$C_T = C_{T0} \exp \left[K_p \ SS(0) \cdot 10^{-6} \left(e^{\frac{-W_s x}{uH_1}} - 1 \right) \right] \qquad \text{(IV-186b)}$$

Eventually, as the solids are depleted from the water column, the total concentration approaches

$$C_T = \frac{C_{T0}}{\exp(K_p SS(0) \cdot 10^{-6})} \qquad \text{(IV-186c)}$$

Under these conditions $(K_p SS(0) \cdot 10^{-6} < 1)$, the total loss from the water column by settling is not likely to be large. For example, if $K_p SS(0) \cdot 10^{-6} = 0.1$, then $C_T = 0.9 \ C_{T0}$.

─── EXAMPLE IV-22 ───

During the August 1981 Flint River survey, the suspended solids profile (Figure IV-67a) indicates that a net deposition of suspended solids was occurring between km 40 and km 70. Based on Equation IV-184, the approximate deposition rate between km 70 and km 40 is:

$$w_s = \frac{0.5 \times 0.2}{30 \times 10^3} \ \ln \left(\frac{10}{4} \right) \times 86400 = 0.26 \ \text{m/day}$$

where the depth (0.5 m) and velocity (0.2 m/sec) are taken from Delos et al. (1983).

Average partition coefficients are also obtained from estimates in Delos et al. (1983) and are:

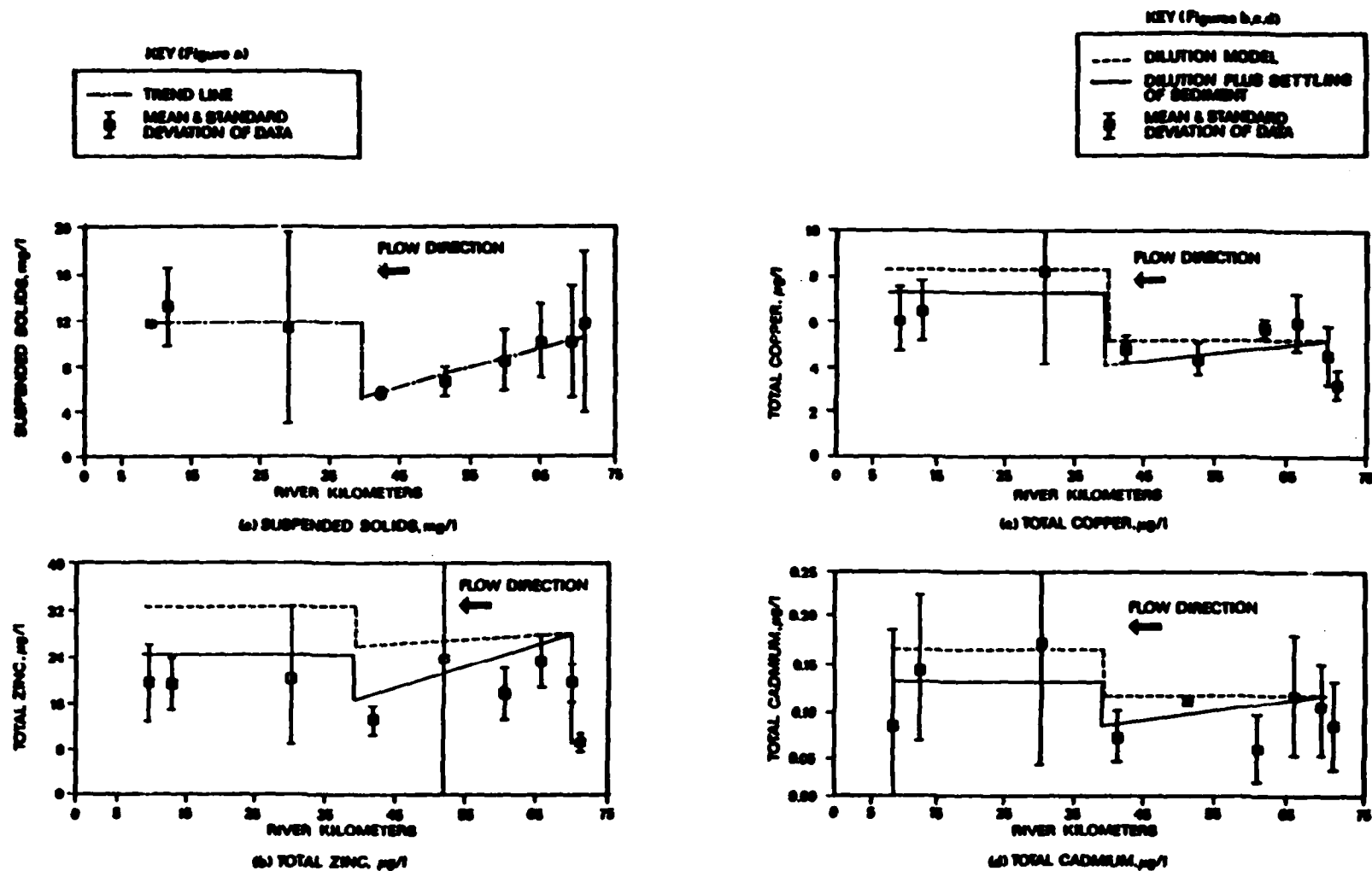| Metal	K (cm^3/gm)
Zinc	0.2 x 10^6
Copper	0.06 x 10^6
Cadmium	0.1 x 10^6

FIGURE IV-67   SUSPENDED SOLIDS AND TOTAL METAL CONCENTRATIONS IN FLINT RIVER, MICHIGAN (AUGUST 1981). (AVERAGE FLOW = 2.66M³/SEC (94 CFS) AT KM 71.9.)

Based on these partition coefficients, the product $K_p SS \cdot 10^{-6}$ is between 0.6 to 2.0 for the metals. Hence, Equation IV-185d is probably more applicable than Equations IV-186a, b, or c. The equation is used to predict the concentration at km 40 based on the boundary concentration calculated in the dilution example (Example IV-20) and the remaining data shown earlier. The calculation is shown in detail for zinc:

Zinc:

$$Zn_T = 26 \exp\left[\ln\left(0.2 \times 10^6 \times 10 \times 10^{-6} + \exp\left(\frac{.26 \times 30000}{.5 \times .2 \times 86400}\right)\right)\right.$$

$$\left. - \ln\left(0.2 \times 10^6 \times 10 \times 10^{-6} + 1\right) - \frac{.26 \times 30000}{.5 \times .2 \times 86400}\right]$$

$$= 26 \ (0.6) = 16 \ \mu g/l$$

Copper:

$$Cu_T = 5 \ (.8) = 4 \ \mu g/l$$

Cadmium:

$$Cd_T = 0.1 \ (.7) = 0.07 \ \mu g/l$$

The results are plotted in Figure IV-67b, c, and d. The predicted values agree more closely with the observed values than do the predictions from the dilution analyses.

—————————————— END OF EXAMPLE IV-22 ——————————————

4.10.3.4 Settling of Metals in Small Impoundments on Rivers

The preceding section presented models which could be used to predict the effects of either settling or scour of solids on trace metal concentrations in rivers. While settling of metal contaminated solids certainly can occur in rivers during low flow conditions, most settling is likely to occur in reservoirs or lakes located on rivers. Investigations frequently reveal that total metal concentrations in river systems, when averaged over a long period of time, decrease with distance. This indicates there is a net loss of metal from the water column, and that perhaps settling is a primary reason. In an extreme approach, some researchers have ignored downstream transport of metals altogether, outside of a small mixing zone, and have hypothesized that metals are rapidly depleted from the water column either by settling

or adsorption to bedded sediments. However, this approach contradicts the results presented earlier which show that metals, even ones which adsorb strongly such as mercury, can be transported downstream.

Solids that are suspended in the water column do tend to settle because of gravitational forces, but also tend to remain in suspension because of turbulence. Evidence shows that suspended solids levels can remain fairly constant over long distances. In reservoirs which are more quiescent than rivers, the turbulent eddies diminish, and often gravitational settling becomes important. Thus for these screening analyses, reservoirs are modeled as sinks of metals.

Based on the idealized reservoir and nomenclature shown in Figure IV-68, mass balances for solids and metals are developed. The solids mass balance is:

$$S^O = \frac{S^i}{\left(\frac{Tw_s}{H} + 1\right)} \tag{IV-187}$$

where

T	=	hydraulic detention time, days
S^i, S^O	=	concentration of suspended solids in inflow and outflow, respectively, mg/l
H	=	mean depth of reservoir, m
w_s	=	settling velocity, m/day.

The total metal concentration leaving the reservoir at steady state can be approximated as:

$$C_T^O = \frac{C_T^i}{1 + \frac{Tw_s}{H} \frac{S^O K_p \cdot 10^{-6}}{\left(1 + S^O K_p \cdot 10^{-6}\right)}} \tag{IV-188a}$$

$$= \frac{C_T^i}{1 + \frac{(S^i - S^O) K_p \cdot 10^{-6}}{1 + S^O K_p \cdot 10^{-6}}} \tag{IV-188b}$$

$$= \frac{C_T^i (1 + S^O K_p \cdot 10^{-6})}{1 + S^i K_p \cdot 10^{-6}} \tag{IV-188c}$$
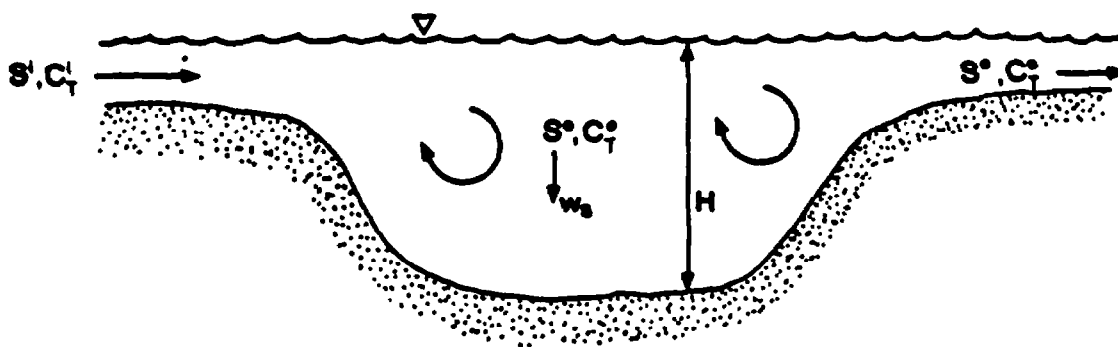
FIGURE IV-68   DEFINITION SKETCH OF IDEALIZED RESERVOIR

The dissolved metal concentration is:

$$c^o = \frac{c^i \, (1 + K_p \, S^i \cdot 10^{-6})}{(1 + K_p \, S^i \cdot 10^{-6})} = \frac{c_T^i}{1 + K_p \, S^i \cdot 10^{-6}} = c^i \quad . \qquad \text{(IV-189)}$$

If the particle sizes of suspended sediments in the inflowing and outflowing waters are significantly different, then the partition coefficient can also be quite different in the two waters. This is primarily because the smaller particles have greater surface area available for adsorption. The following analysis shows how to approximately account for these differences.

For the solids balance, each particle size (e.g., fine silt) can be accounted for individually:

$$S_j^o = \frac{S_j^i}{\left(\dfrac{T \, w_{sj}}{H} + 1\right)} \qquad \text{(IV-190)}$$

where the subscript j denotes particle class.

If the inflowing and outflowing concentrations of particles can be estimated by class size then the settling velocities can be calculated as:

$$w_{sj} = \frac{H}{T}\left(\frac{S_j^i}{S_j^o} - 1\right) \qquad \text{(IV-191)}$$

This approach assumes the internally generated solids in class j are of negligibly small amount.

The linear adsorption isotherm for particle class j is:

$$X_j = K_{pj} \, C \qquad \text{(IV-192)}$$

where

X_j = mass of metal adsorbed per mass of sediment in jth particle class

K_{pj} = partition coefficient for jth particle size

then

$$c_{sj}^0 = K_{pj}\, c^0\, S_j^0 \cdot 10^{-6} \qquad \text{(IV-193)}$$

or

$$c_s^0 = \Sigma c_{sj}^0 = c^0 \Sigma K_{pj}\, S_j^0 \cdot 10^{-6} \quad . \qquad \text{(IV-194)}$$

The concentration of metal in the outflow becomes:

$$c_T^0 = \frac{c_T^i}{1 + \dfrac{\Sigma K_{pj}\,(S_j^i - S_j^0)10^{-6}}{(1 + \Sigma K_{pj} S_j^0 \cdot 10^{-6})}} \qquad \text{(IV-195a)}$$

$$= \frac{c_T^i\,(1 + \Sigma K_{pj} S_j^0 \cdot 10^{-6})}{(1 + \Sigma K_{pj} S_j^i \cdot 10^{-6})} \qquad \text{(IV-195b)}$$

$$= c^i\,(1 + \Sigma K_{pj} S_j^0 \cdot 10^{-6}) \qquad \text{(IV-195c)}$$

and

$$c^0 = \frac{c_T^0}{1 + \Sigma K_{pj}\, S_j^0 \cdot 10^{-6}} = c^i \quad . \qquad \text{(IV-189b)}$$

Equation IV-189b shows that the dissolved fraction of the metal is not affected by the reservoir so that if most of the metal is dissolved, then the reservoir is not an effective sink for the metal.

To handle multiple partition coefficients in a manner amenable to simplified calculation, it is hypothesized that partition coefficients are inversely proportional to specific surface area, or

$$\frac{K_{pr}}{SA_r} = \frac{K_{pj}}{SA_j} \qquad \text{(IV-196)}$$

where

 r denotes a reference particle group (e.g., clay)

 SA = specific surface, m^2/g.

The tabulations below show ranges and typical values for specific areas for sands, silts, and clays.

Solid	Range of Specific Areas (m^2/g)	Typical Value (m^2/g)
Sand	1 - 50	10
Silt	50 - 100	60
Clay	100 - 800	200

Rai et al. (1983) provide a good summary of specific surface areas (and other adsorption related parameters) for a variety of solid surfaces, including metal hydroxides. Using the relationship embodied in Equation IV-196, C_T^o becomes:

$$C_T^o = C_T^i \cdot \frac{1 + \dfrac{K_{pr} \cdot 10^{-6}}{SA_r} \Sigma SA_j \, S_j^o}{1 + \dfrac{K_{pr} \cdot 10^{-6}}{SA_r} \Sigma SA_j \, S_j^i} \qquad (IV-197)$$

EXAMPLE IV-23

Consider a river with two reservoirs located on it (Figure IV-69). The detention time and depth of each reservoir are:

Reservoir	Detention Time (days)	Depth (m)
Haley	3	3
Dell	20	6

Suppose the suspended solids entering the first reservoir from upstream are:

Category	Percent by Weight	Concentration (mg/l)	Settling Velocity (cm/sec)	Specific Surface Area (m^2/g)
Sand	50	100	0.1	10
Silt	25	50	5×10^{-2}	60
Clay	25	50	3×10^{-4}	200

The total zinc concentration in the river upstream of Haley Reservoir is assumed to be 150 μg/l. Find the total zinc concentration in the water column below Haley Reservoir and below Dell Reservoir assuming that the loss from the water column is by sedimentation only.

Assume that a typical partition coefficient for zinc on clays is 10^4 cm^3/gm.
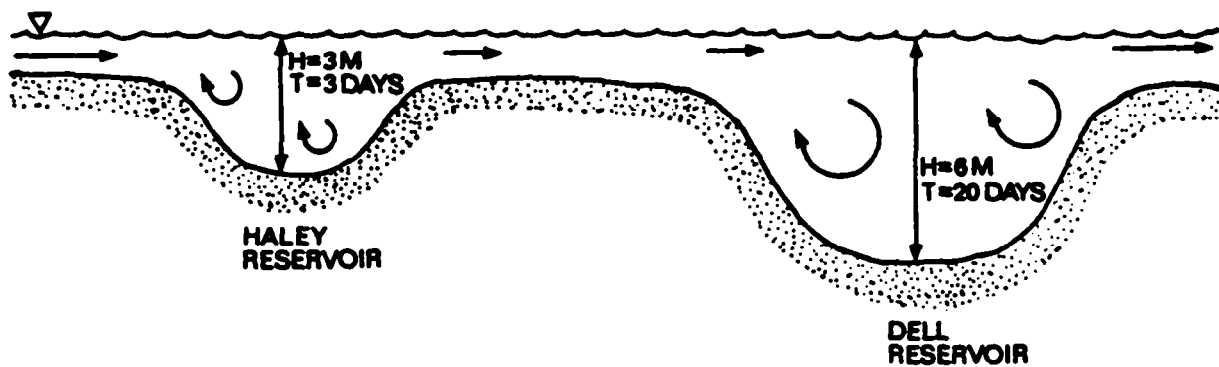
FIGURE IV-69   DEFINITION SKETCH USED IN EXAMPLE IV-23

The specific surface areas of the solids are typical values based on the data presented earlier. The settling velocities are based on Stokes Law, as described in Chapter 5.

From Equation IV-190, the concentrations of the suspended materials leaving Haley Reservoir are:

$$S_{sand} = \frac{100}{\dfrac{3\,(.001)\,86400}{3} + 1} = 1.1 \text{ mg/l}$$

$$S_{silt} = \frac{50}{\dfrac{3 \cdot 5 \cdot 10^{-4}}{3}\,86400 + 1} = 1.1 \text{ mg/l}$$

$$S_{clay} = \frac{50}{\dfrac{3 \cdot 3 \cdot 10^{-6}}{3}\,86400 + 1} = 40 \text{ mg/l} \quad .$$

Nearly all the silt and sand are deposited in the reservoir, but only 20 percent of the clay. The metal concentration in the outflow from Haley Reservoir is:

$$Zn = 150\,\frac{1 + 10^{4-6}/200\,(10 \times 1.1 + 60 \times 1.1 + 200 \times 40)}{1 + 10^{4-6}/200\,(10 \times 100 + 60 \times 50 + 200 \times 50)}$$

$$= 150\,(.83) = 120\,\mu g/l \quad .$$

Considering Dell Reservoir, it is apparent at a glance that the quantity of sand and silt leaving the reservoir is negligible. The concentration of clay leaving the reservoir is:

$$S_{clay} = \frac{40}{\frac{20 \cdot 3 \cdot 10^{-6}}{3} \, 86400 + 1} = 15 \text{ mg/l} \quad .$$

The total metal in the outflow of Dell Reservoir is:

$$Zn = 120 \, \frac{1 + \frac{10^{4-6}}{200} \, 200 \cdot 15}{1 + \frac{10^{4-6}}{200} \, (10 \times 1.1 + 60 \times 1.1 + 200 \times 40)}$$

$$= 120 \, (.82) = 100 \, \mu g/l \quad .$$

It is somewhat surprising that the zinc remains in such high concentrations after passing through two reservoirs. However, consider that the dissolved zinc upstream of the first reservoir is:

$$Zn_{dissolved} = \frac{150}{1 + \frac{10^{4-6}}{200} \, (100 \times 10 + 50 + 60 + 50 + 200)}$$

$$= 88 \, \mu g/l \quad .$$

Hence, most of the zinc remaining in the river downstream of Dell Reservoir is dissolved.

————————————— END OF EXAMPLE IV-23 —————————————

4.10.3.5 Adsorption and Desorption of Metal Between the Water Column and Bedded Sediments

The analyses presented in the previous sections are steady-state analyses, and ignore diffusive transport between the water column and bed. This is justified if the degradation rate of metal is negligible and the partition coefficients in the water column and the bed are the same. From these assumptions, the dissolved phase concentrations of metal are found to be the same in the water column and in the bed. Consequently, there is no net adsorption or desorption between the bedded and suspended materials.

However, situations do occur when the steady-state assumption is not valid. For example, consider a new discharge which begins operation on a previously uncontaminated river reach. As the contaminated water moves downstream, the metal in the water column is in contact with uncontaminated bedded sediment, and some of the dissolved metal can adsorb onto and diffuse into the bedded sediment. During this

process, the concentration in the water column decreases with distance. Figure IV-46 shown previously in this chapter illustrates the converse situation which occurs when an influx of metal is reduced so that the metal in the bedded sediments is no longer in equilibrium with the metal in the water column. Then, desorption tends to occur.

An approach is shown below that can address these situations, and can be used to answer questions such as:

- How long is required for river sediments to be cleansed of excessive metal concentrations by the process of natural desorption?

- If a new source of metal contamination begins discharge, how long is required before the impact of the elevated metal concentrations is fully felt downstream?

The following approach considers adsorption and desorption as the mechanisms of transporting metal between the water column and bed. The effects of resuspension and deposition are not considered mainly because the time frame of interest here is likely to be months to years. Resuspension and deposition rates fluctuate considerably over extended time periods, and tend to negate each other.

Figure IV-70 illustrates the relationship between the dissolved metal concentration in the water column and in the bedded sediments during a period when conditions are not in equilibrium. Near the sediment-water interface, there is likely to exist a relatively thin layer where the dissolved phase concentration is approximately the same as in the water column. Below this mixed layer, vertical diffusion in the sediment controls movement of the dissolved metal. By developing and simultaneously solving mass balance equations for the metal in the water column, in the mixed layer, and in the diffusion layer, the dissolved phase concentration in the water column is found to be:

$$C = \begin{cases} (C_b - C_o) \, G \, (t, \, x) + C_o, & x < \dfrac{t}{B} & \text{(IV-198a)} \\[2mm] C_o & , \, x > \dfrac{t}{B} & \text{(IV-198b)} \end{cases}$$

where

C_o = initial concentration in the water column (at t = 0), $\mu g/l$

C_b = constant background concentration (at x = 0), $\mu g/l$

t = time, days

x = distance below location where C = C_b, m

B = $\dfrac{1}{u} + \dfrac{M_s \, K_p \cdot 10^{-6}}{uH \, (1 + K_p S \cdot 10^{-6})}$, days/ m

u = stream velocity, m/day

M_s = mass of contaminated sediments, per unit area, in thin mixed layer, g/m^2
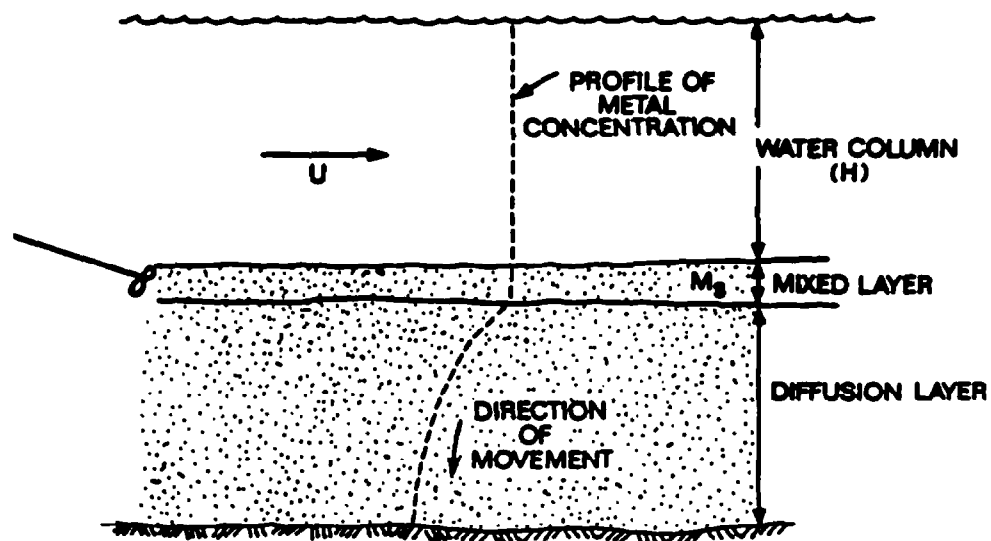
FIGURE IV-70   RELATIONSHIP BETWEEN METAL CONCENTRATION IN
WATER COLUMN AND IN BEDDED SEDIMENTS DURING
A NONEQUILIBRIUM ADSORPTION PERIOD

H   = water depth, m

K_p = partition coefficient, 1/kg

S   = suspended sediment concentration, mg/l

G(t,x)   = an unspecified function of time and distance, unitless.

Equation IV-198b above indicates that the boundary condition $(C = C_b)$ propagates downstream at a speed 1/B which, depending on the magnitude of $M_s K_p$, can be significantly slower than the stream velocity. The quantity 1/B is a useful parameter because it can be used to estimate the time required for the effects of a change in pollutant loading to be propagated downstream.

Equation IV-198 can be used to estimate the residual concentration in a river when the boundary concentration is set equal to zero after a period when metals have been accumulating in the bed (i.e., when $C_b = 0$ and $C_0 > 0$). Conversely, the same equation can be used to predict the adjustment in stream metal concentration following start-up of a discharge where formerly there was none (i.e., when $C_b > 0$, $C_0 = 0$).

To perform these calculations, the function G(t,x) is required. Using an approximation:

$$C \approx (C_b - C_0) \; erfc \left[\frac{\sqrt{U}}{2uH \; (1 + K_p S \cdot 10^{-6}) \sqrt{t - Bx}} \; x \right] + C_0 \; . \qquad (IV-199)$$

where

$$D = \frac{D_m \theta}{\theta + \rho_b K_p}$$

D_m = vertical diffusion coefficient, m^2/day

θ = void fraction

ρ = bulk density, g/m^3

K_p = partition coefficient, $1/kg$.

This is the equivalent of Equation IV-198a, which is valid for large times following a change in mass loading to a river (e.g., one year or greater). The major difficulty in using Equation IV-199 is finding appropriate input data for two of the important unknowns: D (or D_m) and M_s. When $K_p S$ is significantly less than unity and the depth of the mixed layer is small, Equation IV-199 can be further simplified to

$$C = (C_b - C_0) \, erfc\left(\frac{\sqrt{D} \; x}{2uH \sqrt{t}}\right) + C_0 \qquad\qquad (IV-200)$$

Suppose the temporarily changing concentration due to metal desorption from bedded sediments is desired. Set C_b = 0, so

$$\frac{C}{C_0} = erf\left(\frac{\sqrt{D} \; x}{2uH \sqrt{t}}\right) . \qquad\qquad (IV-201)$$

In this case, when the mixed layer is of negligible thickness, substituting typical values of D, u, H into Equation IV-201 shows that $C \ll C_0$. That is, desorption of metal back into the water column produces metal concentrations which are significantly below C_0, so the levels are not likely to be significant enough to be of concern. On the other hand, under these conditions the concentrations in the bed are likely to remain elevated for a long period of time, and could adversely impact the benthic community. In summary, it appears that unless there exists a mixed layer of sediments which can exchange metal with the water column at a rate substantially higher than by diffusion processes alone, desorption of metals from the bed back into the water column is likely to produce concentrations in the water column of secondary importance. Scour of the contaminated sediments is probably more responsible for reintroducing the metal back into the water column at rates where noticeably elevated concentrations may occur.

4.10.3.6 Summary

4.10.3.6.1 Overall Approach

The tools presented in the previous sections can be used to evaluate the influ-

ence of three hydrological conditions (all steady-state) on metal concentrations in rivers. The hydrologic conditions can be defined in terms of the suspended solids levels in rivers:

- a period of net settling
- a period of net scour
- a period of equilibrium (scour and sedimentation balance out each other, or each is negligible).

In order to use these concepts within the screening framework presented here, the annual cycle of events in a river is viewed as a series of steady-state conditions (each of which may be of several months' duration) separated by unsteady transition periods. The term "steady-state" is used cautiously here because each of the pseudo-steady periods may have elements of unsteadiness. For example, consider a high flow condition where metal-contaminated solids are continually being scoured from the bottom. Scouring of contaminated sediments will continue only as long as they are present, i.e., until the depth of contamination is exceeded. After that happens, the solids being scoured no longer contribute metal to the water column. This illustrates that a river's steady-state periods may really have some dependency on a previous steady period. To properly use the steady-state approach in the screening manual requires the user to carefully define the pseudo-steady periods, and select the data appropriate for each period.

To begin the analysis, a dilution approach is recommended, in the case of either single or multiple sources. This implies that multiple sources interact with each other, and downstream concentrations depend on both total mass loading and total dilution. A dilution analysis does not require either suspended solids concentrations or partition coefficients, unless the fraction of dissolved metal is required. Large reservoirs in the river system may require that settling of metal contaminated sediments within the reservoir be calculated, especially if most of the metal is being transported in particulate form.

As a next step, the user may wish to perform a scour analysis to see if metal concentrations become elevated in the water column during scour even though the flow rate is probably higher (thus, more dilution water is available). In such a case, the user might want to perform an anlysis of each hydrologic condition throughout the annual cycle since each condition is not truly independent of the other.

4.10.3.6.2 Uncertainty

Analysis of uncertainty for these screening methods is limited to a perturbation analysis: perturb (or change) the value of a variable within the range of uncertainty and see how the results change. If significant changes occur, the results are sensitive to that variable. At that time, some data could be collected to remedy the situation (see Section 4.10.5). Typically, for analyses discussed in this document,

the variables which require more accurate quantification are background and point sources, flow rates, and partition coefficients.

A particular use of uncertainty analyses is to address the question: Is there a significant difference in the metal concentration in the water column when the dilution approach is used compared to when settling and/or scour occur? For example, a user may have to decide whether concentration levels predicted to be 25 percent higher during a scour period, compared to an equilibrium period when net scour and settling are zero, are really different. By perturbing important variables within the range of realism, their questions can be addressed.

---------------------------- EXAMPLE IV-24 ----------------------------

For the river shown in Figure IV-71, three point sources and three background sources contribute copper to the river system. Calculate the total copper concentration at locations P1, P2, P3, P4, and P5 for the following two conditions. Condition 1 is a moderate to low flow period where the solids within the water column appear to be in equilibrium over distance. Perform a dilution analysis during this period. Condition 2 is a high flow period which follows Condition 1. Data collected reveal that solids are being scoured along the mainstem during Condition 2 as follows:

- ΔSS = 50 mg/l, from point source 1 to P1
- ΔSS = 25 mg/l, from just below tributary B to P2
- ΔSS = 10 mg/l, from just below tributary C to P4.

Determine which condition (the steady-state or scour condition) produces higher instream metal concentrations. Table IV-59 summarizes the required source data.

The dilution analysis (Condition 1) proceeds by applying the mixing equation (Equation IV-156) at each location, working from upstream to downstream:

$$C_{p1} = \frac{C_A \, Q_A + C_1 \, Q_1}{Q_A + Q_1} = \frac{5 \cdot 50 + 500 \cdot 5}{50 + 5} = 50 \ \mu g/l$$

$$C_{p2} = \frac{50 \cdot 55 + 5 \cdot 10}{55 + 10} = 43 \ \mu g/l$$

$$C_{p3} = \frac{C_c \, Q_c + C_2 \, Q_2}{Q_c + Q_2} = \frac{5 \cdot 20 + 75 \cdot 2}{22} = 11 \ \mu g/l$$

$$C_{p4} = \frac{11 \cdot 22 + 43 \cdot 65}{22 + 65} = 35 \ \mu g/l$$
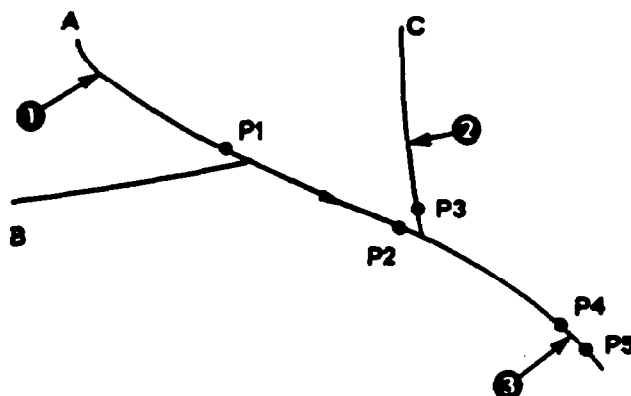
FIGURE IV-71   RIVER SYSTEM FOR EXAMPLE IV-24

TABLE IV-59

SOURCE DATA REQUIRED FOR EXAMPLE IV-24

Source	Condition 1		Condition 2	
	Q(cfs)	Total-Cu(μg/l)	Q(cfs)	Total-Cu(μg/l)
A	50	5	500	5
B	10	5	100	5
C	20	5	200	5
1	5	500	5	500
2	2	75	2	75
3	10	400	10	400

$$C_{p5} = \frac{35 \cdot 87 + 400 \cdot 10}{87 + 10} = 73 \ \mu g/l \quad .$$

The results are summarized in Table IV-60.

For condition 2, the incremental total metal concentration in each of the three reaches of the mainstem is, based on Equation IV-182:

$$\Delta SS \cdot K_p \cdot C_{SS} \cdot 10^{-6}$$

where

K_p = partition coefficient for copper ($\sim 10^4$ l/kg, assumed for this example)

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TABLE IV-60

SUMMARY OF RESULTS OF EXAMPLE IV-24

Location	Condition 1		Condition 2	
	Q(cfs)	Total-Cu(μg/1)	Q(cfs)	Total-Cu(μg/1)
P1	55	50	505	24
P2	65	43	605	28
P3	22	11	202	6
P4	87	35	807	25
P5	97	73	817	30

c_{SS} = steady-state concentration of dissolved copper in the water column during Condition 1.

For c_{SS}, use an average value over the river:

$$\frac{50 + 43 + 35}{3} f_d = 43f_d, \ \mu g/1$$

$$f_d = \frac{1}{1 + 10^4 \cdot 50 \cdot 10^{-6}} = 2/3, \text{ assuming SS} = 50 \text{ mg/1 during}$$
Condition 1.

The incremental copper concentration in each of the three reaches caused by scour are:

Reach 1: $50 \cdot 10^4 \cdot \frac{2}{3} \cdot 43 \cdot 10^{-6} = 14 \ \mu g/1$

Reach 2: $25 \cdot 10^4 \cdot \frac{2}{3} \cdot 43 \cdot 10^{-6} = 7 \ \mu g/1$

Reach 3: $10 \cdot 10^4 \cdot \frac{2}{3} \cdot 43 \cdot 10^{-6} = 3 \ \mu g/1$

To each of these results, the concentration at the upstream end of each reach is added as shown in Equation IV-182. This is done by dilution analysis. For example, below point source 1:

$$C = \frac{5 \cdot 500 + 500 \cdot 5}{505} = 10 \ \mu g/1 \quad .$$

The results at the remaining locations are shown in Table IV-58.

   The total copper levels in the river during the high flow are only 50 percent as high as during the lower flow condition. Apparently, the effects of dilution caused by the higher flow are more important than the scouring effect of the copper contaminated sediments. The fact that the factor $\Delta SS \cdot K_p \cdot 10^{-6}$ is less than unity further indicates that the importance of scour is mitigated by the moderate size (<1) of this product.

--- --- -- -- -- -- -- -- -- END OF EXAMPLE IV-24 --- -- -- -- -- -- -- -- -- -- --- --

4.10.3.6.3 Answers to Questions

   In Section 4.10.2.3 (Selected Case Studies), a number of questions were posed which pertain to the the fate of metals in rivers. Based on the predictive tools just presented, these questions are answered here in a qualitative sense.

- **Is downstream transport of metals important?** Metals can be transported far downstream from their place of input. In some cases, dilution models appear adequate to predict the total metal concentration in the water column. Dilution models are appropriate when scouring of metal contaminated solids or settling of adsorbed metals are of secondary concern.

- **Are metals which are present in the water column present entirely in adsorbed form or is there a significant dissolved fraction?** Depending on the quantity and characteristics of the solids in the water column and the partition coefficient of the metals, the metal can be present in predominantly adsorbed form (>90%) or predominantly in dissolved form (>90%). When most of the metal is dissolved then downstream transport of the metal will be important. However, if most of the metal is adsorbed to suspended solids, downstream transport can <u>still</u> be important unless significant settling of the suspended matter occurs. Note that while solids tend to settle by gravitational forces, they are also kept in suspension by turbulent eddies which are generally present in free flowing rivers. Consequently, solids (and the adsorbed metals) can travel a long distance before settling.

- **What is the relationship between the water column concentrations and concentrations in the bedded sediments?** At steady-state conditions, the following approximation appears to be valid:

$$C_w = C_b$$
$$X_w = X_b$$

where

C_w, C_b = dissolved phase concentration in water column and bed, respectively

X_w, X_b = mass of metal adsorbed per mass of sediment in water column and bed, respectively.

At first glance, these relationships appear to imply that there is no difference in water column and bedded metal concentration. However, this is not true. Based on the above, the following can be concluded:

$$C_{Tw} << C_{Tb}$$

$$C_{sw} << C_{sb}$$

where

C_{Tw}, C_{Tb} = total concentration in water column and in bed, on a unit volume basis, respectively

C_{sw}, C_{sb} = adsorbed phase concentration in water column and in bed, on a unit volume basis, respectively.

On a unit volume basis, then, the metal concentration in the bed (within the contaminated layer, which might be quite thin) is likely to be significantly higher than in the water column. The primary reason for this is that the bed acts as a concentrator for metals that are settling. For example if solids that were suspended in a 1 m deep river settle onto a thin 1 mm layer at the sediment-water interface, then the concentration factor for solids and metals is 1000. Thus, a sorbed phase concentration of 10 µg/l in the water column becomes 10000 µg/l or 10 mg/l in the contaminated bed.

- What is the effect of reservoirs on metal concentrations downstream? If most of the metal that enters the reservoir is adsorbed, then the reservoir can act as a sink for the metal, depending on the hydraulic detention time and depth of the reservoir. If the detention time of the reservoir is relatively short and if the reservoir is shallow, only a small percentage of the total surface area in suspension might settle so that much of the adsorbed metal can still pass through the reservoir. Also, the dissolved fraction of the metal does not settle, so that unless the adsorbed fraction is great and most of it settles, then much of the metal that enters the reservoir can move downstream.

- What is the effect of metal desorption from river beds? Metal desorption from bedded sediments back into the water column appears to occur but at slow rates. If external sources of metals were suddenly cut back, then the equilibrium which may have existed between the bed and water column concentrations is disrupted. Under these conditions there is net desorption of metal into the water column, which tends to provide an internal source until an equilibrium is reestablished again. Complete desorption of metals from bedded sediments may take years, effectively slowing the recovery of the river in response to point source reduction.

These concentrations may be low enough to be of secondary concern to
organisms in the water column, but may be high enough to be of primary
concern to the benthic community.

4.10.4 Speciation of Metals and Equilibrium Modeling

4.10.4.1 Introduction

While the analyses in the preceding sections have proceeded under the assumption
that the fate of metals can be determined based on analysis of a single dissolved
species and a single adsorbed species, metals do not obey such a simplified pattern
of behavior. Figure IV-72 illustrates a more general picture of behavior. Dissolved
metal might be present as the free ion, or as complexes with inorganic or organic
ligands. The adsorbed metal can be adsorbed to a variety of surface types and
appears to obey different adsorption isotherms. If concentrations of metals become
too high, precipitates may form and settle from the solution, or remain suspended in
solution if particle size remains small enough. This section introduces the processes
affecting the speciation of metals. A generic discussion of processes precedes a
metal-by-metal discussion of nine of the priority metals. The generic discussion
emphasizes fate in freshwater environments. It does not detail all processes, but
rather those which are often of greatest importance. This discussion should be
balanced against the screening procedures found earlier in this document. This
second point of view can help the user to see more clearly the simplification and
assumptions made in the screening procedures and to interpret results of the screening
analysis more intelligently.

4.10.4.2 Major Processes Affecting Speciation

This discussion emphasizes the predominant fate processes likely to be of
importance for metals discharged to freshwater rivers and streams under oxic con-
ditions. This scenario, while not completely general, does encompass many commonly
occurring situations and is consistent with the scope of this section. Figure IV-73
shows the general range of pH-pe values considered here, as well as the range which
can be found in different environments. The pH-pe range for each environment are
typical but not all inclusive. Higher pe values in ground water systems are possible,
for example.

It is not necessary that users actually perform calculations relating to the
processes that are discussed here. Rather, the calculations have been performed by a
metal speciation model called MINEQL, which is applied to a number of different water
bodies (Section 4.10.4.4). The major processes that are discussed in this section
include:

   •   Precipitation-dissolution
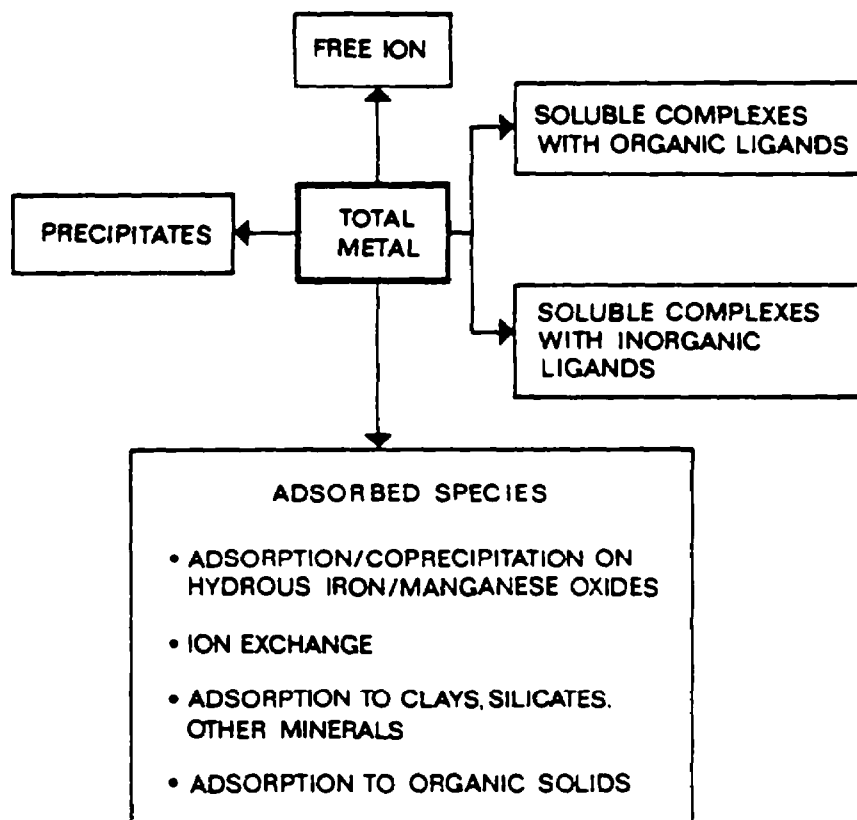
FIGURE IV-72   SPECIATION OF METALS IN THE AQUATIC ENVIRONMENT

- Adsorption
- Oxidation-reduction
- Dilution.

Several other processes of minor importance are also specifically addressed.

Before beginning the process-by-process discussion, some of the important "master variables" (terminology often used by Stumm and Morgan, 1970) that control the fate of the metals are reviewed. These master variables are pH, pe, ionic strength, and water temperature.

The solution pH (= -log $\{H^+\}$, where $\{H^+\}$ is hydrogen ion activity $\approx$ hydrogen ion concentration) is a measure of the hydrogen ion concentration. Typically, in fresh water, pH = 7 denotes neutral conditions, while pH values exceeding 7 denote basic conditions, and pH less than 7 denote acidic conditions. Ocean waters have a relatively constant pH of 8.3-8.5, due to their buffering capacity. The pH of rainwater containing only atmospheric carbon dioxide is typically 5.6-5.7. However, when other acidic inputs are significant, rainwater pH can be lowered to 4.2 or so (acid rain). The pH of river water is more variable than that of the ocean, and most often ranges from 5.2 to 8.0. Solution pH can strongly influence the speciation of metals i.e. their form, such as Cu^{2+} or $CuOH^+$) and hence their fate and toxicity.
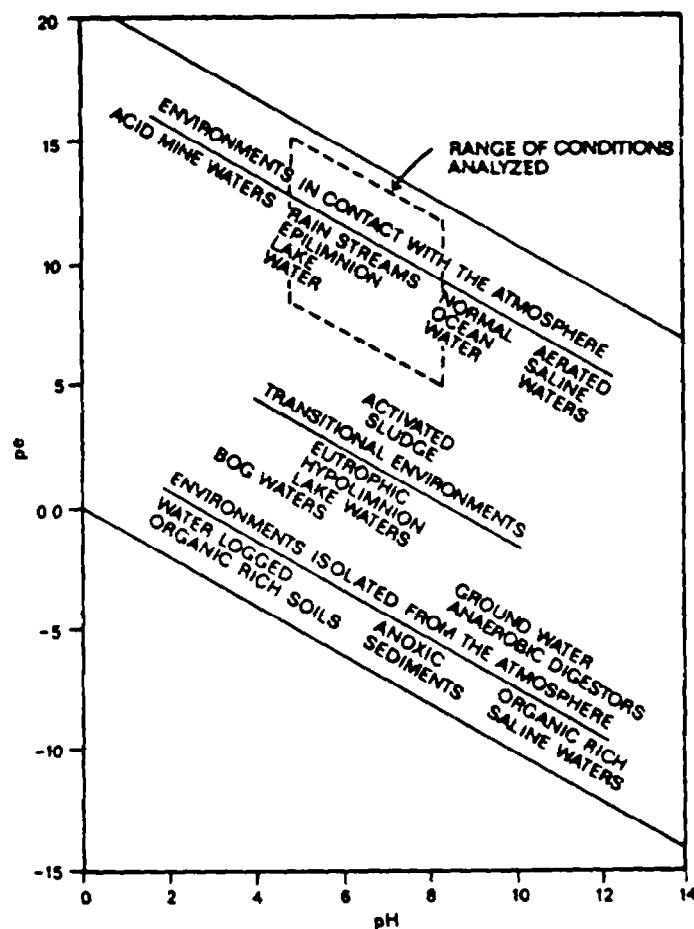
FIGURE IV-73   RELATIVE CHARACTERIZATIONS OF
                ENVIRONMENTS BY PE AND PH

A related concept is pe (= -log |e⁻|, where |e⁻| is the electron activity).
The pe describes the oxidation-reduction status of a water body, and is influential
in dictating species likely to be present in water bodies. Together with pH, pe can
be used to create equilibrium phase diagrams.

Another measure of oxidation-reduction often used is the electrochemical redox
potential, E_H. E_H and pe are related as follows:

E_H (in volts) = 0.059 pe, at 25°C

The dissolved oxygen level can also be related to pe. Based on the oxygen-water
redox reaction, this relationship is:

pe = 1/4 log P_{O_2} + 20.75 -pH

where

P_{O_2} = partial pressure of dissolved oxygen, atmospheres.

For dissolved oxygen levels corresponding to saturation (P_{O_2} = 0.2), pe = 13.6

at pH = 7. For dissolved oxygen levels of about 0.1 mg/1, pe = 13.1 at pH = 7. Hence, in most surface water systems, even in the presence of a small amount of dissolved oxygen, the pe values are typically in the range of 12 to 13.6. Only in anoxic systems (or under nonequilibrium conditions) are pe values negative. While the concept of redox equilibrium is a useful one, the user is cautioned that many natural systems are not likely to be in redox equilibrium.

Ionic strength is a measure of the concentration of ionic species in a solution. In very dilute solutions, with low concentrations of ions, the ions behave independently of each other. However, as the concentrations of ions increase, electrostatic interactions between the ions also increase. Consequently under these conditions, activities rather than concentrations are used in chemical equilibrium equations. Activities are defined as:

$$\{C\} = \gamma \ [C]$$

(IV-202)

where

$\{C\}$ = activity of species C

$[C]$ = concentration of species C

γ = activity coefficient.

For ideal or very dilute solutions, $\gamma = 1$ and activity equals concentration. Figure IV-74 illustrates how activity coefficients change with ionic strength and charge. An ionic strength of 0.5M corresponds to seawater and an ionic strength of 0.0000M corresponds to distilled water. Unless ionic strength is extremely low, activity coefficients are not expected to equal unity, especially for divalent and trivalent ions.

For the analyses here, ionic strength corrections are automatically accounted for in the equilibrium model MINEQL. The user simply has to specify the "typical" water appropriate for the conditions being analyzed (see Section 4.10.4.3).

Ionic strength (I) can be estimated from either total dissolved solids (TDS) or specific conductivity, two commonly available parameters. The appropriate relationship between TDS and ionic strength is:

$$I = 2.5 \cdot 10^{-5} \cdot TDS$$

(IV-203)

where

TDS = total dissolved solids, mg/1.

The relationship between specific conductivity (μmho) and ionic strength is shown in Figure IV-75. The relationships between ionic strength and TDS and between ionic strength and conductivity are valid for ionic strengths less than 0.1, which is more than adequate for fresh water systems. TDS levels for most fresh water in this country are less than 1200 mg/1. Corresponding to Equation (IV-203) above, the ionic strength is:
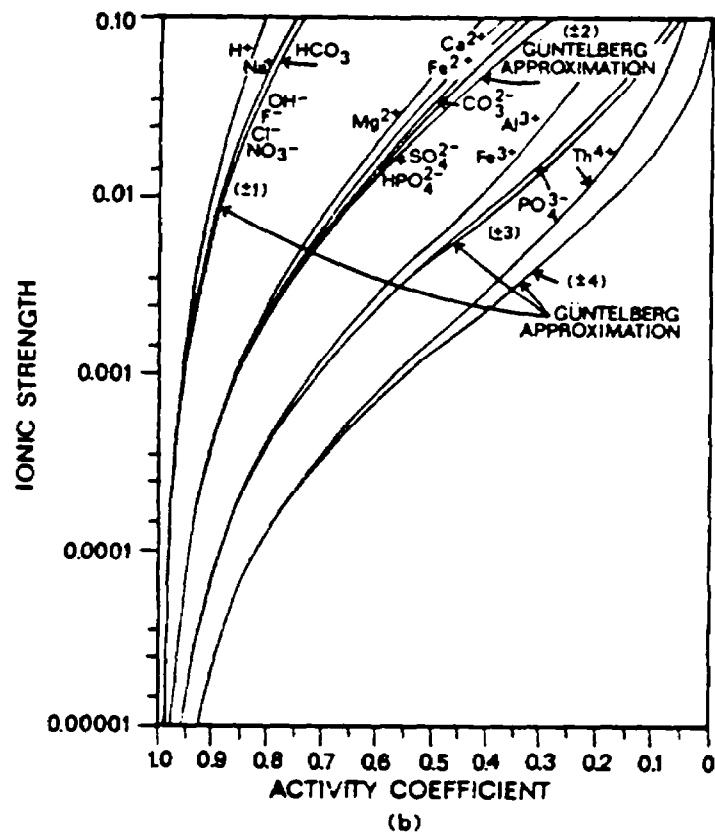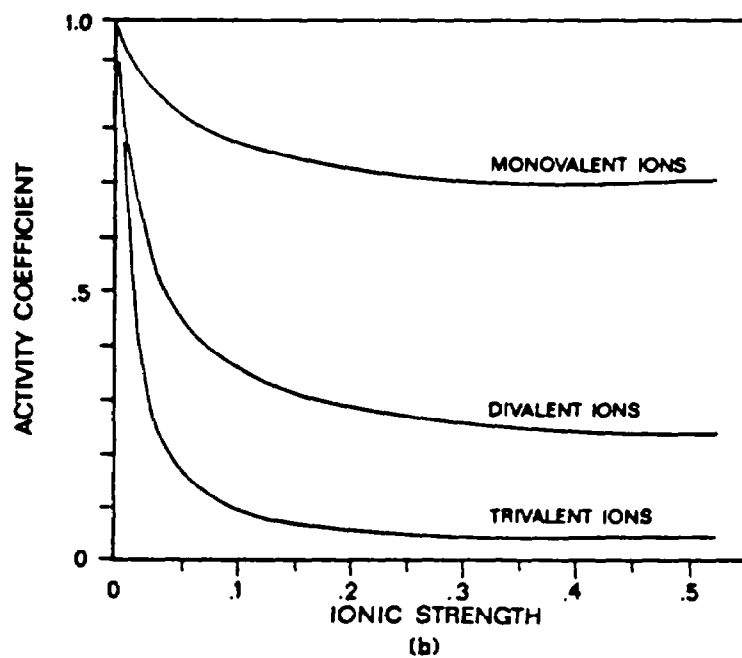
REFERENCE: MOREL AND SCHIFF, 1980, AND SNOEYINK AND JENKINS, 1980

FIGURE IV-74   ACTIVITY COEFFICIENT AND IONIC STRENGTH RELATIONSHIPS
FOR TYPICAL IONS (A) AND SPECIFIC IONS (B).
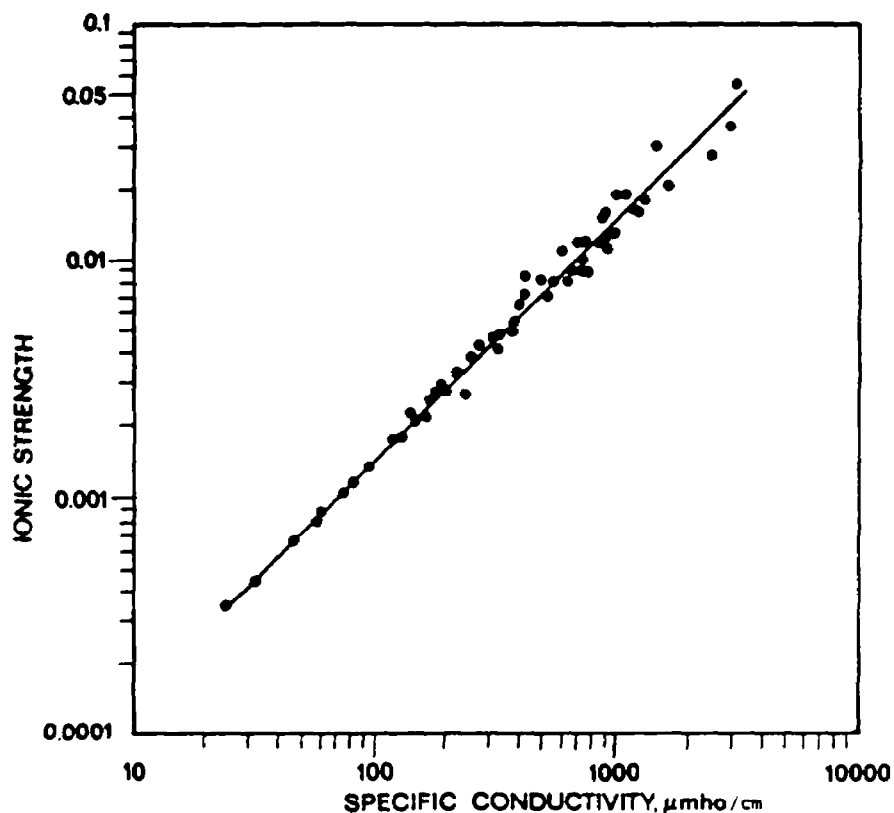
FIGURE IV-75   IONIC STRENGTH VERSUS SPECIFIC CONDUCTIVITY
FOR SURFACE WATERS (FROM LIND, 1970)

$$I = 2.5 \cdot 10^5 \cdot 1200 = 0.03$$

At this ionic strength, activity coefficients are likely to be about 0.8 to 0.9 for monovalent ions, 0.5 to 0.6 for divalent ions, and 0.1 to 0.3 for trivalent ions (see Figure IV-74b).

Water temperature influences virtually every aspect of the chemistry of metals, including solubility and equilibrium constants, and reaction kinetics. Temperature corrections can be used in MINEQL.

4.10.4.2.1 Precipitation and Dissolution

Metals are subject to solubility limitations in natural waters. Should the solubility product (defined below) be exceeded, then that metal tends to precipitate. By precipitating, the metal forms a solid phase (say lead hydroxide, $Pb(OH)_2$'s)) which might remain suspended in the water column if the solid phase particles are small enough and do not grow and if water turbulence is sufficient to keep them in suspension. However, should the solid grow to sufficient size, or be transported to a slowly moving backwater region, then sedimentation of the solid is likely.

The solubility product for a metal cation (a cation is a positively charged ion) with an anion (a negatively charged ion) is represented as:

$$M_aB_b(s) \rightleftharpoons aM^{b+} + bB^{a-} \qquad \text{(IV-204)}$$

where

$M_aB_b(s)$ = the solid phase species

M^{b+} = the positively charged metal cation (with charge b+)

B^{a-} = the anion (with charge a-).

The equilibrium constant for this reaction is defined as:

$$K_{sp} = \frac{\{M^{b+}\}^a \{B^{a-}\}^b}{\{M_aB_b(s)\}} \qquad \text{(IV-205a)}$$

$$= \{M^{b+}\}^a \{B^{a-}\}^b \qquad \text{(IV-205b)}$$

where

$\{M_aB_a(s)\}$ = activity of solid phase, defined as unity by convention

$\{M^{b+}\}$ = activity of metal cation

$\{B^{a+}\}$ = activity of anion

K_{sp} = the equilibrium constant, called the solubility product.

The relationship between activity and concentration can be invoked so that Equation IV-205b can be expressed in terms of concentrations (and activity coefficients) rather than in terms of activities. This is desirable because concentration prediction, rather than activity prediction, is the objective of the analyses. Invoking the definition of activity coefficient as the ratio of activity to concentration, Equation IV-205b can be rewritten as:

$$K_{sp} = \left(\gamma_M\left[M^{b+}\right]\right)^a \left(\gamma_B\left[B^{a-}\right]\right)^b \qquad \text{(IV-206a)}$$

$$= \gamma_M^a \gamma_B^b \left[M^{b+}\right]^a \left[B^{a-}\right]^b \qquad \text{(IV-206b)}$$

where

γ_M, γ_B = activity coefficients for the metal cation and the anion, respectively

$[M^{b+}]$ = concentration of metal cation

$[B^{a-}]$ = concentration of anion.

When $\gamma_M \approx 1$, and $\gamma_B \approx 1$, Equation IV-206b can be written in the simpler, more familiar, form:
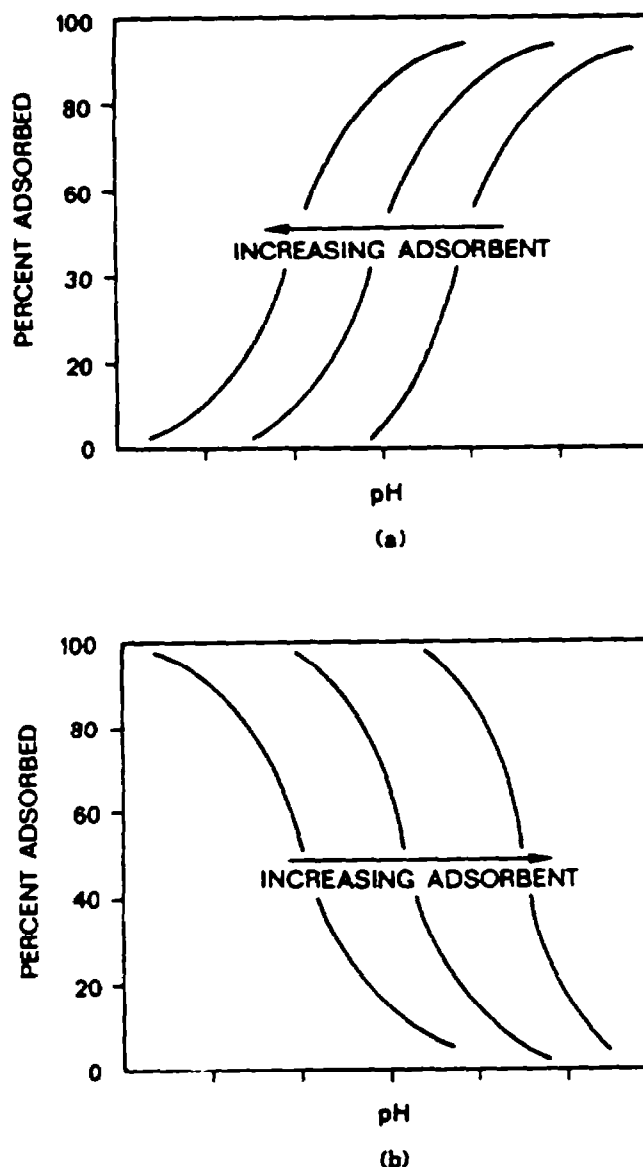
FIGURE IV-76   TYPICAL ADSORPTION CURVES FOR METAL CATIONS (A)
AND ANIONS (B) FOR A RANGE OF pH AND ADSORBENT
LEVELS.

linear and nonlinear equilibrium isotherms or other mechanistic approaches for
predicting adsorption (e.g. electric double-layer theory). For this screening
approach, the linear equilibrium adsorption isotherm is used. Linear partition
coefficients are presented from the literature.

HydroQual, as documented in Delos et al. (1983), has calculated linear partition
coefficients for rivers and lakes for various metals. They analyzed approximately
20,000 records from data bases such as STORET in order to arrive at their predictions.

They found the partition coefficients to be dependent on suspended solids concentrations, but to be independent of pH. Table IV-61 summarizes their results. Under most conditions, the expressions in the table predict that the partition coefficients are likely to exceed 10^4 1/kg, and in some cases, exceed 10^6 1/kg.

Based on linear partitioning, the fraction of metal dissolved is given by:

$$\frac{C}{C_T} = \frac{1}{1+K_p \cdot SS \cdot 10^{-6}} \qquad (IV-208)$$

where

$\frac{C}{C_T}$ = fraction dissolved

K_p = linear partition coefficient, 1/kg

SS = suspended solids, mg/l.

The results of this equation are shown in Table IV-62 for each of the metals in Table IV-61 for a range of suspended solids from 1 mg/l to 1000 mg/l. In most instances, the percent of the metal which is adsorbed exceeds 50 percent. This is in contrast to many toxic organics which often have smaller partition coefficients and, therefore, more of the toxicant is transported in the dissolved state (see, for example, Table II-14).

While the results in Tables IV-61 and IV-62 provide useful information, the possible error associated with the predicted partition coefficients is quite large. Figure IV-77 illustrates this for copper. The envelope of values encompasses an order of magnitude.

Rai et al. (1983) have summarized adsorption data for numerous priority metals. The summary includes K_p values for linear partitioning as well as data for other types of isotherms. As a result of reviewing the work of Rai et al. (1983), and other literature sources it appears that there is generally no consistency as to "expected" values of K_p for a particular as metal in the natural environment. Some researchers report relatively small partition coefficients for metals while others, such as Delos et al. (1983), report significantly larger values. This uncertainty (or variability) emphasizes that site-specific K_p values should be used if possible and that better methods for predicting the importance of partitioning are probably warranted. Based on the fact that metals speciate and each species exhibits different adsorption tendencies, it is not difficult to see why a "K_p approach" is limited in predictive ability. However, the alternative approaches are not well supported either and site-specific data can be quite beneficial, regardless of the approach.

4.10.4.2.3 Oxidation-Reduction

Oxidation-reduction reactions are conceptually analogous to acid-base reactions, except they are significantly slower. Oxidants and reductants are defined as electron
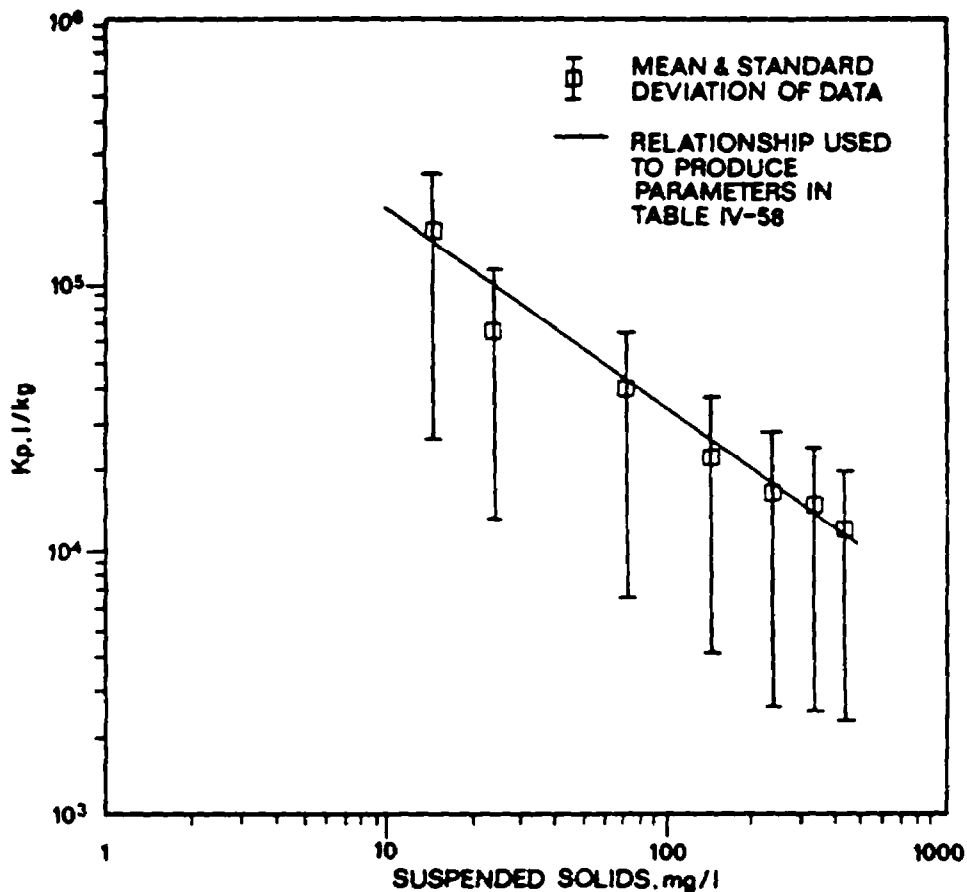
REFERENCE: DELOS ET AL., 1983

FIGURE IV-77   PARTITION COEFFICIENT FOR COPPER IN STREAMS

oxygen is present. The model MINEQL has been run for conditions corresponding to oxidizing environments.

4.10.4.2.4 Dilution

When wastewater is discharged into a river, the metal speciation of the wastewater-river water mixture can be significantly altered compared with metal speciation in the wastewater. This is because the master variables of pH, pe, ionic strength, and temperature in the wastewater-river mixture can be quite different from those of the wastewater alone.

Examples of processes likely to be important during mixing are:

> Solubility changes due to significant changes in species concentrations and redox conditions (say from anoxic conditions where sulfides can control solubility to oxic conditions and where carbonates or hydroxides can control solubility).

- pH changes can influence the fraction of species adsorbed and the relative distribution of the dissolved species.

4.10.4.2.5 Processes of Secondary Importance

Other processes that can influence the fate of a few of the priority metals are volatilization, photolysis, and biodegradation. Each of these processes is discussed in detail in Chapter II of this document as they relate to organic contaminants. Volatilization is the physical transfer of metal from the water column into the atmosphere. Elemental mercury can volatilize and so possibly can arsenic. Photolysis is the chemical process of degradation through absorption of solar energy and may influence the fate of cyanide and mercury. Biodegradation, or the microbial degradation of metal complexes, can influence a number of priority metals. In this section, the processes of volatilization, photolysis, and biodegradation are given minor attention. While photolysis and biodegradation may influence metal speciation, the metal itself can still be present in the water column, although as a complex which may have different toxicity than before.

4.10.4.3 Metal-by-Metal Discussion

This section summarizes the fate of nine priority metals in oxidizing surface water environments. Figure IV-78 shows a periodic table of the elements and illustrates the placement of each of the priority metals discussed (see the circled elements). The common oxidation states of each metal are shown above and to the left of the symbol for each metal. Table IV-63 summarizes the discussion that is to follow. The table shows the metals affected by oxidation-reduction, the primary species which are likely to be present in each environment, the solids controlling solubility, and pH-pe combinations that are conducive to mobilizing the metals (e.g., increasing solubility).

4.10.4.3.1 Arsenic

A source of arsenic in the natural environment in the United States is coal-fuel power plants, which emit approximately 3000 tons of arsenic per year (Nelson, 1977). Arsenic trioxide, $As_2O_3(s)$, is formed and is often the compound which first reaches surface waters. Concentrations of arsenic in surface waters of the United States range from 5 to 340 ppb, with a mean value of 64 ppb (Kopp, 1969). In contrast, average arsenic concentrations in ocean waters are about 2 ppb.

Figure IV-79 is a pe-pH diagram for arsenic, without the influence of organic material, showing its behavior for total arsenic ranging from 10^{-6} to 10^{-3} M (0.1 to 100 ppm). In oxidizing environments likely to exist in most surface waters (i.e. pe

FIGURE IV-78   PERIODIC TABLE OF THE ELEMENTS (FROM SNOEYINK AND JENKINS, 1980)

Mass numbers of the most stable or most abundant isotopes are shown in parentheses.
The elements to the right of the bold lines are called the nonmetals and the elements to the left of the bold line are called the metals.
Common oxidation numbers are given for the representative elements and some transition elements.
* Kurchatovium and Hahnium are tentative names for these elements

values exceeding 8 or so), the pentavalent arsenic species predominate, with $H_2AsO_4^-$ and $HAsO_4^{2-}$ being the most likely anions. Only at relatively low pe values (around 0 or less) at the pH range likely to exist in natural waters will the trivalent form be stable. As evidenced from the pe-pH diagram, arsenic(V) is a triprotic acid, and its behavior is quite similar to that of phosphoric acid.

Arsenic(V) forms a series of salts with alkaline-earth metals (magnesium, calcium, strontium, and barium) and with a number of the heavy metals (such as nickel, copper, zinc, cadmium, and lead) which are quite insoluble. For example, oversaturation with respect to $Pb_3(AsO_4)_2(s)$ at an As(V) concentration of 10^{-5} M can occur when lead concentrations exceed 10^{-5} M at pH = 7. However, 10^{-5} M of either lead or arsenic is high and far exceeds the 1980 U.S. EPA's water quality criteria, and the simultaneous occurrence of both is unlikely. While thermodynamics favor oxida-

TABLE IV-63

SUMMARY OF METAL SPECIATION IN OXIDIZING AND REDUCING ENVIRONMENTS, SOLIDS CONTROLLING
SOLUBILITY, AND pH-pe COMBINATIONS CONDUCIVE TO METAL MOBILIZATION

Element	Unaffected by Oxidation-Reduction	Oxidizing Environment	Reducing Environment	Controlling Solids	Mobilizing Conditions
As		$H_2AsO_4^-$, $HAsO_4^{2-}$	$H_3AsO_3^0$, $H_2AsO_3^-$	$FeAsO_4$, As_2S_3	high pH, high pe
Cd	Cd^{2+}, $CdSO_4^0$, $CdCO_3^0$			$CdCO_3$, $Cd_3(PO_4)_2$, $(Ca,Cd)CO_3$	low pH
Cr		$HCrO_4^{2-}$	Cr^{3+}, CrF^{2+}, $CrOH^{2+}$, $Cr(OH)_3^0$, $Cr(OH)_4^-$	$Cr(OH)_3$, $FeCr_2O_4$	III: low pH, low pe VI: high p high pe
Cu		Cu^{2+}, $CuSO_4^0$, $Cu(OH)_2^0$	Cu^+, $CuCl_2^-$, $Cu(OH)_2^0$	$Cu(OH)_2$, $Cu_3(PO_4)_2$, $Cu_2(OH)_2CO_3$	low pH
Pb	Pb^{2+}, $PbCO_3^0$, $Pb(CO_3)_2^{2-}$			$Pb(OH)_2$, $PbCO_3$, $Pb_3(PO_4)_2$	low pH
Hg		$HgCl_2^0$, $Hg(OH)_2^0$, $HgClOH^0$	Hg^0	HgS	low pH, high Cl^-
Ni	Ni^{2+}, $NiHCO_3^+$, $NiSO_4^0$			NiS, $NiFeO_4$	low pH
Se		SeO_4^{2-}	$HSeO_3^-$, SeO_3^{2-}, HSe^-	$Fe_2(SeO_3)_3$	high pH
Zn	Zn^{2+}, $ZnSO_4^0$, $ZnCO_3^0$, $Zn(CO_3)_2^{2-}$			$Zn(OH)_2$, $ZnCO_3$, $ZnSiO_4$, $ZnFe_2O_4$	low pH
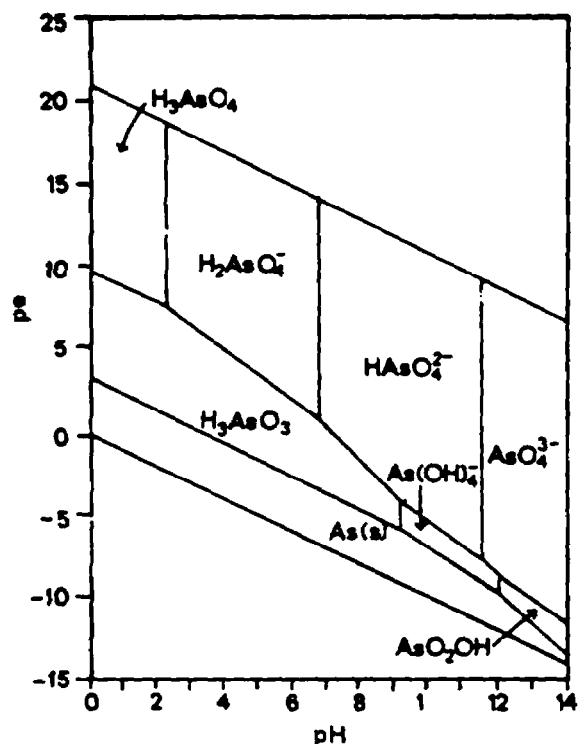
FIGURE IV-79 PE/PH STABILITY FIELD DIAGRAM FOR ARSENIC AT 25^0C

tion of As(III) to As(V) in oxic surface waters, the kinetics of the oxidation process are thought to be such that As(III) can remain in this reduced form for relatively long periods of time; e.g. order of months (Tallman and Shaikh, 1980). As indicated earlier, arsenic from combustion can enter surface waters as $As_2O_3(s)$. This compound then reacts with water to form arsenious acid, H_3AsO_3 which is in the +3 oxidation state (see Figure IV-79). Depending on the rate of the oxidation reaction, the more toxic trivalent arsenic might remain present in the water.

Both As(III) and As(V) species are expected to adsorb onto surfaces, such as oxide surfaces and clays. The As(V) species have greater adsorptive tendency than do the As(III) species. Adsorption generally decreases with increasing pH, indicating that adsorption is more likely to be important in acidic waters.

4.10.4.3.2 Cadmium

In natural fresh water, cadmium can be present in extremely low concentrations (e.g. less than 0.01 $\mu g/l$). Sources of cadmium include both industrial effluents (pigments, plastics, alloys, and electroplating) and municipal effluents industrial sources may account for up to 90 percent of the cadmium released domestically (Environmental Science and Technology, 1971). Cadmium is extremely toxic to fish, and effects on the growth rate have been observed at concentrations between 5 and 10

$\mu g/l$ (Gardiner, 1974). The suggested U.S. EPA criteria for protection of aquatic life are quite low also, varying from 0.01 to 0.05 $\mu g/l$ for waters having hardnesses of 50 and 200 mg/l as $CaCO_3$, respectively.

Cadmium speciation is similar to that of zinc, as might be expected, since they are located in the same group in the periodic table and in adjacent periods 4 and 5 (see Figure IV-78). In oxic surface waters, cadmium is present in the 2+ oxidation state, so that redox reactions are not important for this element.

Cadmium can form complexes with hydroxide, carbonate, chloride, sulfate, and humic materials. Complexes with humic materials can be important when sufficient organic matter is present.

In fresh water, the concentrations of cadmium are usually far below the maximum permitted by its solubility products. Solubility is probably controlled by the carbonate, which should limit the soluble Cd(II) to between 0.1 to 1.0 mg/l. In the pH range of natural waters, hydroxide solubility is about an order of magnitude greater than this.

Figure IV-80 shows the speciation of cadmium in freshwater as a function of pH in the presence of an adsorbate $SiO_2(s)$. The total cadmium present is 10^{-6} M (0.1 mg/l). Even at these high concentrations, cadmium does not begin to precipitate until the pH exceeds about 6.9. The uncomplexed cadmium is the dominant species below this pH.

Adsorption of cadmium appears to follow a linear isotherm at total cadmium concentrations of about 5.0 $\mu g/l$ or less (Gardiner, 1974). Concentrations of cadmium in natural waters are generally less than this, except in cases of extreme pollution.

The proportion of cadmium adsorbed in the water column can be significant. Gardiner (1974) found that between 30 and 46 percent of cadmium in the water column was sorbed at total cadmium levels between 2.1 and 5.5 $\mu g/l$, and at a suspended solids level of 34 mg/l.

According to the work of Gardiner, levels of EDTA, a strong organic complexing agent, below about 30 $\mu g/l$ did not significantly affect cadmium speciation. At higher levels (i.e. 300 $\mu g/l$), the percent adsorbed was decreased by about half.

4.10.4.3.3 Chromium

Background chromium levels in many natural waters are approximately 10^{-8} M (0.5 ppb). Chromium levels in wastewater range up to 10^{-5} M (500 ppb), which is near the solubility for chromium at neutral pH, where $Cr(OH)_3(s)$ can control solubility (for anoxic conditions).

Figure IV-81 is a pe-pH diagram showing the stability of chromium species at a total chromium concentration of 10^{-5} M (The effects of organic species are not included but can be important.) At the pe values normally encountered in river waters (above 5), the free Cr^{3+} ion is expected to be present only in very acidic water (pH < 4).
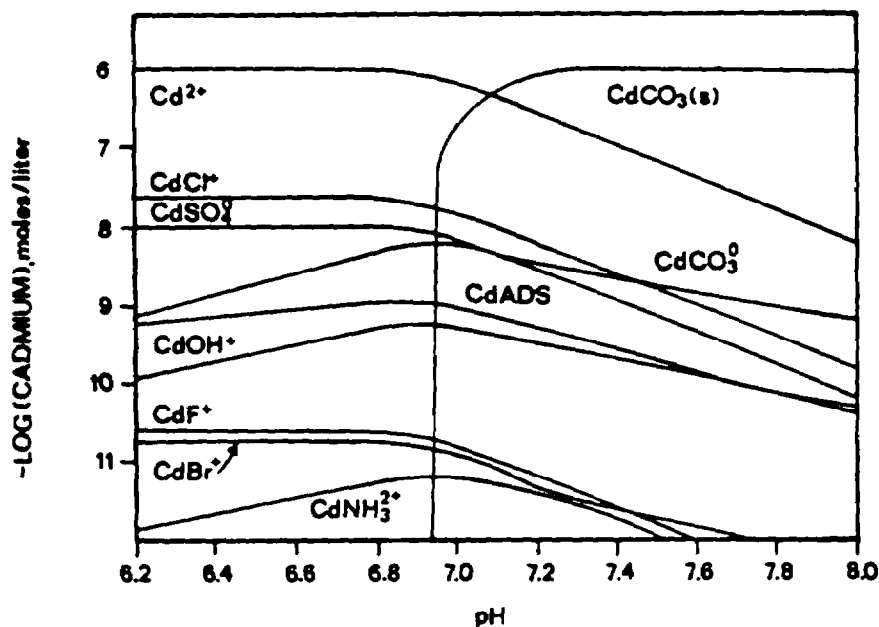
CONSTITUENT	-log MOLAR CONCENTRATION
Cl	3.65
NH_3	5.5
Br	6.62
F	5.5
SO_4	3.9
P_{CO_2}	3.5

REFERENCE: VUCETA AND MORGAN, 1978

FIGURE IV-80   CADMIUM SPECIATION AS A FUNCTION OF pH IN THE PRESENCE OF 1.55 M^2/L $SiO_2(s)$, $Cd_t = 10^{-6}M$.

However, as the pH increases, at low pe, important soluble Cr(III) species are likely to be $CrOH^{2+}$ and $Cr(OH)_2^+$. The most important Cr(VI) species are $HCrO_4^-$ and CrO_4^{2-}, and they are likely to be present at pH values between 6.2 and 8 at high pe values. These anionic forms of chromium are fairly soluble and are relatively mobile in surface waters.

The presence of other metals can control the concentration of Cr(VI). Such metals include barium, calcium, strontium, copper, and lead. Lead concentrations as low as 10^{-7} M (10 ppb) can produce chromate precipitation if concentrations of chromium (VI) exceed 10^{-7} M at pH = 7.

While Cr(VI), in the presence of Fe(III) and dissolved sulfides, can be readily reduced to Cr(III), these compounds are not likely to be present in oxic surface waters. Cr(III) on the other hand can be oxidized by dissolved oxygen, but rather slowly. The fate of chromium depends on its oxidation state: Cr(III) is likely to
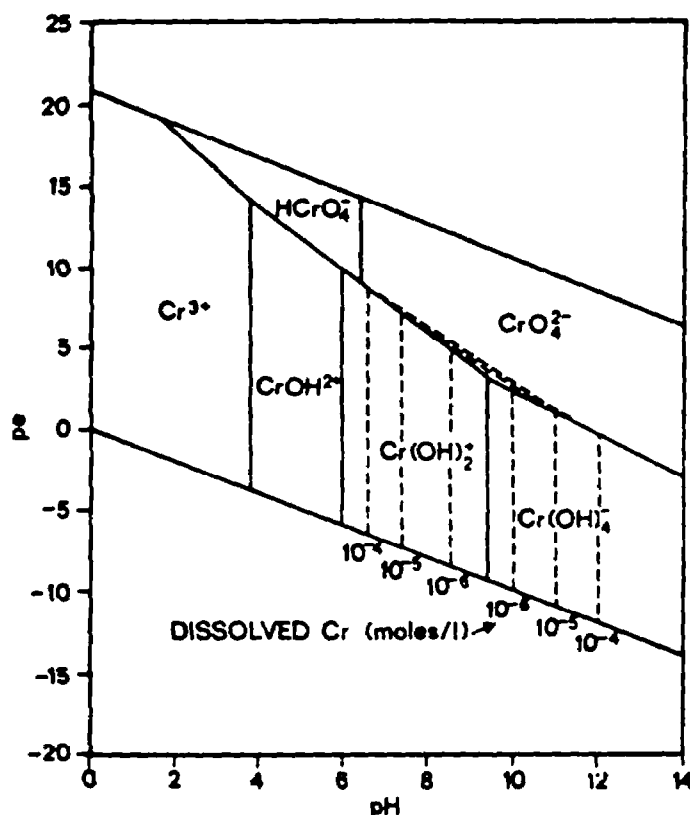
FIGURE IV-81   PE/PH DIAGRAM SHOWING STABILITY OF
CHROMIUM SPECIES FOR $CR_T = 10^{-5}M$.

be sorbed and found in bottom sediments, and Cr(VI) is more likely to be carried in the water column.

4.10.4.3.4 Copper

Elemental copper is a soft metal with an atomic weight of 63.5 and a density of 8.9 g/cm^3. It is a ubiquitous element in rocks and minerals and usually occurs as sulfides and oxides. Its concentrations in natural rocks typically vary from 4 ppm to 55 ppm, and natural background levels are often between 1 to 10 ~g/l in rivers. Industrial sources of copper include smelting and refining industries, copper-wire mills, and iron- and steel-producing industries.

The 2+ valence state is stable in oxic environments, while copper complexes with 1+ valences exist in reducing environments (Figure IV-82). For oxic waters, pe is typically near 10, and the equilibrium valence state is 2+ regardless of pH.

Several different researchers have investigated the equilibrium speciation of copper, both in the presence and in the absence of organic complexing agents. Figure IV-83a shows the predictions of Long and Angino (1977) in fresh water in the presence of the ligands OH^-, Cl^-, CO_3^{2-}, SO_4^{2-}, and HCO_3^-. The results show that either the free
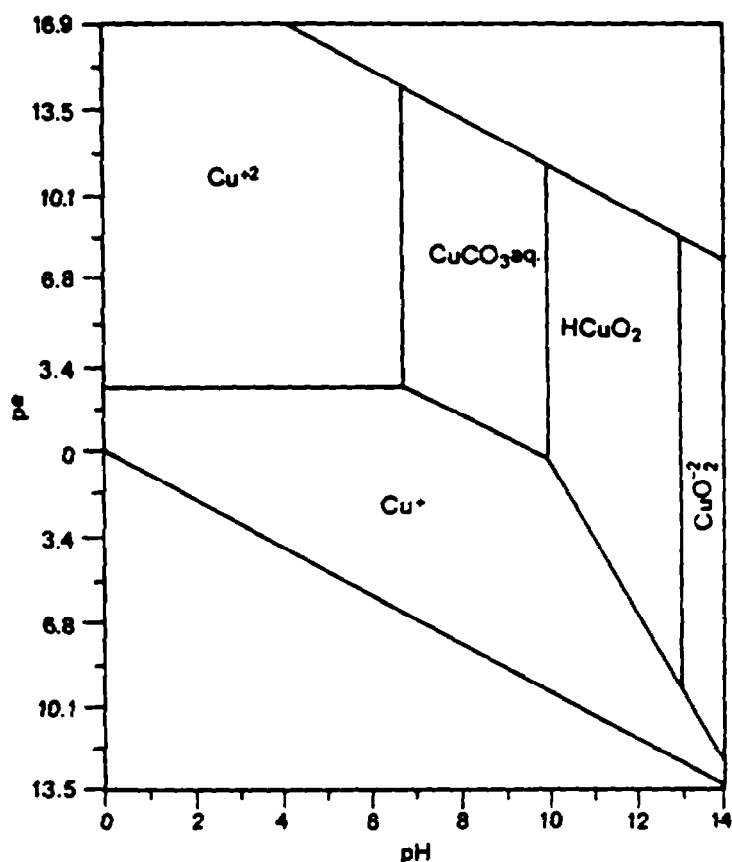
REFERENCE: HEM (1975).

FIGURE IV-82   PE/PH DIAGRAM SHOWING AREAS OF DOMINANCE OF FIVE
SPECIES OF COPPER AT EQUILIBRIUM AT 25°C AND 1 ATM.

copper predominates (at pH values below about 6.5) or $Cu(OH)_2^0$ predominates at higher pH values.

Vuceta and Morgan (1978) investigated the speciation of 10^{-6} M of total copper also in the presence of inorganic ligands, plus an adsorbing surface expressed as SiO_2 (s). Their results are shown in Figure IV-83b, and indicate that for pH≥6.5, the adsorbed form of copper predominates. The free ion is probably present in significant quantities below pH 7 and is the predominant species below pH 6.5. Copper solubility in most fresh water appears to be controlled by malachite $(Cu_2(OH)_2CO_3)$ rather than the hydroxide (Stiff, 1971). However, precipitation of malachite is a slow process.

Organic ligands can complex copper and increase its solubility in water. Vuceta and Morgan (1978) found that when EDTA was added as an organic ligand to their equilibrium model, the adsorbed and organically complexed copper were the predominant species, when at least $10^{-6.3}$ M EDTA was present. At higher amounts of organic

CONSTITUENT	-log MOLAR CONCENTRATION
Cl	3.66
SO₄	3.0
Ca	3.4
Mg	3.8
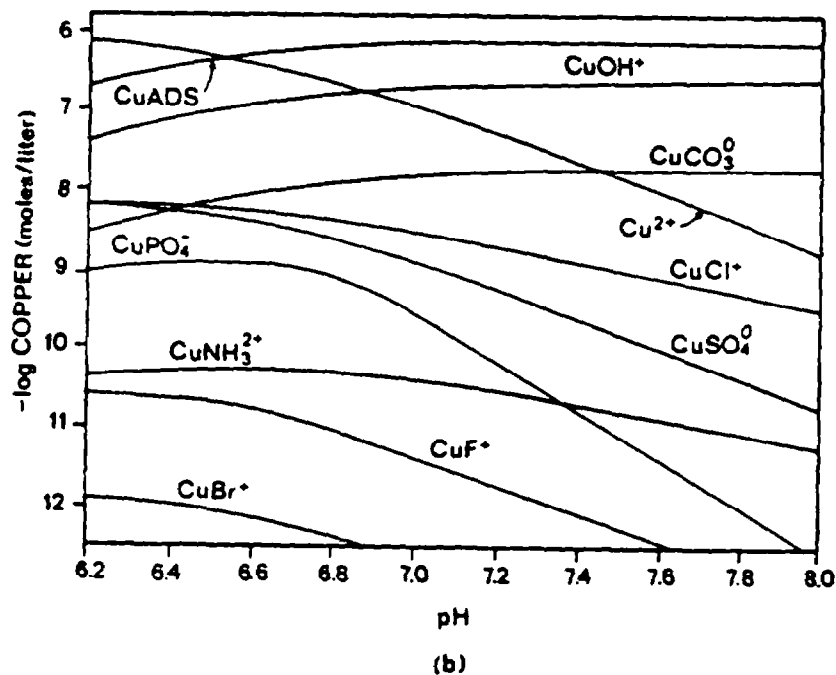
(a)

CONSTITUENT	-log MOLAR CONCENTRATION
Cl	3.65
NH₃	5.5
Br	6.62
F	5.5
SO₄	3.9
P_{CO_2}	3.5

(b)

REFERENCE: (A) LONG AND ANGINO, 1977
(B) VUCETA AND MORGAN, 1978

FIGURE IV-83   COPPER SPECIATION (A) IN THE PRESENCE OF INORGANIC
LIGANDS; (B) IN THE PRESENCE OF INORGANIC LIGANDS
AND AN ADSORBING SURFACE, 1.55 M²/L SiO₂(s).

complexing agents, a greater quantity of adsorbing surface is required for the sorbed phase to be of significance. Gupta and Harrison's (1982) investigations produced similar results. They found that the addition of humic materials reduced the adsorption coefficient, K_p, in a dilute system of kaolin and copper in water. The influence of the humic acid was evident at concentrations below 1 mg/l (Figure IV-84).

4.10.4.3.5 Lead

Lead is a constituent of hundreds of natural minerals, and its average abundance in the earth's crust is 15 ppm. Natural background levels of lead in inland waters typically average 1 μg/l or less. However, areas impacted by man, such as from lead mining, can have concentrations on the order of 50 μg/l. Lead is used in metal products (with storage batteries being a primary use), pigments, gasoline antiknock additives, and other miscellaneous uses.

While lead exists in three oxidation states (0, 2^+, and 4^+), the 2^+ oxidation state predominates in natural surface waters. Long and Angino (1977) evaluated the equilibrium speciation of lead in a freshwater environment containing only the inorganic ligands OH^-, Cl^-, CO_3^{2-}, SO_4^{2-}, and HCO_3^-. Figure IV-85a shows their results. The Pb^{2+} ion is the predominant specie at pH ≤ 7, while at $7 \leq pH \leq 9$, $PbCO_3^0$ is the major specie.

Vuceta and Morgan (1978) also used an equilibrium model approach for lead speciation in fresh water in the presence of inorganic ligands plus an adsorbing surface. Figure IV-85b shows their results. Again, Pb^{2+} predominates below pH $= 7$, and $PbCO_3^0$ predominates at higher pH. For the amount of adsorbing surface used in the analysis (1.55 m^2/l $SiO_2(s)$), the concentration of adsorbed lead was approximately an order of magnitude below the dissolved phase concentration. Small additions of iron and manganese oxides to the model data base, which provide further adsorption surfaces, did not appreciably change the results.

Lead can precipitate as a number of compounds including $PbSO_4(s)$, $PbCO_3(s)$, $Pb(OH)_2(s)$, $PbS(s)$, and $Pb_3(PO_4)_2$. The $PbCO_3(s)$ can control solubility in natural waters. Near pH $= 8$, the lead solubility is probably between 30 to 100 μg/l, and rapidly increases at lower pH values. In soft waters at low pH values, lead solubility can be quite high so that using such a water type for drinking may be a health hazard if lead pipes comprise the water distribution system.

Lead readily forms complexes with organic ligands, which tend to increase the amount of lead which can be dissolved in water. In Vuceta and Morgan's equilibrium modeling results (1978), they found that when a strong complexing agent such as EDTA exceeded about $10^{-6.3}$ M, more of the lead was complexed than was not. The total lead present was 10^{-7} M (20 μg/l).
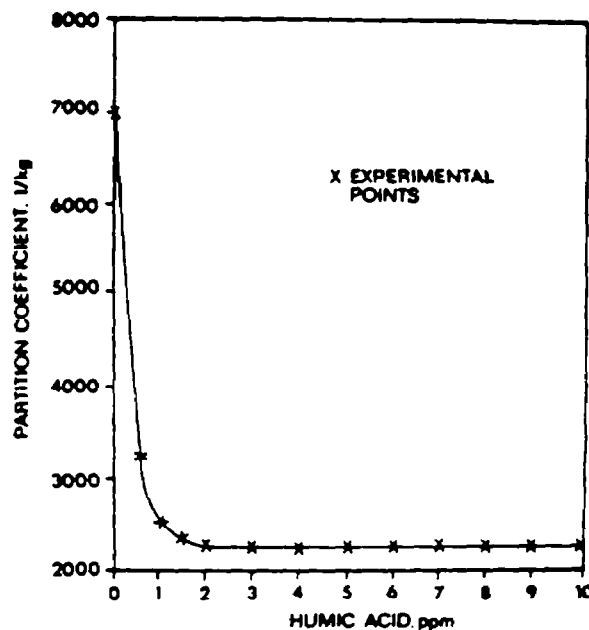
FIGURE IV-84   EFFECT OF HUMIC ACID ON PARTITIONING OF COPPER.
                (NOTE. THE HUMIC ACID WAS OBTAINED FROM THE
                ALDRIDGE CHEMICAL COMPANY; NA-SALT, WATER
                SOLUBLE.)

Lead is readily adsorbed to numerous solid surfaces, including organic matter, clay, silica, and iron and manganese oxides. Lead adsorption is pH dependent and the adsorption edge occurs at lower pH than that of either copper or zinc.

4.10.4.3.6 Mercury

Elemental mercury is a silver-white metal and is a liquid at room temperature. It has a specific gravity of 13.5 and a vapor pressure of 0.0012 torr. It is used in the electrolytic preparation of chlorine and caustic soda, in electrical apparatus such as mercury battery cells, in control instruments such as thermometers, in laboratory applications, and in other industrial applications. Concentrations of mercury in natural rocks range from about 5 to 1000 ppb, with 80 ppb being a typical value. Typical background mercury levels in natural surface waters average 0.01 to 0.1 μg/l.

Mercury can exist in the natural environment in one of three oxidation states: 0 (the metallic form), 1+ (mercurous), or 2+ (mercuric). Figure IV-86 illustrates for the predominant inorganic species present in water under equilibrium conditions (Gavis and Ferguson, 1972).

For typical pe-pH values in surface waters, either the chloride or hydroxide

CONSTITUENT	-log MOLAR CONCENTRATION
Cl	3.66
SO$_4$	3.0
Ca	3.4
Mg	3.8

CONSTITUENT	-log MOLAR CONCENTRATION
Cl	3.65
NH$_3$	5.5
Br	6.62
F	5.5
SO$_4$	3.9
P$_{CO_2}$	3.5
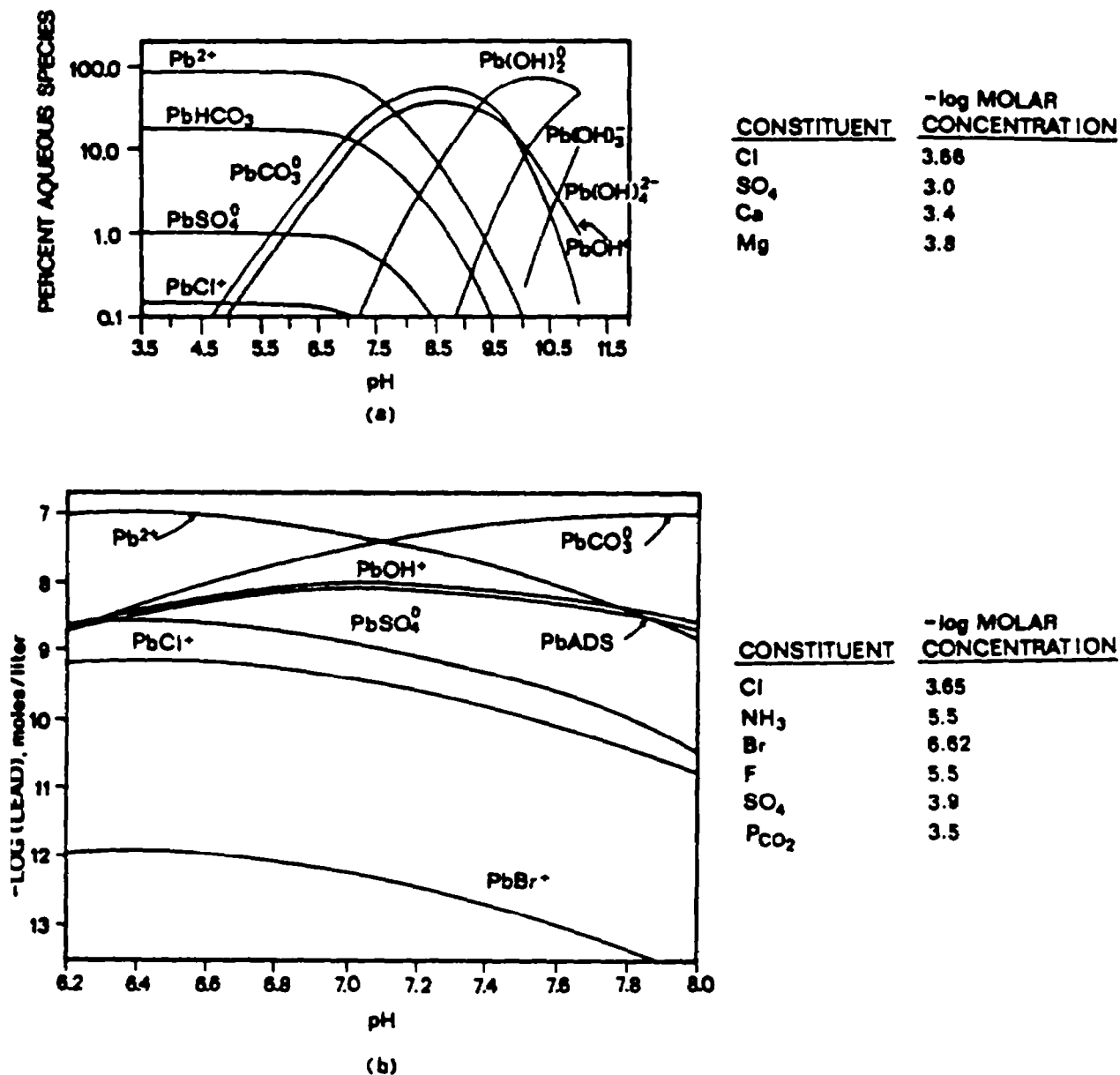
REFERENCES: (A) LONG AND ANGINO (1977)
            (B) VUCETA AND MORGAN (1978)

FIGURE IV-85   LEAD SPECIATION (A) IN THE PRESENCE OF INORGANIC
               LIGANDS; (B) IN THE PRESENCE OF INORGANIC LIGANDS
               AND A SOLID ADSORBING SURFACE (1.55 M^2/L SiO$_2$(s)).
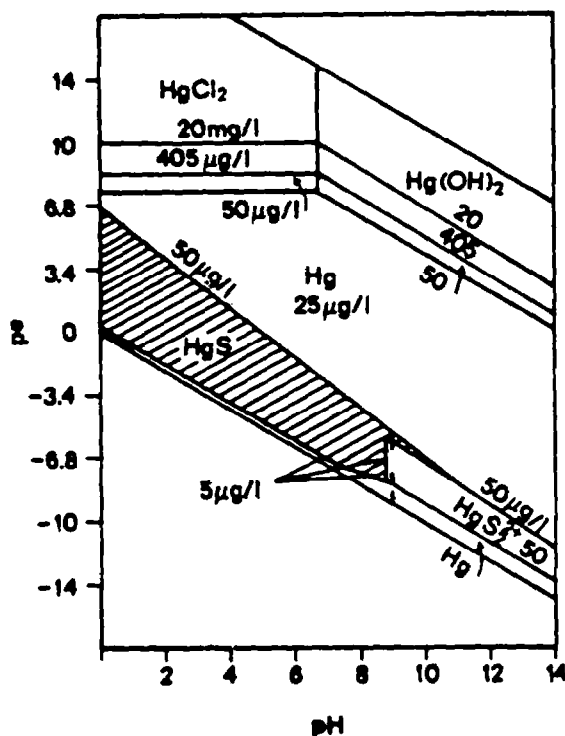
FIGURE IV-86   PE/PH DIAGRAM FOR HG, SHOWING PREDOMINANT SPECIES
IN SOLUTION FOR CONCENTRATIONS OF TOTAL HG
GREATER THAN 5 µG/L.

species predominate for the conditions shown. The solubilities of these compounds are great enough that precipitation of mercury in oxidizing environments is usually not a concern.

Mercury possesses an affinity for sulfhydryl groups (-SH) and can form organic sulfhydryl complexes. Mercury also forms compounds with alkyl groups (e.g. dimethyl mercury). The methyl mercury ion (CH_3Hg^+) can be discharged from industrial effluents and can be synthesized from inorganic mercury by bacteria which reside in sediments.

Mercury strongly adsorbs to a variety of solids, including organics, clays, metal oxides, and sand. Halide ions (e.g. Cl^-, Br^-, I^-) appear to suppress mercury adsorption.

Based on elemental mercury solubility of 19.2 µg/l at 50°C and 81.3 µg/l at 30°C and a vapor pressure of 0.0012 torr, the calculated Henry's Law constant lies between 10^{-2} to 10^{-3} atm·m^3/mole. Elemental mercury is relatively volatile. Both organic and inorganic mercury compounds exhibit volatility.

4.10.4.3.7 Nickel

Nickel is present in the earth's crust at an average concentration of approximately 80 ppm. Background levels in surface waters are 1 µg/l or less. Although nickel forms compounds with valences of 0, 1+, 2+, 3+, and 4+, the important valence state is 2+.

Nickel can precipitate as the hydroxide and carbonate, as studied by Patterson et al. (1977). Figure IV-87 shows the solubility limits for nickel carbonate and nickel hydroxide in the presence of $10^{-1.2}$ M total inorganic carbon (TIC). While this amount of total carbon is significantly greater than found in natural rivers, the figure does illustrate that neither nickel carbonate nor the hydroxide is likely to limit solubility in the natural environment except at high nickel concentrations.

Nickel can be adsorbed by a variety of substances, including iron and manganese oxides and organics. However, nickel is thought to be relatively mobile in the aquatic environment, especially in comparison with other metals. The work of Vuceta and Morgan (1978) appear to substantiate this. They evaluated the chemical speciation and adsorption of $10^{-6.5}$ M (19 $\mu g/l$) of total nickel in the presence of inorganic ligands which included OH^-, CO_3^{2-}, and SO_4^{2-} and a solid surface expressed as $SiO_2(s)$ (the equivalent of 310 mg/l). They found that at pH = 7, practically all of the Ni (18 $\mu g/l$) was present on the free divalent cation and that only a small amount was adsorbed. Adding small amounts of $Fe(OH)_3(s)$ and $MnO_2(s)$ had little influence on the amount of nickel adsorbed; the free ion again was the predominant species.

Complexation with organic ligands can be very important for nickel, and tends to further increase the mobility of this metal. Vuceta and Morgan (1978) found that $10^{-6.5}$ M (90 $\mu g/l$) of EDTA added to natural water at pH = 7 complexed about 50 percent of the nickel, with the remainder present as the free ion.

4.10.4.3.8 Silver

Elemental silver is a white ductile metal having an atomic weight of 107.9. It is primarily used in electroplating, as a conductor, in alloys, paints, jewelry, silverware, and mirror production. Background levels of silver are low in the aquatic environment, ranging from about 0.09 $\mu g/l$ to 0.6 $\mu g/l$ (Kharkov et al., 1968). In the earth's crust, silver typically occurs in concentrations of about 0.1 ppm.

Silver is quite toxic to bacteria, invertebrates, and fish. Chronic toxicity to freshwater aquatic life may occur at concentrations as low as 0.12 $\mu g/l$. Of the heavy metals only mercury is considered more toxic.

Silver can have valence states of 0, 1+, 2+, and 3+. The 0 and 1+ valence states are the most prevalent in the aquatic environment.

Solubility controls in the aquatic environment are probably not exerted by either the oxide or carbonates. However, silver halides are quite insoluble and can control solubility. Hem (1970) states that chloride concentrations as low as 10^{-3} M (35 mg/l) can limit solubility to below about 10 $\mu g/l$.

Silver adsorbs to a variety of surfaces, including ferric hydroxides, clay minerals, and organics. Also, adsorption to manganese dioxide can be significant (Kharkov et al., 1968).
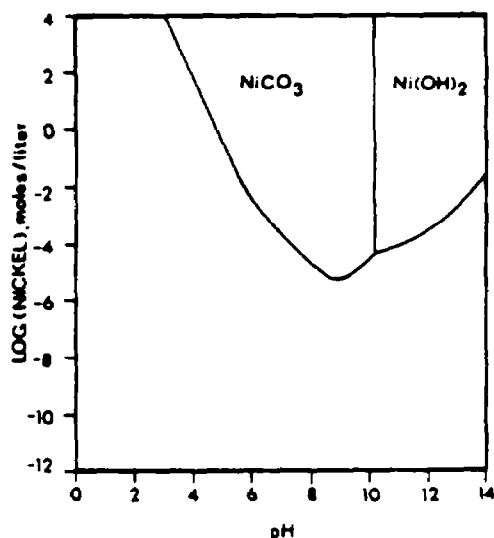
REFERENCE: PATTERSON ET AL. (1977).

FIGURE IV-87   NICKEL CARBONATE AND NICKEL HYDROXIDE
SOLUBILITY PHASE DIAGRAM (TIC = $10^{-1.2}$M).

4.10.4.3.9 Zinc

The chemistry of zinc is similar to that of cadmium, which is found directly below it in the periodic table. Zinc, however, is more abundant than cadmium; and is an essential element in trace quantities for building tissues. In oxic aqueous systems, zinc exists in the 2+ oxidation state.

Typical concentrations of zinc in soils range from 10 to 300 ppm, with the average being approximately 50 ppm (Bowen, 1966). The median concentration of Zn in surface waters of the United States is approximately 20 μg/l (Durum et al., 1971).

Zinc is used as an oxide pigment in rubber and paint, in agricultural fertilizers and sprays, in the textile industry, and battery production. The major metallurgical uses are in the galvanizing of metal and production of brass and other alloys.

Figure IV-88 from Vuceta and Morgan (1978) shows zinc speciation as a function of pH, assuming the total zinc is 10^{-7} M (7 μg/l), and in the presence of an adsorbing surface, expressed as SiO_2(s). Throughout the pH range shown (6.2 to 8.0), the free metal ion predominates. The next most predominate species are sulfate and carbonate, even more prevalent than the adsorbed zinc.

Models of zinc speciation based on inorganic ligands are altered in the presence of organic matter, which appear to increase soluble zinc. The results of Vuceta and Morgan (1978) suggest that organic complexation is important at pH values below approximately 6 and at ligand concentrations exceeding 100 μg/l.

Zinc is normally undersaturated in natural waters. Potential solubility controls

4.10.4.4 Equilibrium Modeling Analysis

4.10.4.4.1 Introduction

The analysis in Section 4.10.3 treats metals as pollutants which speciate into either adsorbed or dissolved form. Based on this approach, the distribution of metals in the water column or in the bedded sediments can be estimated using a relatively modest amount of data, particularly with respect to the chemical characteristics of the water which transports the metals. In contrast to this simplified picture of metal behavior, the previous section showed that metals can form a large number of compounds, soluble and insoluble, with organic and inorganic ligands and can become adsorbed to organic or inorganic solids.

Although approaches that consider metal speciation require more information to implement, they can also address questions that the analyses in Section 4.10.3 can not. For example:

- How do the chemical properties of the river water affect metal speciation?
- What are likely to be the predominant species of metal present?
- When is precipitation likely to occur?
- Under what conditions are the more toxic species likely to be present?

Equilibrium models provide a key for answering these questions since they can calculate the species' distribution of metals for a specific set of receiving water conditions. The models assume that rate-limited processes are so fast that the species quickly come to a state of equilibrium. While equilibrium models themselves are not transport models, they can be combined with transport models. That equilibrium models rather than rate models have been developed by researchers indicates that knowledge is still quite limited regarding the fate of metals in aquatic systems and that rate models do not appear to be feasible at present.

Based on the foregoing, the approach selected here is to choose an equilibrium model and to apply it to a variety of water types found throughout the United States. The results are tabulated for easy reference.

4.10.4.4.2 Choice of Typical Waters

Typical waters chosen for the purposes of this report are based on the United States Geological Survey's National Water Quality Network (NASQAN; Briggs and Ficke, 1977). That report is based on the 1975 water year and is their most recent report. Figure IV-90 shows the USGS's water resources regions within the United States.

Fifteen stations were selected within these regions based on regional representation, population, and interrelationships of the chemical constituents in the rivers. They are also shown in Figure IV-90.

The characteristics of the waters at the selected stations are shown in Table IV-64. The standard deviation as well as mean values are given for water temperature,

01 New England
02 Mid Atlantic
03 South Atlantic-Gulf
04 Great Lakes
05 Ohio
06 Tennessee
07 Upper Mississippi
08 Lower Mississippi
09 Souris-Red-Rainy
10 Missouri Basin
11 Arkansas-White-Red

12 Texas-Gulf
13 Rio Grande
14 Upper Colorado
15 Lower Colorado
16 Great Basin
17 Pacific Northwest
18 California
19 Alaska
20 Hawaii
21 Caribbean

①★ Station Locations
    Selected
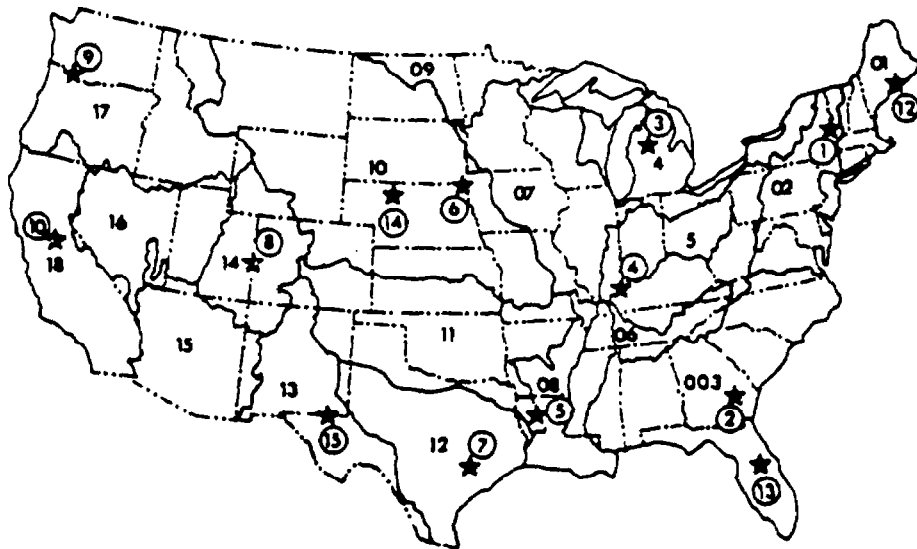
FIGURE IV-90   WATER RESOURCES REGIONS OF THE UNITED STATES

suspended solids, and pH. The range, rather than the mean, is shown for total organic carbon.

For comparison against the standard waters, a low pH water at the outlet of Woods Lake in the Adirondack Mountains in New York State has been added. The pH of the water averages 4.7, the alkalinity is -10 μeq/l, and the water is very soft (hardness = 6 mg/l as $CaCO_3$). In such a water, metals might tend to dissolve, and due to the low hardness, criteria levels would be quite low for the metals whose standards relate to hardness.

4.10.4.4.3 Equilibrium Model Chosen

A variety of equilibrium models capable of predicting metal speciation have been developed in the past decade. Summaries of the performance and capabilities of the

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TABLE IV-64

CHARACTERISTICS OF RIVER WATERS CHOSEN FOR ANALYSIS

Station No.	Region No.	River	USGS Station No.	Temperature °C	Suspended Solids[a] mg/l	Percent Silt-Clay	Total Dissolved Solids mg/l	Specific Conductance μmho	Total Organic Carbon[b] mg/l	pH[a]	Dissolved Calcium mg/l	Dissolved Magnesium mg/l	Dissolved Sodium mg/l	Dissolved Potassium mg/l	Dissolved Iron mg/l	Total Hardness mg/l as CaCO₃	Total NO₂+NO₃ mg/l-N	Total Phosphorus mg/l-P	Bicarbonate mg/l	Dissolved Sulfate mg/l	Dissolved Chloride mg/l
1	2	Hudson	01372043	15.±8.	13.±7.	88.	82.	178.	2.-16.	7.7±0.2	19.	3.	6.	1.	0.06	60.	0.7	0.07	66.	18.	10.
2	3	Oyocheo	02202100	18.±7.	14.±13.	-	45.	54.	6.-12.	6.9±1.2	7.	1.	4.	1.	0.7	11.	0.07	0.04	23.	5.	5.
3	4	Muskegon	04123030	10.±8.	21.±9.	95.	203.	357.	5.-12.	8.1±0.2	41.	13.	10.	1.	0.07	163.	0.2	0.03	185.	19.	19.
4	5	Ohio	03612500	17.±9.	78.±66.	87.	160.	282.	4.-5.	7.2±0.6	33.	8.	10.	2.	0.02	117.	0.9	0.23	80.	46.	13.
5	8	Mississippi	00267000	17.±18.	17.±17.	-	157.	274.	7.-12.	7.9±0.3	36.	12.	4.	2.	0.12	146.	0.1	0.05	161.	7.	7.
6	10	Missouri	00618000	12.±11.	1130.±1100.	50.	440.	720.	4.-12.	8.0±0.2	61.	21.	59.	6.	0.5	240.	0.8	0.3	213.	164.	18.
7	12	Brazos	00136650	21.±7.	770.±660.	91.	300.	700.	5.-32.	7.0±0.5	57.	11.	63.	4.	0.1	190.	0.4	0.4	170.	62.	90.
8	14	Colorado	00163630	13.±8.	2450.±1440.	-	690.	1000.	5.	8.1±0.2	96.	13.	66.	4.	0.03	374.	0.7	0.10	172.	200.	60.
9	17	Columbia	14120000	10.±5.	23.±16.	84.	95.	180.	2.-11.	7.6±0.4	18.	6.	6.	1.	0.06	60.	0.4	0.05	77.	13.	3.
10	18	Sacramento	11447650	16.±5	100.±100.	64.	82.	119.	3.-8.	7.0±0.4	14.	5.	8.	1.	0.03	47.	0.00	0.11	60.	7.	4.
11	1	Woods Lake, NY	---	11.±7.	1.	-	10.	25.	5.	4.7±0.2	2.	0.2	0.6	0.7	0.3	6.	2.0	0.00	0	6.0	0.3
12	1	Penobscot	01030500	9.±9.	5.±2.	98	30.	59.	3.-9.5	6.6±0.2	6.6	1.4	3.1	0.6	0.1	22.	.045	0.02	14.	8.6	3.0
13	3	St. Marys	02231000	20.±5.	5.±3.	-	30.	47.	10.-32.	5.1±1.0	3.3	1.2	3.4	0.4	0.5	13.	0.05	0.05	7.5	5.9	8.6
14	10	Grand	06357000	16.±10.	5222.±1860.	-	1376.	1885.	5.-25.	8.7±0.5	42.	29.	376.	10.	0.01	276.	0.10	0.30	880.	966.	130.
15	13	Pecos	00407500	19.±7.	32.±19.	71.	8080.	11520.	6.-14.	8.3±0.3	467.	213.	2073.	73.	0.15	7000.	0.4	0.07	129.	1725.	3425.

Source: Briggs and Ficke, 1977.

[a] Mean ± one standard deviation.

[b] Range.

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models can be found in Nordstrom et al., 1979. The model selected for this project is MINEQL.

MINEQL (Westall et al., 1976) has evolved over the years and is based on an earlier equilibrium model called REDEQL. The version of MINEQL used in this chapter is called MINEQL+STANFORD, in recognition of modifications done at Stanford University.

MINEQL uses the equilibrium constant approach (in contrast to the direct minimization of the Gibbs free energy function) to attain equilibrium composition of species. The model is quite versatile and allows the user numerous options. For example, redox reactions can be considered or not at the discretion of the user. Adsorption can be modeled using the electrical double layer theory, which considers the interaction of charged ions in solution and at a solid surface. Precipitation can be considered at the discretion of the user, or suppressed as desired.

4.10.4.4.4 Results

Tables IV-65 through IV-79 summarize the predictions of MINEQL for the 15 natural waters selected. For each metal, a range of concentrations is analyzed beginning at typical background levels and continuing for concentrations well above the water quality criteria. Concentrations are expressed as -log molar and μg/l.

Organic ligands have not been included in this analyses. Organics are not included because major uncertainties exist as to the effects of organics on metals (particularly how to quantify the effects) and not because they are unimportant.

In selecting surface waters for analysis, the primary variables that should be considered by the user include pH, hardness, bicarbonate (an approximate measure of alkalinity), and specific conductivity. By cross-comparing results from several similar rivers, sensitivity to parameters can be estimated.

While Tables IV-65 through IV-79 are straightforward in their use, a number of features of the tables may not be readily apparent, and are listed here.

1. The concentrations of numerous metals are elevated enough in model simulations so that they precipitate in some rivers. For example, in the Hudson River, 81 percent of the lead is predicted to precipitate as $Pb(OH)_2(s)$ when the total lead is 1000 μg/l (see Table IV-65). The solubility of lead as limited by this process would be 0.19 (1000) = 190 μg/l.

2. If the metals are present in low enough concentrations so that precipitation does not occur, the percent metal speciation is largely independent of total metal concentration. For example, Table IV-65 shows that speciation of zinc in the Hudson River at concentrations below 1000 μg/l can be predicted by knowing that approximately 72 percent is Zn^{2+}, 15 percent is $ZnCO_3^0$, 8 percent is $ZnHCO_3^+$, and 2 percent is $ZnOH^+$. Thus, the user has the flexibility of ignoring precipitates

TABLE IV-65
METAL SPECIATION IN THE HUDSON RIVER

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Arsenic	8.9-5.4 (0.1-540 $\mu g/l$)	74% $HAsO_4^{2-}$
		26% $H_2AsO_4^{-}$
Cadmium	9.5-6.2 (0.1-70 $\mu g/l$)	95% Cd^{2+}
		2% $CdSO_4^{0}$
		2% $CdCl^{+}$
Chromium(III) (without redox)	5.0 (520 $\mu g/l$)	96% $Cr(OH)_3(s)$*
		3% $Cr(OH)_2^{+}$
		2% $Cr(OH)_4^{-}$
	5.6 (130 $\mu g/l$)	81% $Cr(OH)_3(s)$*
		11% $Cr(OH)_2^{+}$
		7% $Cr(OH)_4^{-}$
	6.0 (40 $\mu g/l$)	23% $Cr(OH)_3(s)$*
		47% $Cr(OH)_2^{+}$
		30% $Cr(OH)_4^{-}$
	8.7-6.6 (0.1-4 $\mu g/l$)	61% $Cr(OH)_2^{+}$
		38% $Cr(OH)_4^{-}$
Chromium(VI)	8.7-5.0 (0.1-520 $\mu g/l$)	93% Cr_4^{2-}
		7% $HCrO_4^{-}$
Copper	4.8 (1000 $\mu g/l$)	95% $Cu_2(OH)_2CO_3(s)$*
		3% $Cu(OH)_2^{0}$
		1% $CuCO_3^{0}$
	5.4 (250 $\mu g/l$)	81% $Cu_2(OH)_2CO_3(s)$*
		12% $Cu(OH)_2^{0}$
		6% $CuCO_3^{0}$
		1% Cu^{2+}

TABLE IV-65 (Continued)

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Copper (Continued)	6.0 (60 $\mu g/l$)	49% $Cu(OH)_2^o$
		24% $CuCO_3^o$
		21% $Cu_2(OH)_2CO_3(s)$ *
		4% Cu^{2+}
	8.5-6.6 (0.2-16 $\mu g/l$)	62% $Cu(OH)_2^o$
		31% $CuCO_3^o$
		6% Cu^{2+}
		1% $Cu(OH)^+$
Lead	5.3 (1000 $\mu g/l$)	81% $Pb(OH)_2(s)$ *
		16% $PbCO_3^o$
		1% $Pb(OH)^+$
	5.8 (316 $\mu g/l$)	52% $PbCO_3^o$
		41% $Pb(OH)_2(s)$ *
		4% $Pb(OH)^+$
		3% Pb^{2+}
	8.3-6.3 (0.4-100 $\mu g/l$)	88% $PbCO_3^o$
		7% $Pb(OH)^+$
		4% Pb^{2+}
Mercury	12-9 (0.0002-0.2 $\mu g/l$)	84% $Hg(OH)_2^o$
		15% $HgClOH^o$
Nickel	7.8-4.8 (1-1000 $\mu g/l$)	94% Ni^{2+}
		4% $NiOH^+$
		2% $NiSO_4^o$
Silver	8.8-6.2 (0.1-70 $\mu g/l$)	65% Ag^+
		33% $AgCl^o$
Zinc	7.3-4.8 (2-1000 $\mu g/l$)	72% Zn^{2+}
		15% $ZnCO_3^o$
		8% $ZnHCO_3^+$
		2% $ZnOH^+$

*Predicted solubility limitations.

TABLE IV-66
METAL SPECIATION IN THE OGEECHEE RIVER

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Arsenic	8.9-5.4 (0.1-540 $\mu g/l$)	54% $H_2AsO_4^-$
		46% $HAsO_4^{2-}$
Cadmium	9.5-6.2 (0.1-70 $\mu g/l$)	98% Cd^{2+}
		1% $CdCl^+$
Chromium(III) (without redox)	5.0 (520 $\mu g/l$)	91% $Cr(OH)_3(s)^*$
		9% $Cr(OH)_2^+$
	5.5 (160 $\mu g/l$)	61% $Cr(OH)_3(s)^*$
		35% $Cr(OH)_2^+$
		2% $Cr(OH)_4^-$
		1% $Cr(OH)^{2+}$
	8.7-6.0 (0.1-50 $\mu g/l$)	90% $Cr(OH)_2^+$
		6% $Cr(OH)_4^-$
		4% $CrOH^{2+}$
Chromium(VI)		77% CrO_4^{2-}
		23% $HCrO_4^-$
Copper	4.8 (1000 $\mu g/l$)	93% $Cu_2(OH)_2CO_3(s)^*$
		3% $Cu(OH)_2^o$
		2% Cu^{2+}
		1% $CuCO_3^o$
	5.4 (250 $\mu g/l$)	72% $Cu_2(OH)_2CO_3(s)^*$
		11% $Cu(OH)_2^o$
		10% Cu^{2+}
		6% $CuCO_3^o$
	8.5-6.5 (0.2-60 $\mu g/l$)	40% $Cu(OH)_2^o$
		36% Cu^{2+}
		22% $CuCO_3^o$
		3% $CuOH^+$

TABLE IV-66 (Continued)

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Lead	5.3 (1000 $\mu g/l$)	72% $PbCO_3(s)$[*]
		16% $PbCO_3^o$
		8% Pb^{2+}
		4% $PbOH^+$
	5.8 (316 $\mu g/l$)	52% $PbCO_3^o$
		23% Pb^{2+}
		13% $PbOH^+$
		11% $PbCO_3(s)$[*]
	8.3-6.3 (0.4-100 $\mu g/l$)	58% $PbCO_3^o$
		26% Pb^{2+}
		15% $PbOH^+$
Mercury	12-9 (0.0002-0.2 $\mu g/l$)	77% $Hg(OH)_2^o$
		23% $HgClOH^o$
Nickel	7.8-4.8 (1-1000 $\mu g/l$)	98% Ni^{2+}
		1% $NiOH^+$
Silver	8.8-6.2 (0.1-70 $\mu g/l$)	79% Ag^+
		21% $AgCl^o$
Zinc	7.3-4.8 (2-1000 $\mu g/l$)	92% Zn^{2+}
		4% $ZnHCO_3^+$
		2% $ZnCO_3^o$

[*]Predicted solubility limitations.

TABLE IV-67

METAL SPECIATION IN THE MUSKEGON RIVER

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Arsenic	8.9-5.4 (0.1-540 $\mu g/l$)	94% $HAsO_4^{2-}$
		6% $H_2AsO_4^-$
Cadmium	6.2 (70 $\mu g/l$)	50% Cd^{2+}
		46% $CdCO_3(s)^*$
		2% $CdCl^+$
		1% $CdSO_4^0$
		1% $CdCO_3^0$
	9.5-6.8 (0.1-20 $\mu g/l$)	91% Cd^{2+}
		4% $CdCl^+$
		2% $CdSO_4^0$
		2% $CdCO_3^0$
Chromium(III) (without redox)	5.0 (520 $\mu g/l$)	91% $Cr(OH)_3(s)^*$
		7% $Cr(OH)_4^-$
	5.6 (130 $\mu g/l$)	62% $Cr(OH)_3(s)^*$
		36% $Cr(OH)_4^-$
		2% $Cr(OH)_2^+$
	8.7-6.3 (0.1-20 $\mu g/l$)	94% $Cr(OH)_4^-$
		6% $Cr(OH)_2^+$
Chromium(VI)	8.7-5.0 (0.1-520 $\mu g/l$)	99% CrO_4^{2-}
		1% $HCrO_4^-$
Copper	4.8 (1000 $\mu g/l$)	95% $Cu_2(OH)_2CO_3(s)^*$
		4% $Cu(OH)_2^0$
		1% $CuCO_3^0$
	5.4 (250 $\mu g/l$)	80% $Cu_2(OH)_2CO_3(s)^*$
		16% $Cu(OH)_2^0$
		4% $CuCO_3^0$

TABLE IV-67 (Continued)

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Copper (Continued)	6.0 (60 $\mu g/l$)	65% $Cu(OH)_2^o$
		18% $CuCO_3^o$.
		16% $Cu_2(OH)_2CO_3(s)$*
	8.5-6.6 (0.2-16 $\mu g/l$)	77% $Cu(OH)_2^o$
		21% $CuCO_3^o$
Lead	5.3 (1000 $\mu g/l$)	92% $Pb(OH)_2(s)$*
		7% $PbCO_3^o$
	5.8 (316 $\mu g/l$)	75% $Pb(OH)_2(s)$*
		23% $PbCO_3^o$
	6.3 (100 $\mu g/l$)	72% $PbCO_3^o$
		22% $Pb(OH)_2(s)$*
		3% $PbOH^+$
		3% $Pb(CO_3)_2^{2-}$
	8.3-6.9 (0.4-15 $\mu g/l$)	93% $PbCO_3^o$
		4% $Pb(OH)^+$
		3% $Pb(CO_3)_2^{2-}$
Mercury	12-9 (0.0002-0.2 $\mu g/l$)	94% $Hg(OH)_2^o$
		6% $HgClOH^o$
Nickel	4.8 (1-1000 $\mu g/l$)	93% $Ni(OH)_2(s)$*
		6% Ni^{2+}
		1% $NiOH^+$
	5.3 (300 $\mu g/l$)	77% $Ni(OH)_2(S)$*
		18% Ni^{2+}
		4% $NiOH^+$
	5.8 (90 $\mu g/l$)	58% Ni^{2+}
		28% $Ni(OH)_2(s)$*
		12% $NiOH^+$
		1% $NiSO_4^o$
	7.8-6.3 (1-15 $\mu g/l$)	80% Ni^{2+}
		17% $NiOH^+$
		2% $NiSO_4^o$

TABLE IV-67 (Continued)

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Silver	6.2 (70 $\mu g/l$)	41% Ag^+
		10% $AgCl^0$
		17% $AgCl(s)^*$
		2% $AgCl_2^-$
	8.8-6.7 (0.1-15 $\mu g/l$)	50% Ag^+
		48% $AgCl^0$
		3% $AgCl_2^-$
Zinc	4.8 (1000 $\mu g/l$)	58% $ZnCO_3(s)^*$
		21% $ZnCO_3^0$
		10% $Zn(CO_3)_2^{2-}$
		7% Zn^{2+}
		2% $ZnHCO_3^+$
	7.3-5.3 (2-320 $\mu g/l$)	49% $ZnCO_3^0$
		23% $Zn(CO_3)_3^{2-}$
		17% Zn^{2+}
		6% $ZnHCO_3^+$
		3% $Zn(OH)_2^0$
		2% $ZnOH^+$

*Predicted solubility limitations.

TABLE IV-68

METAL SPECIATION IN THE OHIO RIVER

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Arsenic	8.9-5.4 (0.1-540 $\mu g/l$)	66% $HAsO_4^{2-}$
		34% $H_2AsO_4^-$
Cadmium	9.5-6.2 (0.1-70 $\mu g/l$)	93% Cd^{2+}
		5% $CdSO_4^o$
		3% $CdCl^+$
Chromium(III) (without redox)	5.0 (520 $\mu g/l$)	94% $Cr(OH)_3(s)^*$
		4% $Cr(OH)_2^+$
		1% $Cr(OH)_4^-$
	5.5 (160 $\mu g/l$)	76% $Cr(OH)_3(s)^*$
		18% $Cr(OH)_2^+$
		5% $Cr(OH)_4^-$
	6.0 (50 $\mu g/l$)	75% $Cr(OH)_2^+$
		19% $Cr(OH)_4^-$
		4% $Cr(OH)_3(s)^*$
		2% $CrOH^+$
	6.5-8.7 (0.1-8 $\mu g/l$)	79% $Cr(OH)_2^o$
		20% $Cr(OH)_4^-$
		2% $CrOH^+$
Chromium(VI)	8.7-5.0 (0.1-520 $\mu g/l$)	90% CrO_4^{2-}
		10% $HCrO_4^-$
Copper	4.8 (1000 $\mu g/l$)	95% $Cu_2(OH)_2CO_3(s)^*$
		2% $CuCO_3^o$
		2% $Cu(OH)_2^o$

TABLE IV-68 (Continued)

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Copper (Continued)	5.3 (300 $\mu g/l$)	81% $Cu_2(OH)_2CO_3(s)$*
		8% $CuCO_3^0$
		8% $Cu(OH)_2^0$
		2% Cu^{2+}
	5.8 (100 $\mu g/l$)	35% $CuCO_3^0$
		34% $Cu(OH)_2^0$
		21% $Cu_2(OH)_2CO_3(s)$*
		9% Cu^{2+}
	8.5-6.5 (0.2-15 $\mu g/l$)	44% $CuCO_3^0$
		43% $Cu(OH)_2^0$
		11% Cu^{2+}
Lead	5.3 (1000 $\mu g/l$)	81% $PbCO_3(s)$*
		16% $PbCO_3^0$
		1% Pb^{2+}
	5.8 (316 $\mu g/l$)	52% $PbCO_3^0$
		41% $PbCO_3(s)$*
		3% Pb^{2+}
		3% $PbOH^+$
	6.3-8.3 (0.4-100 $\mu g/l$)	88% $PbCO_3^0$
		6% Pb^{2+}
		6% $Pb OH^+$
Mercury	12-9 (0.0002-0.2 $\mu g/l$)	72% $Hg(OH)_2^0$
		27% $HgClOH^0$
		1% $HgCl_2^0$
Nickel	7.8-4.8 (1-1000 $\mu g/l$)	93% Ni^{2+}
		5% $NiSO_4^0$
		2% $NiOH^+$
Silver	8.8-6.2 (0.1-70 $\mu g/l$)	93% Ag^+
		38% $AgCl^0$
		1% $AgCl_2^0$

TABLE IV-68 (Continued)

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Zinc	7.3-4.8 (2-1000 $\mu g/l$)	72% Zn^{2+}
		11% $ZnCO_3^0$
		10% $ZnHCO_3^+$
		4% $ZnSO_4^0$

*Predicted solubility limitations.

TABLE IV-69
METAL SPECIATION IN THE MISSISSIPPI RIVER

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Arsenic	8.9-5.4 (0.1-540 $\mu g/l$)	90% $HAsO_4^{2-}$
		10% $H_2AsO_4^-$
Cadmium	6.2 (70 $\mu g/l$)	91% Cd^{2+}
		6% $CdCO_3(s)^*$
		1% $CdCO_3^0$
	9.5-6.7 (0.1-20 $\mu g/l$)	97% Cd^{2+}
		1% $CdCO_3^0$
Chromium(III) (without redox)	5.0 (520 $\mu g/l$)	94% $Cr(OH)_3(s)^*$
		6% $Cr(OH)_4^-$
	5.5 (160 $\mu g/l$)	74% $Cr(OH)_3(s)^*$
		23% $Cr(OH)_4^-$
		4% $Cr(OH)_2^+$
	6.3-8.7 (0.1-20 $\mu g/l$)	86% $Cr(OH)_4^-$
		14% $Cr(OH)_2^+$
		1% $HgClOH^0$

TABLE IV-69 (Continued)

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Chromium(VI)	8.7-5.0 (0.1-520 $\mu g/l$)	98% CrO_4^{2-}
		2% $HCrO_4^-$
Copper	4.8 (1000 $\mu g/l$)	95% $Cu_2(OH)_2CO_3(s)^*$
		3% $Cu(OH)_2^0$
		1% $CuCO_3^0$
	5.4 (250 $\mu g/l$)	81% $Cu_2(OH)_2CO_3(s)^*$
		14% $Cu(OH)_2^0$
		5% $CuCO_3^0$
	6.0 (60 $\mu g/l$)	56% $Cu(OH)_2^0$
		22% $Cu_2(OH)_2CO_3(s)^*$
		21% $CuCO_3^0$
	8.5-6.6 (0.2-16 $\mu g/l$)	71% $Cu(OH)_2^0$
		27% $CuCO_3^0$
Lead	5.3 (1000 $\mu g/l$)	87% $Pb(OH)_2(s)^*$
		12% $PbCO_3^0$
	5.8 (316 $\mu g/l$)	60% $Pb(OH)_2(s)^*$
		37% $PbCO_3^0$
	8.3-6.4 (0.4-100 $\mu g/l$)	94% $PbCO_3^0$
		4% $PbOH^+$
		2% $PbCO_3^{2-}$
Mercury	12-9 (0.0002-0.2 $\mu g/l$)	99% $Hg(OH)_2^0$

TABLE IV-69 (Continued)

Metal	Tested Range of Total Metal Concentrations as pM$_T$ and µg/l	Species
Nickel	4.8 (1000 µg/l)	83% Ni(OH)$_2$(s)*
		15% Ni^{2+}
		2% NiOH$^+$
	5.3 (320 µg/l)	47% Ni(OH)$_2$(s)*
		46% Ni^{2+}
		6% NiOH$^+$
	7.8-5.8 (1-40 µg/l)	87% Ni^{2+}
		12% NiOH$^+$
Silver	8.8-6.2 (0.1-70 µg/l)	91% Ag$^+$
		9% AgCl^0
Zinc	4.8 (1000 µg/l)	55% ZnCO$_3$(s)*
		21% ZnCO$_3^0$
		14% Zn^{2+}
		5% Zn(CO$_3$)$_2^{2-}$
		4% ZnHCO$_3^+$
	7.3-5.3 (2-320 µg/l)	46% ZnCO$_3^0$
		30% Zn^{2+}
		12% Zn(CO$_3$)$_2^{2-}$
		2% ZnOH$^+$

*Predicted solubility limitations.

TABLE IV-70
METAL SPECIATION IN THE MISSOURI RIVER

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Arsenic	8.9-5.4 (0.1-540 $\mu g/l$)	93% $HAsO_4^{2-}$
		7% $H_2AsO_4^-$
Cadmium	6.2 (70 $\mu g/l$)	66% Cd^{2+}
		21% $CdCO_3(s)^*$
		10% $CdSO_4^o$
		2% $CdCl^+$
	9.5-6.8 (0.1-20 $\mu g/l$)	83% Cd^{2+}
		12% $CdSO_4^o$
		3% $CdCl^+$
		1% $CdCO_3^o$
Chromium(III) (without oxidation-reduction)	5.0 (520 $\mu g/l$)	92% $Cr(OH)_3(s)^*$
		7% $Cr(OH)_4^-$
	5.6 (100 $\mu g/l$)	67% $Cr(OH)_3(s)^*$
		30% $Cr(OH)_4^-$
		3% $Cr(OH)_2^+$
	8.7-6.3 (0.1-20 $\mu g/l$)	91% $Cr(OH)_4^-$
		9% $Cr(OH)_2^+$
Chromium(VI)	8.7-5.0 (0.1-520 $\mu g/l$)	77% CrO_4^{2-}
		1% $HCrO_4^-$
Copper	4.8 (1000 $\mu g/l$)	95% $Cu_2(OH)_2CO_3(s)^*$
		3% $Cu(OH)_2^o$
		1% $CuCO_3^o$
	5.4 (250 $\mu g/l$)	81% $Cu_2(OH)_2CO_3(s)^*$
		13% $Cu(OH)_2^o$
		5% $CuCO_3^o$
	6.0 (60 $\mu g/l$)	55% $Cu(OH)_2^o$
		22% $Cu_2(OH)_2CO_3(s)^*$
		21% $CuCO_3^o$

TABLE IV-70 (Continued)

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Copper (Continued)	8.5-6.6 (0.2-16 $\mu g/l$)	72% $Cu(OH)_2^0$
		30% $CuCO_3^0$
		1% $Cu(CO_3)_2^{2-}$
Lead	5.3 (1000 $\mu g/l$)	89% $Pb(OH)_2(s)^*$
		10% $PbCO_3^0$
	5.8 (316 $\mu g/l$)	66% $Pb(OH)_2(s)^*$
		31% $PbCO_3^0$
		1% $Pb(CO_3)_2^{2-}$
		1% $Pb(OH)^+$
	8.3-6.3 (0.4-100 $\mu g/l$)	93% $PbCO_3^0$
		3% $Pb(CO)_2^{2-}$
		3% $Pb(OH)^+$
Mercury	12-9 (0.0002-0.2 $\mu g/l$)	93% $Hg(OH)_2^0$
		7% $HgClOH^0$
Nickel	4.8 (1-1000 $\mu g/l$)	86% $Ni(OH)_2(s)^*$
		10% Ni^{2+}
		2% $NiSO_4^0$
		2% $NiOH^+$
	5.3 (300 $\mu g/l$)	56% $Ni(OH)_2(S)^*$
		33% Ni^{2+}
		5% $NiSO_4^0$
		5% $NiOH^+$
	7.8-5.8 (1-90 $\mu g/l$)	77% Ni^{2+}
		12% $NiOH^+$
		11% $NiSO_4^0$
Silver	6.2 (70 $\mu g/l$)	53% Ag^{2+}
		40% $AgCl^0$
		5% $AgCl(s)^*$
	8.8-6.8 (0.1-20 $\mu g/l$)	55% Ag^{2+}
		42% $AgCl^0$
		1% $AgSO_4^0$

TABLE IV-70 (Continued)

Metal	Tested Range of Total Metal Concentrations as pM_T and μg/l	Species
Zinc	4.8 (1000 μg/l)	53% $ZnCO_3(s)^*$
		21% $ZnCO_3^o$
		10% Zn^{2+}
		10% $Zn(CO_3)_2^{2-}$
		2% $ZnSO_4^o$
		3% $ZnHCO_3^+$
	7.3-5.3 (2-320 μg/l)	44% $ZnCO_3^o$
		21% Zn^{2+}
		21% $Zn(CO_3)_2^{2-}$
		7% $ZnHCO_3^+$
		4% $ZnSO_4^o$
		2% $ZnOH^+$
		2% $Zn(OH)_2^o$

*Predicted solubility limitations.

TABLE IV-71

METAL SPECIATION IN THE BRAZOS RIVER

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Arsenic	8.9-5.4 (0.1-540 $\mu g/l$)	57% $HAsO_4^{2-}$
		43% $H_2AsO_4^-$
Cadmium	9.5-6.2 (0.1-70 $\mu g/l$)	81% Cd^{2+}
		15% $CdCl^+$
		4% $CdSO_4^0$
Chromium(III) (no redox)	5.0 (520 $\mu g/l$)	92% $Cr(OH)_3(s)^*$
		7% $Cr(OH)_2^+$
	5.6 (130 $\mu g/l$)	66% $Cr(OH)_3(s)^*$
		30% $Cr(OH)_2^+$
		3% $Cr(OH)_4^-$
	8.7-6.3 (0.1-20 $\mu g/l$)	88% $Cr(OH)_2^+$
		9% $Cr(OH)_4^-$
		4% $CrOH^{2+}$
Chromium(VI)	8.7-5.0 (0.1-520 $\mu g/l$)	88% CrO_4^{2-}
		12% $HCrO_4^-$
Copper	4.8 (1000 $\mu g/l$)	95% $Cu_2(OH)_2CO_3(s)^*$
		4% $CuCO_3^0$
		1% $Cu(OH)_2^0$
	5.3 (300 $\mu g/l$)	77% $Cu_2(OH)_2CO_3(s)^*$
		15% $CuCO_3^0$
		5% $Cu(OH)_2^0$
		3% Cu^{2+}
	6.0 (60 $\mu g.l$)	60% $CuCO_3^0$
		29% $Cu(OH)_2^0$
		14% Cu^{2+}
		4% $Cu_2(OH)_2CO_3(s)^*$

TABLE IV-71

(Continued)

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species	
Copper (Continued)	8.5-6.6 (0.2-16 $\mu g/l$)	63%	$CuCO_3^o$
		21%	$Cu(OH)_2^o$
		15%	Cu^{2+}
Lead	5.3 (1000 $\mu g/l$)	82%	$PbCO_3(s)$*
		16%	$PbCO_3^o$
	5.8 (316 $\mu g/l$)	52%	$PbCO_3^o$
		42%	$PbCO_3(s)$*
		3%	Pb^{2+}
		2%	$PbOH^+$
	8.3-6.3 (0.4-100 $\mu g/l$)	90%	$PbCO_3^o$
		5%	Pb^{2+}
		3%	$PbOH^+$
Mercury	12-9 (0.0002-0.2 $\mu g/l$)	60%	$HgClOH^o$
		25%	$HgCl_2^o$
		15%	$Hg(OH)_2^o$
Nickel	7.8-4.8 (1-1000 $\mu g/l$)	93%	Ni^{2+}
		5%	$NiSO_4^o$
		1%	$NiOH^+$
Silver	6.2 (70 $\mu g/l$)	41%	$AgCl(s)$*
		40%	$AgCl^o$
		10%	$AgCl_2^-$
		9%	Ag^+
	8.8-6.8 (0.1-15 $\mu g/l$)	67%	$AgCl^o$
		17%	$AgCl_2^-$
		16%	Ag^+
Zinc	7.3-4.8 (2-1000 $\mu g/l$)	66%	Zn^{2+}
		17%	$ZnHCO_3^+$
		11%	$ZnCO_3^o$
		4%	$ZnSO_4^o$

* Predicted solubility limitations.

TABLE IV-72
METAL SPECIATION IN THE COLUMBIA RIVER

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Arsenic	8.9-5.4 (0.1-540 μg/1)	82% $HAsO_4^{2-}$
		18% $H_2AsO_4^{-}$
Cadmium	9.5-6.2 (0.1-70 μg/1)	97% Cd^{2+}
		2% $CdSO_4^{0}$
Chromium(III) (no redox)	5.0 (520 μg/1)	96% $Cr(OH)_3(s)^{*}$
		3% $Cr(OH)_4^{-}$
		2% $Cr(OH)_2^{+}$
	5.6 (130 μg/1)	82% $Cr(OH)_3(s)^{*}$
		11% $Cr(OH)_4^{-}$
		7% $Cr(OH)_2^{+}$
	6.3 (20 μg/1)	47% $Cr(OH)_4^{-}$
		30% $Cr(OH)_2^{+}$
		24% $Cr(OH)_3(s)^{*}$
	8.7-6.8 (0.1-5 μg/1)	61% $Cr(OH)_4^{-}$
		39% $Cr(OH)_2^{+}$
Chromium(VI)	8.7-5.0 (0.1-520 μg/1)	95% CrO_4^{2-}
		4% $HCrO_4^{-}$
Copper	4.8 (1000 μg/1)	95% $Cu_2(OH)_2CO_3(s)^{*}$
		3% $Cu(OH)_2^{0}$
		1% $CuCO_3^{0}$
	5.4 (250 μg/1)	81% $Cu_2(OH)_2CO_3(s)^{*}$
		14% $Cu(OH)_2^{0}$
		5% $CuCO_3^{0}$

TABLE IV-72 (Continued)

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/1$	Species
Copper (Continued)	6.0 (60 $\mu g/1$)	57% $Cu(OH)_2^o$
		21% $CuCO_3^o$
		20% $Cu(OH)_2CO_3(s)^*$
		2% Cu^{2+}
	8.5-6.6 (0.2-16 $\mu g/1$)	71% $Cu(OH)_2^o$
		20% $CuCO_3^o$
		3% Cu^{2+}
Lead	5.3 (1000 $\mu g/1$)	88% $Pb(OH)_2(s)^*$
		11% $PbCO_3^o$
	5.8 (316 $\mu g/1$)	61% $Pb(OH)_2(s)^*$
		35% $PbCO_3^o$
		3% $PbOH^+$
		1% Pb^{2+}
	8.3-6.3 (0.4-100 $\mu g/1$)	90% $PbCO_3^o$
		7% $PbOH^+$
		3% Pb^{2+}
Mercury	12-9 (0.0002-0.2 $\mu g/1$)	97% $Hg(OH)_2^o$
		3% $HgClOH^o$
Nickel	4.8 (1000 $\mu g/1$)	57% Ni^{2+}
		39% $Ni(OH)_2(s)^*$
		4% $NiOH^+$
	7.8-5.3 (1-250 $\mu g/1$)	92% Ni^{2+}
		6% $NiOH^+$
		2% $NiSO_4^o$
Silver	8.8-6.2 (0.1-70 $\mu g/1$)	86% Ag^{2+}
		13% $AgCl^o$
Zinc	4.8 (1000 $\mu g/1$)	55% Zn^{2+}
		21% $ZnCO_3^o$
		12% $ZnCO_3(s)^*$
		7% $ZnHCO_3^+$
		2% $ZnOH^+$

TABLE IV-72 (Continued)

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Zinc (Continued)	7.3-5.3 (2-200 $\mu g/l$)	62% Zn^{2+}
		24% $ZnCO_3^o$
		8% $ZnHCO_3^+$
		2% $ZnOH^+$
		1% $ZnCO_3^o$
		1% $ZnSO_4^o$
		1% $Zn(OH)_2^o$

*Predicted solubility limitations.

TABLE IV-73
METAL SPECIATION IN THE SACRAMENTO RIVER

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Arsenic	8.9-5.4 (0.1-540 $\mu g/l$)	53% $HAsO_4^{2-}$
		47% $H_2AsO_4^-$
Cadmium	9.5-6.2 (0.1-70 $\mu g/l$)	98% Cd^{2+}
Chromium(III) (no redox)	5.0 (520 $\mu g/l$)	92% $Cr(OH)_3(s)$*
		7% $Cr(OH)_2^+$
	5.6 (130 $\mu g/l$)	68% $Cr(OH)_3(s)$*
		28% $Cr(OH)_4^+$
		3% $Cr(OH)_4^-$
	8.7-6.3 (0.1-20 $\mu g/l$)	88% $Cr(OH)_2^+$
		9% $Cr(OH)_4^-$
		3% $CrOH^{2+}$

TABLE IV-73 (Continued)

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Chromium(VI)	8.7-5.0 (0.1-520 $\mu g/l$)	82% CrO_4^{2-}
		18% $HCrO_4^-$
Copper	4.8 (1000 $\mu g/l$)	95% $Cu_2(OH)_2CO_3(s)$*
		2% $CuCO_3^0$
		2% $Cu(OH)_2^0$
		1% Cu^{2+}
	5.4 (250 $\mu g/l$)	78% $Cu_2(OH)_2CO_3(s)$*
		9% $CuCO_3^0$
		8% $Cu(OH)_2^0$
		5% Cu^{2+}
	6.0 (60 $\mu g/l$)	37% $CuCO_3^0$
		32% $Cu(OH)_2^0$
		19% Cu^{2+}
		10% $Cu_2(OH)_2CO_3(s)$*
	8.5-6.6 (0.2-16 $\mu g/l$)	41% $CuCO_3^0$
		36% $Cu(OH)_2^0$
		21% Cu^{2+}
		2% $CuOH^+$
Lead	5.3 (1000 $\mu g/l$)	79% $PbCO_3(s)$*
		16% $PbCO_3^0$
		2% Pb^{2+}
		2 $PbOH^+$
	5.8 (316 $\mu g/l$)	52% $PbCO_3^0$
		35% $PbCO_3(s)$*
		8% Pb^{2+}
		5% $PbOH^+$
	8.3-6.4 (0.4-100 $\mu g/l$)	80% $PbCO_3^0$
		12% Pb^{2+}
		8% $PbOH^+$

TABLE IV-73 (Continued)

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Mercury	12-9 (0.0002-0.2 $\mu g/l$)	84% $Hg(OH)_2^o$
		10% $HgClOH^o$
Nickel	7.8-4.8 (1-1000 $\mu g/l$)	97% Ni^{2+}
		2% $NiOH^+$
Silver	8.8-6.2 (0.1-70 $\mu g/l$)	83% Ag^{2+}
		17% $AgCl^o$
Zinc	7.3-4.8 (2-1000 $\mu g/l$)	83% Zn^{2+}
		9% $ZnHCO_3^+$
		6% $ZnCO_3^o$

* Predicted solubility limitations.

TABLE IV-74
METAL SPECIATION IN THE COLORADO RIVER

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Arsenic	8.9-5.4 (0.1-540 $\mu g/l$)	95% $HAsO_4^{2-}$
		5% $H_2AsO_4^-$
Cadmium	6.2 (70 $\mu g/l$)	69% Cd^{2+}
		18% $CdSO_4^o$
		9% $CdCl^+$
		3% $CdCO_3(s)$ *
	8.7-6.8 (0.1-20 $\mu g/l$)	71% Cd^{2+}
		18% $CdSO_4^o$
		9% $CdCl^o$

TABLE IV-74 (Continued)

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/1$	Species
Chromium(III) (no redox)	5.0 (520 $\mu g/1$)	90% $Cr(OH)_3(s)^*$
		9% $Cr(OH)_4^-$
	5.6 (130 $\mu g/1$)	60% $Cr(OH)_3(s)^*$
		38% $Cr(OH)_4^-$
		2% $Cr(OH)_2^o$
	8.7-6.3 (0.1-20 $\mu g/1$)	94% $Cr(OH)_4^-$
		6% $Cr(OH)_2^o$
Chromium(VI)		99% CrO_4^{2-}
Copper	4.8 (1000 $\mu g/1$)	95% $Cu_2(OH)_2CO_3(s)^*$
		4% Cu^{2+}
	5.4 (250 $\mu g/1$)	79% $Cu_2(OH)_2CO_3(s)^*$
		17% $Cu(OH)_2^o$
		4% $CuCO_3^o$
	6.0 (60 $\mu g/1$)	70% $Cu(OH)_2^o$
		17% $CuCO_3^o$
		12% $Cu_2(OH)_2CO_3(s)^*$
	8.5-6.6 (0.2-16 $\mu g/1$)	79% $Cu(OH)_2^o$
		19% $CuCO_3^o$
		3% Cu^{2+}
Lead	5.3 (1000 $\mu g/1$)	95% $Pb(OH)_2(s)^*$
		4% $PbCO_3^o$
	5.8 (316 $\mu g/1$)	85% $Pb(OH)_2(s)^*$
		14% $PbCO_3^o$
	6.3 (100 $\mu g/1$)	51% $Pb(OH)_2(s)^*$
		44% $PbCO_3^o$
		3% $PbOH^+$
	8.3-6.8 (0.4-60 $\mu g/1$)	91% $PbCO_3^o$
		6% $PbOH^+$

TABLE IV-74 (Continued)

Metal	Tested Range of Total Metal Concentrations as pM_T and g/l	Species
Mercury	12-9 (0.0002-0.2 μg/l)	81% $Hg(OH)_2^o$
		19% $HgClOH^o$
Nickel	4.8 (1000 μg/l)	90% $Ni(OH)_2(s)^*$
		7% Ni^{2+}
		2% $NiSO_4^o$
	5.3 (300 μg/l)	68% $Ni(OH)_2(s)^*$
		22% Ni^{2+}
		6% $NiSO_4^o$
		4% $NiOH^+$
	7.8-5.8 (1-40 μg/l)	69% Ni^{2+}
		18% $NiSO_4^o$
		13% $NiOH^+$
Silver	6.2 (70 μg/l)	40% $AgCl(s)^+$
		40% $AgCl^o$
		13% Ag^{2+}
		8% $AgCl^-$
	8.8-6.8 (0.2-15 μg/l)	66% $AgCl^o$
		21% Ag^{2+}
		13% $AgCl_2^-$
Zinc	4.8 (1000 μg/l)	50% $ZnCO_3(s)^*$
		21% $ZnCO_3^o$
		10% $Zn(CO_3)_2^{2-}$
		10% Zn^{2+}
		3% $ZnSO_4^o$
		2% $ZnHCO_3^+$

TABLE IV-74 (Continued)

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Zinc (Continued)	7.3-5.3 (2-250 $\mu g/l$)	42% $ZnCO_3^0$
		21% Zn^{2+}
		21% $Zn(CO_3)_2^{2-}$
		6% $ZnSO_4^0$
		5% $ZnHCO_3^+$
		3% $Zn(OH)_2^+$
		2% $ZnOH^+$

[+]Predicted solubility limitations.

TABLE IV-75
METAL SPECIATION IN WOODS LAKE OUTLET

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Arsenic	8.9-5.4 (0.1-540 $\mu g/l$)	99% $H_2AsO_4^-$
Cadmium	9.5-6.2 (0.1-70 $\mu g/l$)	99% Cd^{2+}
		1% $CdSO_4^0$
Chromium(III) (without redox)	8.7-5.0 (520 $\mu g/l$)	73% $CrOH^{2+}$
		12% $CrSO_4^+$
		11% $Cr(OH)_2^+$
		3% Cr^{3+}
Chromium(VI)	8.7-5.0 (0.1-520 $\mu g/l$)	66% $CrOH^{2+}$
		11% $CrSO_4^+$
		11% $HCrO_4^-$
		10% $Cr(OH)_2^+$
		3% Cr^{3+}
Copper	8.5-4.8 (0.2-1000 $\mu g/l$)	99% Cu^{2+}
		1% $CuSO_4^0$

TABLE IV-75 (Continued)

Metal	Tested Range of Total Metal Concentrations as pM_T and $\mu g/l$	Species
Lead	8.3-5.3 (1-1000 $\mu g/l$)	97% Pb^{2+}
		1% $PbSO_4^o$
Mercury	12-9 (0.0002-0.2 $\mu g/l$)	60% $HgClOH^o$
		22% $Hg(OH)_2^o$
		18% $HgCl_2^o$
Nickel	7.8-4.8 (1-1000 $\mu g/l$)	99% Ni^{2+}
		1% $NiSO_4^o$
Silver	8.8-6.2 (0.1-70 $\mu g/l$)	98% Ag^+
		2% $AgCl^o$
Zinc	7.3-4.8 (2-1000 $\mu g/l$)	99% Zn^{2+}
		1% $ZnSO_3^o$

TABLE IV-76

METAL SPECIATION IN PENOBSCOT RIVER, MAINE

Metal	Concentration Range	Species
Arsenic	0.3 - 1000 $\mu g/l$	70% $H_2AsO_4^-$
		30% $HAsO_4^{2-}$
Cadmium	0.008 - 80 $\mu g/l$	98.1% Cd^{2+}
		1.3% $CdSO_4^o$
Chromium III (without redox)	solubility = 95 $\mu g/l$	$Cr(OH)_3(s)$ is solubility control
	<95 $\mu g/l$	91% $Cr(OH)_2^+$
		8% $Cr(OH)^{2+}$
		1% $Cr(OH)_4^-$
Chromium VI	0.1 - 500 $\mu g/l$	63% CrO_4^{2-}
		37% $HCrO_4^-$

TABLE IV-76 (Continued)

Metal	Concentration Range	Species
Copper	solubility = 130 μg/l	$Cu_2(OH)_2CO_3(s)$ is solubility control
	<130 μg/l	66% Cu^{2+}
		18% $Cu(OH)_2^o$
		13% $CuCO_2^o$
		2% $CuOH^+$
Lead	solubility = 510 μg/l	$Pb(OH)_2(s)$ is solubility control
	<510 μg/l	44% Pb^{2+}
		42% $PbCO_3^o$
		13% $PbOH^+$
		2% $PbSO_4^o$
Mercury	0.0002 - 0.2 μg/l	73% $Hg(OH)_2^o$
		26% $HgClOH^o$
Nickel	1. - 1000 μg/l	98% Ni^{2+}
		1% $NiSO_4^o$
Silver	0.03 - 100 μg/l	86% Ag^+
		14% $AgCl^o$
Zinc	1. - 1000 μg/l	95% Zn^{2+}
		3% $ZnHCO_3^+$
		2% $ZnSO_4^o$

TABLE IV-77

METAL SPECIATION IN ST. MARYS RIVER, FLORIDA

Metal	Concentration range	Species
Arsenic	0.3-1000 μg/l	99% $H_2AsO_4^-$
		1% $HAsO_4^{2-}$
Cadmium	0.008-80 μg/l	97% Cd^{2+}
		2% $CdCl^+$
Chromium III (without redox)	0.1-500 μg/l	69% $CrOH^{2+}$
		25% $Cr(OH)_2^+$
		4% $CrSO_4^+$
		1% Cr^{3+}
Chromium VI	0.1-500 μg/l	92% $HCrO_4^-$
		5% CrO_4^{2-}
		2% $CrOH^{2+}$
Copper	0.1-1000 μg/l	99% Cu^{2+}
Lead	0.1-1000 μg/l	96% Pb^{2+}
		2% $PbSO_4^0$
Mercury	0.0002-0.2 μg/l	71% $HgCl_2$
		23% $HgClOH^0$
		1% $Hg(OH)_2^0$
Nickel	0.1-1000 μg/l	99% Ni^{2+}
Silver	0.1-70 μg/l	74% Ag^+
		26% $AgCl^0$
Zinc	0.1-1000 μg/l	97% Zn^{2+}
		1% $ZnHCO_3^+$

TABLE IV-78
METAL SPECIATION IN GRAND RIVER, SOUTH DAKOTA

Metal	Concentration Range	Species
Arsenic	1-1000 μg/l	99% $HAsO_4^{2-}$
		1% $H_2AsO_4^-$
Cadmium	solubility = 10 μg/l	$CdCO_3(s)$ is solubility control
	<10 μg/l	57% Cd^{2+}
		20% $CdSO_4^o$
		12% $CdCl^+$
		9% $CdCO_3^o$
		2% $Cd(OH)^+$
Chromium III	solubility = 240 μg/l	$Cr(OH)_3(s)$
	<240 μg/l	99% $Cr(OH)_4^-$
Chromium VI	1-500 μg/l	100% CrO_4^{2-}
Copper	solubility = 70 μg/l	$Cu_2(OH)_2CO_3(s)$ is solubility control
	<70 μg/l	86% $Cu(OH)_2^o$
		10% $CuCO_3^o$
		5% $Cu(CO_3)_2^{2-}$
Lead	solubility = 35 μg/l	$Pb(OH)_2(s)$ is solubility control
	<35 μg/l	56% $PbCO_3^o$
		44% $PB(CO_3)_2^{2-}$
Mercury	0.002-0.2 μg/l	92% $Hg(OH)_2^o$
		8% $HgClOH^o$
Nickel	solubility = 30 μg/l	$Ni(OH)_2(s)$ is solubility control
	<30 μg/l	43% Ni^{2+}
		35% $NiOH^+$
		15% $NiSO_4^o$
		6% $Ni(OH)_2^o$

TABLE IV-78 (Continued)

Metal	Concentration Range	Species
Silver	solubility = 60 μg/l	AgCl(s) is solubility control
	<60 μg/l	64% AgCl^0
		24% AgCl$_2^-$
		11% Ag$^+$
Zinc	1-1000 μg/l	84% Zn(CO$_3$)$_2^{2-}$
		13% ZnCO$_3^0$
		2% Zn(OH)$_2^0$

TABLE IV-79

METAL SPECIATION IN PECOS RIVER, NEW MEXICO

Metal	Concentration Range	Species
Arsenic	1-1000 μg/l	98% HAsO$_4^{2-}$
		2% H$_2$HsO$_4^-$
Cadmium	0.1-80 μg/l	59% CdCl$^+$
		17% Cd^{2+}
		17% CdCl$_2^0$
		6% CdSO$_4^0$
Chromium III	solubility = 85 μg/l	Cr(OH)$_3$(s) is solubility control
	<85 μg/l	98% Cr(OH)$_4^-$
		2% Cr(OH)$_2^+$
Chromium VI	1-500 μg/l	99% CrO$_4^{2-}$
Copper	solubility = 70 μg/l	Cu$_2$(OH)$_2$CO$_3$(s) is solubility control
	<70 μg/l	90% Cu(OH)$_2^0$
		9% CuCO$_3^0$

TABLE IV-79 (Continued)

Metal	Concentration Range	Species
Lead	solubility = 8 μg/l	$Pb(OH)_2(s)$ is solubility control
	<8 μg/l	83% $PbCO_3^0$
		9% $Pb(CO_3)_2^{2-}$
		4% $PbOH^+$
Mercury	0.002-0.2 μg/l	37% $HgClOH^0$
		24% $HgCl_2^0$
		18% $HgCl_3^-$
		15% $HgCl_4^{2-}$
		6% $Hg(OH)_2^0$
Nickel	solubility = 90 μg/l	$Ni(OH)_2(s)$ is solubility control
	<90 μg/l	60% Ni^{2+}
		23% $NiSO_4^0$
		11% $NiOH^+$
		6% $NiCl^+$
Silver	0.1-70 μg/l	65% $AgCl_2^-$
		18% $AgCl_4^{3-}$
		11% $AgCl_3^{2-}$
Zinc	Solubility = 800 μg/l	$ZnCO_3(s)$ is solubility control
	<800 μg/l	26% $ZnCO_3^0$
		24% $Zn(CO_3)_2^{2-}$
		23% Zn^{2+}
		10% $ZnSO_4^0$
		4% $Zn(OH)_2^0$
		4% $ZnClOH^0$
		2% $ZnOH^+$

and being able to estimate metal speciation at these higher concentrations exactly the same way as for lower concentrations.

3. The tables do not consider the influence of adsorption. While MINEQL can simulate adsorption using electric double-layer theory, this option was not utilized. However, adsorption can be superimposed on the results in the table as follows. First consider the case without precipitation, the case most likely to be of concern for these screening analyses. The information required to account for adsorption is the partition coefficient, K_p, and suspended solids concentration, S, so that the dissolved fraction can be calculated:

$$\frac{C}{C_T} = \frac{1}{1+K_p S \cdot 10^{-6}}$$

where

   C_T = total metal in water column
   C = total dissolved phase concentration.

The dissolved species can be approximated using the same percent distributions present when no adsorption occurs, except the percents in the tables become the percent of total dissolved metal, not total metal. As an example, consider the results from MINEQL shown below for a river when pH = 8.

Species	Without Adsorption	With Adsorption (Area=6.9 m^2/1)
Cu-Adsorbed	0.0%	98.1%
$Cu(OH)_2^0$	95.6%	1.8% (95.6)
$CuCO_3^0$	2.1%	<< 1% (2.1)
Cu^{2+}	1.1%	<< 1% (1.1)
$CuOH^+$	0.6%	<< 1% (0.6)
$CuSO_4^0$	0.5%	<< 1% (0.5)

Without adsorption, 95.6% of the total copper is present as $Cu(OH)_2^0$. When 6.9 m^2/1 of adsorbing surface is added for the conditions simulated, about 98% of the copper adsorbs, leaving only 2% dissolved. However, the percentage distributions of the dissolved species (the percents are shown in parentheses) are the same percent distributions without adsorption (e.g. 95.6 percent of the dissolved copper is $Cu(OH)_2^0$). Figure IV-91 provides a mathematical justification for the procedure suggested above.

4. Now consider adsorption at metal concentrations where precipitation is predicted to occur. The sketch below will help to explain the species shift when adsorption occurs.
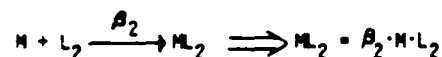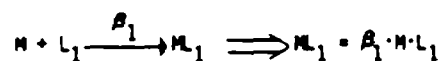
- **Consider a system with 3 dissolved metal species**

    M (free ion)

    ML_1 (1st metal-ligand complex)

    ML_2 (2nd metal-ligand complex)

    where $M + ML_1 + ML_2$ = total dissolved metal = M_{To}

- **The equilibrium reactions are:**

$$M + L_1 \xrightarrow{\beta_1} ML_1 \implies ML_1 = \beta_1 \cdot M \cdot L_1$$

$$M + L_2 \xrightarrow{\beta_2} ML_2 \implies ML_2 = \beta_2 \cdot M \cdot L_2$$

- **The equilibrium speciation fraction for free metal ion is:**

$$\frac{M}{M_{To}} = \frac{1}{1 + \dfrac{\beta_1 \cdot L_{1T}}{1 + \beta_1 M} + \dfrac{\beta_1 L_{2T}}{1 + \beta_2 M}}$$

    If $1 \gg \beta_1 M$, $1 \gg \beta_2 M$ (typically true in many natural systems)

    Then:

$$\frac{M}{M_{To}} = \frac{M}{M_{Total}} \cdot \frac{M_{Total}}{M_{To}} = \frac{M}{M_{Total}} \cdot \frac{1}{\alpha} = \frac{1}{1 + \beta_1 L_{1T} + \beta_2 L_{2T}} = \text{constant for each river analyzed}$$

$$\alpha = \text{fraction dissolved} \left(e.g., \frac{1}{1 + K_p \cdot S \cdot 10^{-6}} \right)$$

    So $\quad M = (M_{Total}) \cdot (\alpha) \cdot \left(\dfrac{1}{1 + \beta_1 L_{1T} + \beta_2 L_{2T}} \right)$

    Concentration of total metal in river, based on procedures summarized in Table IV-58

    Determine from local data or use Table IV-62

    These are the fractional species in Tables IV-65 through IV-79

- **Summary:**

    To account for adsorption, use Tables IV-65 through IV-79 directly but consider the percent species to be **dissolved metal** rather than **total metal.**

FIGURE IV-91   EXAMPLE PROCEDURE FOR SUPERPOSITION OF ADSORPTION

As an adsorbing species is added to a water where dissolved and precipitated species are in equilibrium, some of the dissolved species become adsorbed. In turn, precipitates begin to re-dissolve to satisfy solubility conditions. As long as an excess of precipitates are present, the concentrations of total dissolved species will not change with or without adsorption. However, when all of the precipitated solids re-dissolve, then the concentration of dissolved species will decrease compared to the case with no adsorption. The tabulations below illustrate an example from MINEQL for a total copper concentration of $5 \cdot 10^{-6}$ M (318 μg/l).

Species	No Adsorption	Adsorption (Area=0.69 m^2/l)	Adsorption (Area=69 m^2/l)
Cu-Adsorbed	0.0%	15.4%	98.7%
$Cu(OH)_2(s)$	58.3%	42.9%	0.0%
$Cu(OH)_2^0$	39.9%	39.9%	1.2%

When a relatively small amount of adsorbing species is added (0.69 m^2/l), 15.4% of the copper adsorbs, and the total precipitated copper decreases from 58.3% to 42.9%. However, the total dissolved copper remains constant at 39.9%. When significantly more surface area is added, more copper adsorbs until eventually the dissolved copper in the water column is below solubility, and all of the precipitated copper redissolves. Based on the above illustration, the following procedure is suggested to account for the possibility of simultaneous precipitation and adsorption. Using the total concentration C_T of interest from the appropriate table, find

$$C = \frac{C_T}{1+K_p S \cdot 10^{-6}}$$

If C is less than C_{sol}, the solubility of the metal which can be found as described previously in step (1), then all of the precipitate is re-dissolved and only the adsorbed and dissolved species exist. Thus,

both C and C_s ($=C_T-C$) are known, and the species of C can be found as described in step (3).

If C> C_{sol}, the dissolved metal concentration becomes C_{sol}, and the total dissolved plus adsorbed concentration, C_T', is:

$$C_T' = C_{sol} \, (1+K_p S \cdot 10^{-6})$$

where C_T' is less than C_T. The precipitated metal is $C_T - C_{sol} \cdot (1 + K_p S \cdot 10^{-6})$. Again, the species distribution of C_{sol} can be found using step (3). The following tabulations summarize the two cases:

	$C > C_{sol}$	$C < C_{sol}$
Amount dissolved	C_{sol}	C
Amount adsorbed	$K_p S C_{sol} \cdot 10^{-6}$	$K_p S C \cdot 10^{-6}$
Amount precipitated	$C_T - C_{sol} - K_p S C_{sol} \cdot 10^{-6}$	0

As mentioned previously, the results in the tables are valid for oxidizing conditions, with one exception. Chromium (III), which is thermodynamically stable under reducing conditions, was allowed to exist by not involving redox reactions. The oxidation of chromium (III) to chromium (VI) is thought to be very slow, so if chromium enters a river as the III+ ion, it may persist. However, chromium(III) is relatively insoluble in most waters (from 30 to 50 µg/l) and is also less toxic than chromium(VI) so that chromium(III) is likely to be of secondary importance.

Throughout the range of metal concentrations examined, some of the metals did not precipitate at all. Those metals are: arsenic, chromium(VI), and mercury. The remaining metals precipitate under at least some of the conditions, and the precipitates are:

- Cd: $CdCO_3(s)$
- Cr(III): $Cr(OH)_3(s)$
- Cu: $Cu_2(OH)_2CO_3(s)$
- Pb: $Pb(OH)_2(s)$ or $PbCO_3(s)$
- Ni: $Ni(OH)_2(s)$
- Ag: $AgCl(s)^2$
- Zn: $ZnCO_3(s)$

The only natural water where no metal precipitation occurred was at Woods Lake outlet, where the pH is 4.7. Also, in Woods Lake, most of the chromium is likely to be present as Cr(III) regardless of pe because of the low pH.

The fact that MINEQL (or any other equilibrium model) predicts certain metals will precipitate under certain conditions must be interpreted with a certain amount

of judgment because of the supersaturation possibility and because of uncertainty in solubility products. For example, the solubility products used by MINEQL for Pb(OH)(s) and Ni(OH)$_2$(s) appear to be on the lower end of an acceptable scale which spans 3 to 4 orders of magnitude for the solubility product (Sillen, 1966), i.e. the solubilities are taken to be lower rather than higher. Hence, predicted hydroxide solubility limitations for lead and nickel, which occur in a number of the surface waters chosen, should be interpreted with this in mind.

While the mathematical tools presented in Section 4.10.3 can be used independently of metal species distribution, the results from MINEQL can also be used in conjunction with the mathematical tools. The approach is as follows:

1. Using the transport-fate expressions in Section 4.10.3, find the temporal and spatial distributions of the metal(s) of interest. Record C_T (total concentration), C (the dissolved concentration), and C/C_T (the fraction dissolved) at each location of interest.

2. Select an appropriate natural water from Tables IV-65 through IV-79, and enter the table using the total metal concentration found from step (1) at each location of interest in the water body (if three locations are of interest, for example, the procedure outlined here is repeated three times).

3. Since the effects of adsorption are not directly included in the tables, the procedure outlined earlier should be used to account for adsorption and to find the percent distribution and amount of each dissolved species. Note that C/C_T values (see step (1)) do not have to be recalculated for the earlier procedure.

4. In all likelihood, the percent distribution of the dissolved species will not change significantly within a given river, although the total dissolved concentration can change. (An exception is an acid-mine-drainage situation, where pH can change significantly over distance.) When this is the case, the first three steps have to be completed only one time. The percentages found are then multiplied by C at each location to find the species distribution at each location.

————————————————————— EXAMPLE IV-25 ——————————————————————

This example illustrates some differences in lead speciation likely to exist between two of the river waters shown earlier in Table IV-64: the Ogeechee River in Georgia and the Colorado River in Colorado. Some of the water quality characteristics of the rivers are summarized below.

River	pH	Suspended Solids, mg/l	Total Hardness
Ogeechee	6.9	14	21.
Colorado	8.1	2450	374.

The water in the Colorado is quite hard while the Ogeechee River water is very soft. Consequently, hardness-related water quality criteria are different for the two rivers. For example, the 24-hour average criteria levels for cadmium and lead are 20 and 870 times higher in the Colorado than in the Ogeechee, respectively.

Lead solubility in the Ogeechee is controlled by the carbonate (see Table IV-66) while in the Colorado, the hydroxide controls (see Table IV-74). The lead solubility in the Ogeechee appears to be about 220 μg/l. This is found from the prediction by MINEQL that 11 percent of the total lead of 250 μg/l is present as $PbCO_3(s)$. The remaining 89%, or 220 μg/l, is dissolved.

In the Colorado River, the $Pb(OH)_2(s)$ limits the total soluble lead to appproximately 50 μg/l (49 percent of 100 μg/l is soluble). Note that in the absence of precipitation, the percent distribution of lead is independent of the total lead in the water column. As shown in Tables IV-66 and IV-74, the predominant species of dissolved lead are:

River	Species
Ogeechee	58% $PbCO_3^o$
	26% Pb_{2+}
	15% $PbOH^+$
Colorado	91% $PbCO_3^o$
	6% $PbOH^+$

Now, consider adsorption of lead to the suspended matter in the rivers. Based on the suspended solids levels and typical partition coefficients, it is assumed that 70 percent of the lead is adsorbed in the Ogeechee River and 99 percent in the Colorado River (see Table IV-62). Because such high fractions of the metals adsorb, it is unlikely that precipitates form even at high concentrations of metal, based on the procedure described earlier in this section. As an example, consider a total lead concentration of 60 μg/l in the Colorado River. In the absence of adsorption, precipitation of $Pb(OH)_2(s)$ is predicted. However, if 99 percent of the 60 μg/l is adsorbed, then only 1 percent or 0.6 μg/l of the lead is dissolved in the water column. This is considerably below the 50 μg/l solubility of lead, so that precipitation does not occur. According to Table IV-74, nearly all (91 percent) of the 0.6 μg/l dissolved lead is present as $PbCO_3^o$

—————————————— END OF EXAMPLE IV-25 ——————————————————

4.10.5 Execution of Limited Field Reconnaissance and Sampling Program

4.10.5.1 Introduction

Since a screening level analysis is intended to make use of a minimal amount of existing data to estimate where severe water quality problems are likely to occur and where problems are unlikely to occur, the suggestion that a limited field reconnaissance and sampling program be conducted appears incongruous with the intent of the approach. However, a limited field reconnaissance and sampling program may be useful on a screening level for a number of reasons.

Perhaps the most important is the complexity of the problem of predicting fate of metals. Researchers are still far from developing a well accepted unified theory which can be used to predict the fate of metals in the natural aquatic environment. A review of the literature quickly reveals the divergency of views that now exist, particularly in the area of quantification. A good example is the partitioning of metals onto solids. Ignoring the fact that a variety of approaches exist related to adsorption, and considering only the linear isotherm adsorption approach used in this chapter, documented results show that the adsorption coefficient, K_p, is quite variable for a given metal under the conditions encountered in natural rivers. While in groundwater systems this variability may not be as important because of the large amount of solids surface area for the metal to adsorb (i.e., well over 99 percent of the metal is likely to be adsorbed for $K_p > 10^3$ l/kg), in surface water the available solid surface area is typically only about 0.01 to 0.02 percent as great as in groundwater systems. With these much smaller surface areas, the percent metal that is dissolved can vary considerably.

For example, at a suspended solids level of 100 mg/l, a metal is 91 percent dissolved when $K_p = 10^3$ l/kg and 9 percent dissolved when $K_p = 10^5$ l/kg. In the first instance, much of the metal is transported downstream and is influenced to a small degree by solids settling or scour. Under these conditions, multiple waste sources on a river interact with each other to produce gradually elevating levels of metals over distance (unless dilution is important).

On the other hand, when only 9 percent of the metal is dissolved, then settling zones in the river tend to remove the metal from the water column, and downstream sources can act independently of each other. Thus, the partition coefficient becomes an important parameter to quantify.

The best way of interpreting K_p for metals is to consider the coefficient as a parameter (not necessarily of solid scientific validity) that relates concentrations of solid and particulate metals and is likely to be highly variable from one set of conditions to another. Because of its importance, local determination of K_p is recommended.

A second reason for local sampling is the importance and variability of natural metal sources. In some cases, natural sources of metals may be largely or entirely

responsible for exceeding standards. Thus, removing a large percentage of point source contributions may have a negligible impact on levels of metals.

Before undertaking a field reconnaissance and sampling program, the following questions should be answered:

1. Have all potential sources of information been accessed? Delos et al. (1983) summarize likely sources.

2. Have the available data been summarized, categorized, and compared against the information needs required to conduct a screening analysis? Table IV-80 shows the kinds of information required to carry out the screening analyses presented in this document. While supporting information may be useful for other purposes envisioned by the user, they are not likely to be critical for the purposes of these screening procedures.

3. Have preliminary screening analyses been carried out to see whether the missing, or poorly quantified data are important? The proposed screening analyses should be performed first with "best judgment" data to verify that the missing information do make a significant difference. If not, there is no reason, within the scope of the objectives of this chapter, to collect that kind of data.

4. Have the objectives of the field reconnaissance/sampling program been defined and have these activities been planned thoroughly? Before setting foot into the field, all the reasons for doing so should have been carefully thought out. Pre-planning will save time and money, and more likely produce the intended results. Particularly, personnel requirements and assignments and equipment needs (including backup equipment) should be carefully addressed.

4.10.5.2 Field Reconnaissance

A field reconnaissance is a firsthand survey of the system under investigation. A reconnaissance can be used to verify, if only in a qualitative sense, some of the data which are being used for the screening analysis. In particular, this kind of data can consist of:

- Identification and locations of point sources
- Locations of appropriate upstream and downstream boundaries
- Estimation of water depths in different reaches of the river
- Estimation of surface widths in different reaches of the river
- Identification of free-flowing reaches, backwater areas, and locations and sizes of lakes or reservoirs
- Visual (photographic) documentation of the system.

TABLE IV-80

SUMMARY OF DATA REQUIREMENTS FOR SCREENING OF METALS IN RIVERS

Data	Methodology Where Data Are Used[a]	Remarks
Hydraulic Data		
1. Rivers:		
• River flow rate, Q	D, R, S, L	An accurate estimation of flow rate is very important because of its dilution capability.
• Cross-sectional area, A	D, R, S	
• Water depth, H	D, R, S, L, AD	The average water depth is volume divided by surface area.
• Reach lengths, x	R, S, AD	Watershed subareas can be used to estimate flow rates.
• Watershed areas by tributary drainage, A_w	D	
• Stream velocity, U	R, S, AD	The required velocity is distance divided by travel time. It can be approximated by Q/A only when A is representative of the reach being studied.
2. Lakes:		
• Hydraulic residence time, T		Hydraulic residence times of lakes can vary seasonally as the flow rate through the lakes' changes.
• Mean depth, H		
Source data		Source data include both natural and anthropogenic sources.
1. Background		
• Metal concentrations, C_{uT}	D, R, S, L	Background concentrations should generally not be set to zero without justification.
• Boundary flow rates, Q_u	D, R, S, L	
• Boundary suspended solids, S_u	D, R, S, L, AD	One important reason for determining suspended solids concentrations is to determine the dissolved concentration, C, of metals, based on C_T, S, and K_p. However, if C is known along with C_T and S, use this information to find K_p rather than using literature values.
• Silt, clay fraction of suspended solids	L	
• Locations	D, R, S, L	
2. Point Sources		
• Locations	D, R, S, L	
• Flow rate, Q_w	D, R, S, L	
• Metal concentration, C_{Tw}	D, R, S, L	
• Suspended solids, S_w	D, R, S, L, AD	
Bed Data		
• Depth of contamination		For the screening analysis, the depth of contamination is most useful during a period of prolonged scour when metal is being input into the water column from the bed.
• Porosity of sediments, n		
• Density of solids in sediments (e.g., 2.7 for sand), ρ_s		
• Metal concentration in bed during prolonged scour period, C_{T2}		
Derived Parameters		
• Partition coefficient, K_p	All	The partition coefficient is a very important parameter. Local determination is preferable.
• Settling velocity, w_s	S, L	This parameter is derived based on Equation IV-184.
• Resuspension velocity, w_{rs}	R	This parameter is derived based on Equation IV-181.
Equilibrium Modeling		
Water quality characterization of river:	E	Table IV-64 summarizes the chemical characteristics chosen to characterize 14 rivers and 1 lake throughout the United States.
• pH		
• Suspended solids		
• Conductivity		
• Temperature		
• Hardness		Water quality criteria for many metals are keyed to hardness, and increase with increasing hardness (see Table IV-41).
• Total organic carbon		
• Other major cations and anions		

[a] D - dilution
R - dilution and resuspension
S - dilution and settling
L - lake on river
AD - adsorption/desorption rates
E - equilibrium modeling

One of the primary purposes of the reconnaissance, in addition to verifying data used in the screening analyses, is to gain a feel for the importance of settling and scour of solids, as a function of reach, throughout the study area. If there are extensive settling zones where a high percentage of the solids settle, and if the partition coefficients of the metals under investigation are high, then much of the metals are likely to settle also. On the other hand, if the suspended solids are transported downstream with relatively little settling or if $K_p S \cdot 10^{-6}$ is small (e.g., < 1) then downstream transport of metals is likely to be significant. Comparison of the behavior of the surface water with predicted metal distributions go hand in hand, and provide an opportunity for the user to obtain a consistency between prediction and observation.

As part of characterizing settling zones, samples of bottom sediments (the top 1 to 3 inches) can be collected for visual observation. A qualitative comparison of grain size and texture might confirm whether fine, as well as coarse, particles settle in quiescent zones in rivers.

The very limited field reconnaissance described above requires little data collection, with the exception of water depths and widths. The appropriate water depth is the average depth across a section. If the section is approximately parabolic, then the average depth approximately equals 2/3 of the maximum depth. An added benefit of knowing average depths and surface widths is that the cross-sectional area can be estimated which can directly be used to find stream velocity. Choosing "typical" sections for characterizing width and depths means that the calculated velocity is likely to be typical as well.

The next question to be addressed in a field reconnaissance is when to go into the field. A variety of possibilities exist, with the major candidate situations being:

- Steady, low to moderate flow conditions
- Pseudo-steady high flow conditions, such as snow runoff periods during spring melt or during a long, low intensity storm
- Highly unsteady conditions when stream flow is rapidly changing due to a transient high intensity storm event.

Without question, the steady, low to moderate flow condition is most appropriate for a first, low effort reconnaissance, even if this is not the most critical water quality condition. Generally the results obtained during a steady-state period are more readily and accurately interpretable because time variability is not a consideration. Additionally, results from a field reconnaissance conducted at steady-state can help to determine critical conditions.

4.10.5.3 Sampling Guidelines

Table IV-80 shown earlier summarizes the data required for the screening procedures contained in this document. Based on a comparison between the data available and the data required to perform a screening analyses, sampling priorities can be

generated. While it is not possible to always decide beforehand what are the most important parameters for a particular situation, some preliminary calculations with the screening tools will be useful to reveal what appears most important. In many cases, the magnitude of the partition coefficient is likely to play an important role. The partition coefficient is not measured directly, but is calculated from measured values of adsorbed metal per unit suspended solids (X) and dissolved metal (C); i.e., $K_p = X/C$.

If resources permit, a comprehensive survey where samples are collected at the system boundaries and at important sources at a single point in time is generally very useful for predictive purposes. If the survey is performed during steady-state conditions, all samples do not have to be collected in a truly simultaneous fashion. The principal advantage of a comprehensive survey over repeated sampling at one or two stations is that the information collected can be used to more accurately reconstruct overall cause and effect mechanisms, understand better system responses and thus more reliably predict concentrations throughout the system.

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