disposal of residues on land

Proceedings of the

NATIONAL CONFERENCE ON DISPOSAL OF RESIDUES ON LAND

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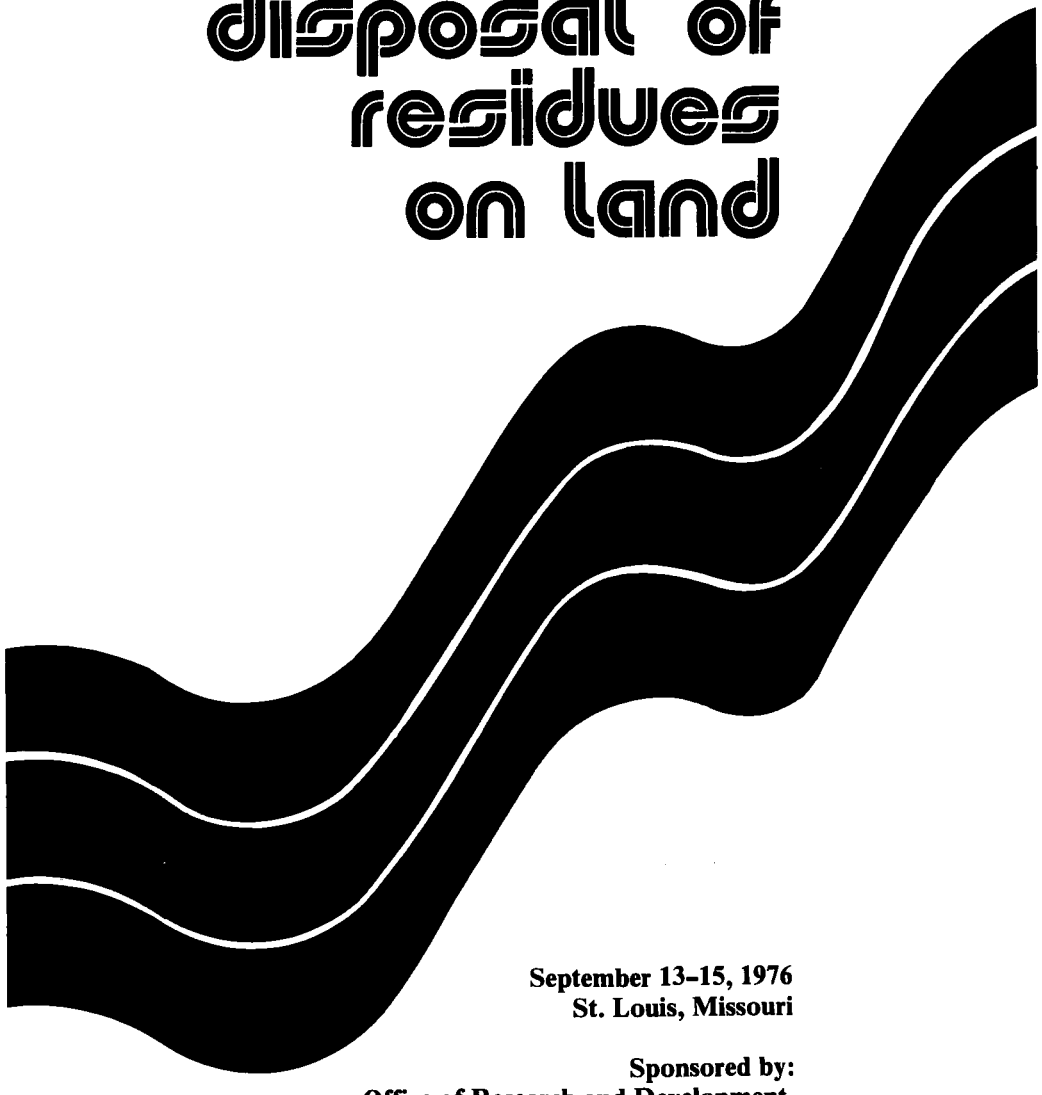

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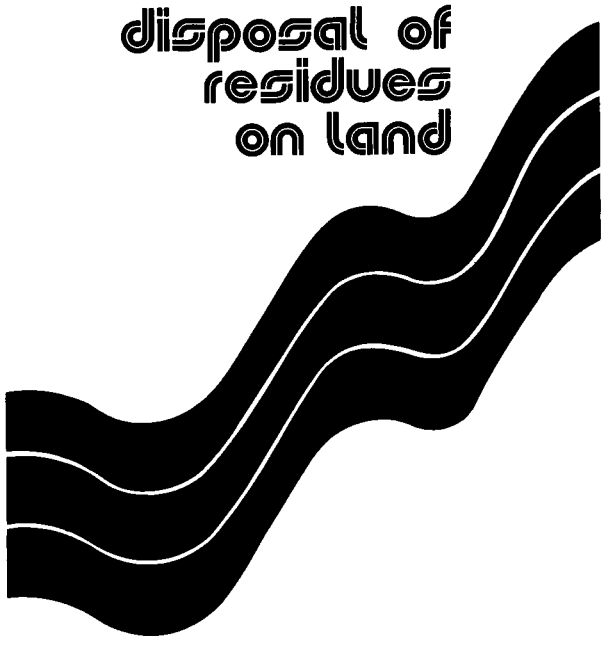
disposal of
residues
on land

The Institutional Challenges to Residual Management

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INTRODUCTION

Residuals are a problem of gargantuan size as well as complexity. The Office of Solid Waste Management Programs has presented testimony to the U. S. House of Representatives concerning the quantity and composition of the non-hazardous and hazardous discarded materials stream. This includes 1.783 billion tons of mining wastes, 687 million tons of agricultural wastes, 135 million tons of municipal wastes, 260 million tons of industrial wastes, and 7.3 million tons of sewage sludges. This imposing number of three to four billion tons of solid waste must be disposed of predominantly on land. EPA has further documented over 23 million tons of potentially hazardous waste produced by eight groups of industries. The growth of sludges as a result of air and water pollution control standards may take dramatic jumps if the 1977 and 1983 mandates of Public Law 92-500 are met. We also expect an increase in potentially hazardous waste by 1983 of 31 million tons by dry weight, an increase of over 33 percent in nine years; and, the growth of all solid wastes are increasing between 2.5 and 4.5 percent per year.

We must examine the technical issues on residuals management and to help narrow the gap between what we know and what we need to know. This I am confident we can do—R&D on safe, beneficial methods to dispose of residuals will ultimately lead to standards and methodology.

Concurrently, we must develop less cumbersome, more effective institutional processes. The problem from social, political, and economic influences, in some respects surpass the technical in difficulty to master. They are complex and often illogical and frustrating.

The institutional factors which will affect residuals management can be segmented into:

- Legal and regulatory
- Social and political—and the bonds of existing practice.

Each of the residuals has a particular set of issues, institutional arrangements and economic considerations which govern the resolution (or lack of resolution) of problems.

Industrial Residues

Industrial residues represent one of the largest in volume—they are being produced in increasing quantities and complexities. They are a result of both public and private sector activities and their disposal on land is controlled basically by the states. The role of EPA has been primarily one of technical and financial assistance to the states. The states have the primary regulatory function which a few states have exercised very adroitly, but others have failed to act.

The institutional framework for controls is complicated by the media approach of our pollution control efforts—(independently). The following discussion by media presents the primary sources of industrial residues and the roles of different governmental levels and the private sector in their disposal.

Air

The Federal regulatory program established by the Clean Air Act of 1974 has considerable impact on production and controls of residuals by industry. During the past, the actual impact of air pollution regulations—and technology—have been assessed poorly if done at all. However, the background documents "Standards Support and Environmental Impact Statements" (SSEIS) will in the future contain assessments of residuals and economic analysis. Fortunately, it is expected that residuals production from air pollution control will increase much more gradually than from water pollution controls.

The disposal of materials collected by air pollution devices can be divided into sludges or solids basically collected as particulate matter. The sludges are primarily sulfur oxide sludges which are not hazardous but represent a voluminous, special land disposal problem. The particulates are primarily dust, dirt, and fly ash. In the Region VII states, Iowa has developed guidance for the disposal of fly ash under the solid waste disposal law. The other three states in Region VII have not developed guidance for fly ash disposal and none of the Region VII states have developed guidance for sulfur oxide sludge disposal. In our Region it is a problem of minor proportions.

Water

On the other hand—industrial residues from water pollution controls under PL 92-500 already present a challenge.

The production of *industrial sludges* has been estimated at 35 million tons per year on a dry-weight basis and is greater than municipal waste water sludges. Ten *major industrial* sectors were estimated to produce in excess of 7 million tons of sludge for disposal *on land* in 1971. These ten will increase disposal on land requirements to *13 million tons in 1977* when the best practical treatment (BPT) is installed. All industries may increase their disposal on land requirements to *25 million tons* by 1983.

The role of the Environmental Protection Agency with regard to industrial sludge management will follow the same basic pattern as described for municipal sludge, but will impact the private sector rather than the public.

The EPA draft residuals sludge management strategy paper includes two "immediate action" tasks with regard to industrial sludge, namely: "(1) development of detailed program plan for industrial sludge management by 12/76 and (2) development of

a guidance document for the utilization/disposal of industrial sludges to be used by the regional offices, states, and localities by 12/77." In addition, several issues directly related to industrial sludges require further evaluation: (1) the determination of the public health consequences of various disposal mechanisms to define the risk/benefit relationships and (2) the technological problems of dewatering, recovery, operations, and maintenance. The effects of sludge are intermedia, therefore must be investigated on an intermedia basis. The lack of adequate data on and guidance on adequate practices, market information for selected sludges, *and* recognition of the impact of the sludge management problem created by legislation on the state and federal level will be overcome through research, investigation and dissemination of information. These issues *are* being investigated by a variety of methods including the definition of the roles of the EPA, USDA, and FDA with the states and the establishment of communication channels for information flow. In addition. issue papers or similar documents outlining EPA's policy and procedures will be developed as rapidly as possible in order to provide the needed guidance to states, local agencies, and the private sector.

The role of the states includes operation of the water pollution control permit program in the states which are delegated such authority. In Region VII, Nebraska, Missouri, and Kansas, the permit programs have been delegated. The state agencies have the primary regulatory authority for industrial sludge disposal on land and the local agencies or private firms have the operational, financial, and technical responsibilities. The activities of the Region VII states will be described later in the municipal sludge section.

Solid Waste

The production of industrial solid waste other than mining has been estimated by EPA's Office of Solid Waste Management Programs to be between 140 and 270 million tons per year. Unfortunately wide variations in the production of solid wastes make estimates a dynamic statistic. We have to remember this in developing control strategies. The dynamics of estimates can be illustrated; e.g., original estimates had been made that the hazardous waste stream amounted to 10 million tons/year. However, further investigations have placed the quantity of hazardous waste produced at closer to *23 million tons/year.* As a result of the BPT and best available treatment (BAT) requirements, this total is expected to increase to over 26 million tons in 1977 and over 30 million tons in 1983. Although the nonhazardous industrial solid waste stream is not well documented or defined, it is estimated to amount to 270 million tons/year and *will be increasing at a rate of between 2.5 and 4.5 percent per year.*

The role of the Region VII states in regulating industrial solid wastes has traditionally been to treat them much the same as municipal solid waste unless it contained a hazardous material The states of Kansas, Missouri, Iowa, and Nebraska regulate solid waste disposal sites by requiring a permit for construction and operation of the sites. The state agencies review the site design and operation plan which should include a description of any industrial solid waste to be accepted. If, in the judgment of the agency the site is designed to adequately handle industrial waste, approval to receive specific materials is provided with the permit. If special conditions for receipt of the industrial waste are judged necessary, the conditions for accepting the wastes are included in the permit.

Basic data on hazardous waste production in Region VII is now being developed: In Iowa, the Department of Environmental Quality is conducting a hazardous waste survey to determine the extent of hazardous waste generation, handling, and disposal problems within the state. They have developed and proposed to the state legislature a bill which would provide the state agency with the authority to control the treatment, disposal, and storage of hazardous wastes and require reporting on generation.

In Kansas, a hazardous waste survey of 450 industries has just been completed by the state solid waste management agency. The agency is drafting a report on the findings of the the survey and also plans to develop recommendations for legislation. State personnel are appearing today (September 13) before the legislative committee to discuss these needs. State regulations already provide for limited control of hazardous waste land disposal and can be expanded.

In Missouri, the Department of Natural Resources is also completing a hazardous waste survey of over 400 industries and is at the same time working with an ad hoc committee to develop consensus hazardous waste management legislation. The state agency currently has authority over hazardous waste treatment and disposal operations and three sites are permitted to receive various types of hazardous wastes on an "as requested" basis for each waste. The new legislation will be directed toward insuring that all hazardous wastes generated are reported and disposed of properly.

In Nebraska, the Department of Environmental Control has the primary authority over solid waste disposal from first-class cities and at all private sites. Other agencies, such as the Department of Health and Highway Department, also have some jurisdiction over such sites, but agreements are under development to avoid duplicate jurisdiction. The state solid waste agency has completed a survey of approximately 90 generators of hazardous wastes and is in the process of developing a survey report with recommendations for needed legislation. The state environmental protection act contains several sections relating to hazardous and toxic pollutants which require a legal opinion pertaining to their scope before recommendations on legislation can be developed.

In the hazardous waste management area, the states in Region VII are responding to the challenge. Nationally, California has led the way but Minnesota and Oregon also have relatively new comprehensive hazardous waste management laws, regulations, and programs. Illinois, Oklahoma, Washington, and Maryland have hazardous waste management acts in various stages of implementation, and Pennsylvania, Massachusetts, and other states are exercising through other acts limited control over hazardous wastes. Georgia and Kentucky have issued guidance concerning the handling, treatment, and disposal of hazardous wastes, which is another approach to the problem. As you can see, our states are developing programs without a federal mandate, on a heterogeneous pattern. A uniform national program is needed.

The private sector to be regulated has had numerous opportunities for input to a national hazardous waste management program. With the growth and diversity of state programs, little overt opposition to the hazardous waste management provisions of Senate Bill 2150 and House Bill 14496 has developed signaling to EPA that perhaps the time has arrived.

The two bills have no substantial differences: They would establish criteria and designation of hazardous waste; regulations for disposal, treatment, and storage; criteria for a system of manifests; and minimum criteria for state programs authorized to operate the permit, regulatory, and enforcement activities. In addition, the bills would authorize the Administrator to seek injunctions for imminent hazards caused by disposal of solid or hazardous wastes and provide for enforcement of the regulations and standards established under the hazardous waste management portion of the act.

Implementation of the hazardous waste management provisions would take place over an 18-month period and would extend program support to those states that met the requirements for state programs. In addition, the definition of "hazard-

ous" would not be limited to solids but would include solids, liquids, and contained gases, making the provision intermedia and establishing a program concerned with these wastes regardless of form.

Municipal Sludges

The role of the federal government in control of land disposal of the municipal sludges is one of financial and technical assistance to states, local government, and industry in the development of technology for proper disposal. However, the impact of the Federal Water Pollution Control Act, P. L. 92-500, goes considerably further.

The impact of P. L. 92-500 was reported in detail by Harold Bernard at the Second Annual National Conference on Municipal Sludge Management and Disposal. Briefly, he listed nine specific sections of the Act which will significantly increase sludge production by 1977 and 1983, and/or will require stricter enforcement.

Shortly after passage of the Act in late 1972, EPA formed a sludge management working group including USDA and FDA to develop recommendations on proper municipal sludge practices.

At the June 9 and June 10 meeting of this year, the regional requirements subcommittee developed a statement concerning the major needs in the area of residual sludge management. The highest priority is the development of a national policy including an interim policy on industry pretreatment requirements for heavy metals. Technical guidance which provides limits on contaminants discharged to land was the next priority, followed closely by the need for states to develop sludge management guidelines.

This imposing list of major recommendations provides a good summary of the state of the sludge management program. It requires a major commitment of resources. A draft strategy paper for residual sludge management has just been completed for internal review by the working group. Several of you have seen the draft—we look for its publication in the near future.

Also, on June 3, 1976, in the *Federal Register,* the Environmental Protection Agency issued a technical bulletin on the environmental factors in municipal sludge management. The objective of the bulletin is to provide design information on sludge management options and factors on environmental acceptability.

The state role in the area of municipal sludge disposal on land will be regulatory. Many state agencies which control solid waste management have broad control over land disposal which should be expanded, with the assistance of air and water pollution control programs, to encompass disposal of all wastes on land.

Although several states have advanced further in municipal sludge guidance than those of Region VII, our states are moving (at different rates) to establish a regulatory control program over the land disposal of municipal and industrial sludges. The state of Iowa has proposed to develop guidance for land disposal of municipal and selected industrial sludges. The state of Kansas allows the disposal of municipal waste treatment sludges in sanitary landfills. This disposal practice is proposed to be evaluated under the funds available under section 208 of P. L. 92-500. The state of Missouri allows the disposal of municipal waste water treatment sludges in sanitary landfills designed for receipt of such sludges. They have proposed to evaluate land disposal of sludges under their section 208 grant also. The state of Nebraska allows disposal of municipal sludge in sanitary landfills which are permitted by the state agency. They are examining the possibility of control over municipal sludge disposal through regulations aimed at the source rather than the method of disposal.

Cities must adopt specific pretreatment requirements in order to be eligible for federal construction grant funds. The national pollutant discharge elimination system (NPDES) requirements and permit program will also require communities not involved in the construction grant programs to meet the pretreatment requirements for noncompatible wastes.

New (and substantial) funds have been made available for planning residual management in an intermedia context under the 208 planning program under P. L. 92-500. Basically, the state 208 programs will allow state agencies to focus on municipal and industrial sludge management concepts. The state agencies should develop rules and regulations and technical guidance covering these sludges as part of the statewide 208 planning program and can exercise guidance over institutional arrangements through matching grant provisions of state law. The local role will be primarily limited to municipal sludge management.

Municipal Refuse

The production of solid waste has been correlated with the growth of the gross national product by Professor Zaltzman of West Virginia. The post-consumer solid waste production figure for 1971 was 125 million tons and for 1973 grew to 135 million tons on a wet basis. Of primary concern is that the vast majority of this waste stream is disposed of on land and that controls on these operations are becoming more intensive.

In 1965 when the federal involvement began with the passage of the Solid Waste Disposal Act, only five states had solid waste management programs and employed a total of 13 people. As of 1976, all 50 states had active programs employing over 400 persons. But this is not a measure of progress in itself. A real measure of progress is in the number of state permitted land disposal sites, which for Region VII has increased from 27 in 1970 to 380 in 1976, serving 84 percent of the population. This dramatic growth indicates the increasing concern for the manner in which we dispose of residuals on land. The initial permitting and control of disposal practices is being rapidly completed with the establishment of properly engineered sanitary landfills. However, we are beginning to ask whether the practices we have established are environmentally adequate.

National legislation is being considered to require a national ban on open dumping. It would be implemented in a cooperative fashion between the federal and state governments with the federal government providing financial and technical assistance and the states providing the legal, regulatory, and permitting activities. The focus of the Environmental Protection Agency with regard to residuals management has, until very recently, concentrated on the disposal of municipal solid waste. Designation of the Office of Solid Waste Management programs as the lead office concerning all sludge management and their investigations of hazardous waste management problems has expanded the scope of residuals disposal programs within EPA.

The role of state government in the land disposal of solid waste is as the regulatory body. The states have accepted the challenge to develop and operate a variety of comprehensive solid waste management programs which have resulted in dramatic progress. They have developed regulations governing solid waste disposal sites and are continuing to evolve better standards of construction and operation. The state programs in the Region VII states have limitations depending on the political and social pressures within the state, but, for the most part, they have evolved dynamic programs for land disposal. The challenge they now face after their initial success is to continue to improve and to spur the local and private agencies to upgrade their operations. Their cooperation and institution of adequate disposal practices is vital to protection of the environment. Their investment of resources in adequate facilities has contributed to the development of sound land disposal practices and will continue to fare into the future.

Agricultural chemicals represent a special category—at the federal level, there is an institutional mishmash. The Environ-

mental Protection Agency has the primary responsibility for the regulation of pesticides through registration and use control. The U. S. Department of Agriculture, an advocate for agriculture, assists farmers in pesticide selection and other pest control methods. The Food and Drug Administration enforces the pesticide residue tolerance limits and regulates the use of veterinary drugs. Finally, National Institute of Occupation, Safety and Health (NIOSH) establishes, and Occupational Safety and Health Administration (OSHA) enforces the health and safety standards for workers, both farm and manufacturing, from the adverse effects of pesticides.

The EPA regulatory program established under the new federal insecticide, fungicide, and rodenticide act (FIFRA) is a far reaching concept with social as well economic consequences. The Act makes the user responsible for his action in pesticide use including proper storage and disposal of pesticides and containers. Proposed regulations on this subject were published in the *Federal Register* on October 15, 1974, and final regulations are expected by the end of Fiscal Year 1976 (this month). Basically, the disposal regulations would ban open dumping, including land disposal; open burning which does not provide adequate environmental and public health protection; and well injection which does not have prior state agency approval. The regulations apply or will apply to both containers and pesticides, which are viewed as equally serious problems. Incidentally, an estimated 250,000,000 pesticide containers require disposal each year.

(Without legislation which requires some type of a collection system and provides an incentive for return of the containers, the pesticide container disposal problem will continue to mount. Pressure must be applied: (1) to the manufacturer to develop reusable containers; (2) to dealers or collection centers requiring them to accept containers for return to the manufacturer; and (3) consumers (farmers) must be provided a deposit return on containers at a level sufficient to make them return the empties.)

SUMMARY

The definition of residuals for this proceedings focuses on industrial and municipal sludges, municipal refuse, irrigation salts, mining residuals and salts, and agricultural fertilizers. The element common to all is their application to land. Yet the land varies from sand to clay in proportions which can change in a few feet. The complexity of developing a set of criteria to protect the land quality will be enormous. In addition, the constituents of every sludge can vary with every facility and may change on a daily basis. The disposition of these by-products should be carefully tailored to the receiving soil or, if not suited for this disposal method, should be diverted to a long-term, secure disposal site or adequate treatment facility.

To paraphrase Tom Hayden, "The earth is a closed system—there is no 'away' to throw things." The responsibility for developing safe and economical disposal methods for residuals rests with both the public and private sectors. The public (government) must prescribe reasonable requirements for residuals handling, transport, treatment, and disposal. The private sector must provide the means to accomplish environmentally acceptable treatment and disposal. The research and development of methods involves both sectors.

The division of responsibility for the purpose of defining land use, treatment methods, and standards is divided, as it should be, among local, federal, and state governments with participation of the populace at each level. Generally, the treatment standards for land disposal have been established at the state level of government. However, increasing concern with hazardous wastes and their environmental and health impact have led to the recommendation that a nationwide hazardous waste management program be developed. Senate Bill 2150, and House Bill 14496, incorporate a national hazardous waste management program to be administered by the Environmental Protection Agency and would provide—at last—a rational institutional framework to all levels.

Residue Disposal Onto Land— An Overview

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Environmental Quality Systems Inc.
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The purpose of this Conference is to review those aspects of the residue disposal on land that are known and that can be used immediately for disposal operations, to determine the confidence level of usefulness, and to indicate the areas for additional information prior to use.

The aspects that are of concern at this Conference are the transport, fate and effects of the nitrogen, phosphorus, heavy metals, inorganic salts, and organic compounds in residues, and the potential health effects produced by the disposal of these residues on the land.

There are many sources of waste. They can, however, be broken down into basic constituents of concern and their respective impact on the environment. Wastes can be considered in regard to their pollution potential, such as organic-BOD, organic-COD, complexed organics, inorganics-high salts, inorganics-heavy metals, phosphates, and nitrogen compounds. In addition, these can be considered in terms of surface runoff, leachate into and through the root zone, uptake and impact on plants, movement of leachate through the unsaturated zone of the soil column and finally movement in aquifers as shown in Figure 1. Looked at in this manner, residues have a commonality of constituents, transport phenomena and effects that can be interchanged.

This does not suggest that one can expect an exact exchange of data from one residue source and site to another. It is recognized that the combination of a residue and a specific site are unique, but they are unique to degree, not to kind. That is to say a site and waste will react similarly from one site to another, but not exactly the same.

Figure 2 indicates the relative annual contribution of mining, agriculture, and industrial residues, sludges from the industrial treatment of industrial wastewaters, sludges from the treatment of municipal wastewaters, municipal refuse and water plant sludges. Note that industrial and municipal sources of residue constitute only 415 million tons of the total annual production of 2885 million tons, or about 14%. For the agricultural and mining sources, the major source of waste is the sediment runoff.

The fate of the constituents in the residues, i.e. the nitrogen or the phosphate, the organics, heavy metals, inorganics, are generally similar, as shown in Figure 1. Of concern is vaporization, runoff, leaching into the ground and subsequent uptake through the roots and back up into the plants which are eventually harvested or die off. The percolate continues down through the unsaturated zone into the saturated zone, or the water table, where it moves generally horizontally down gradient hydraulically to resurface in a stream or be extracted in a well.

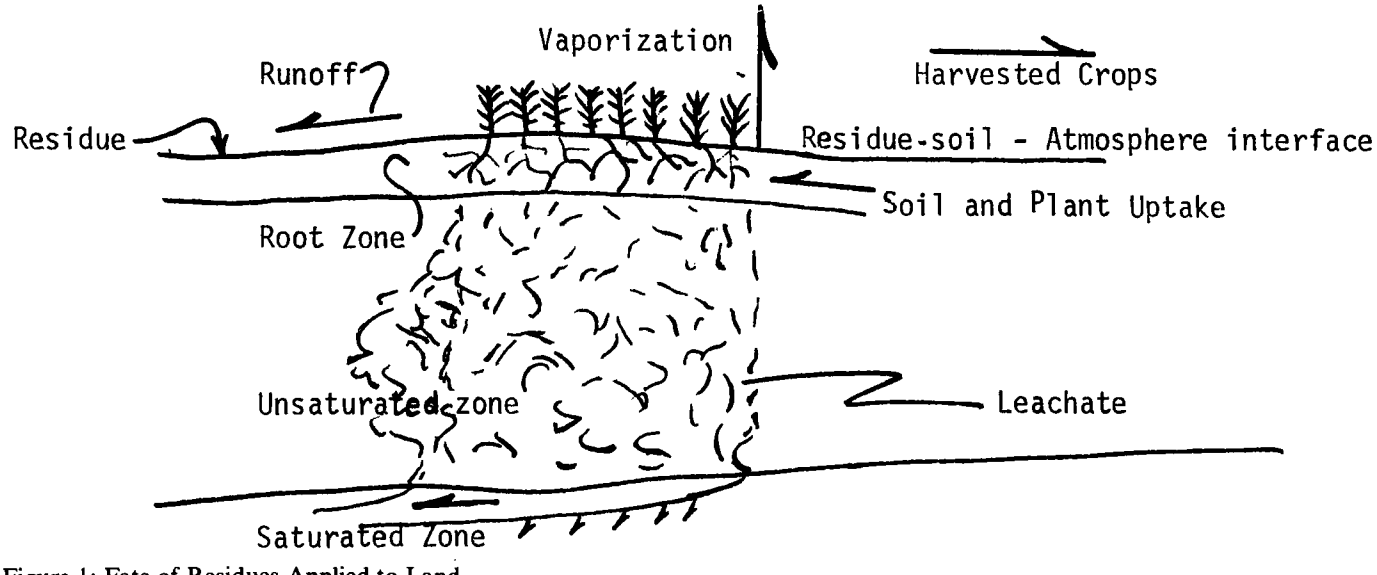

Figure 1: Fate of Residues Applied to Land

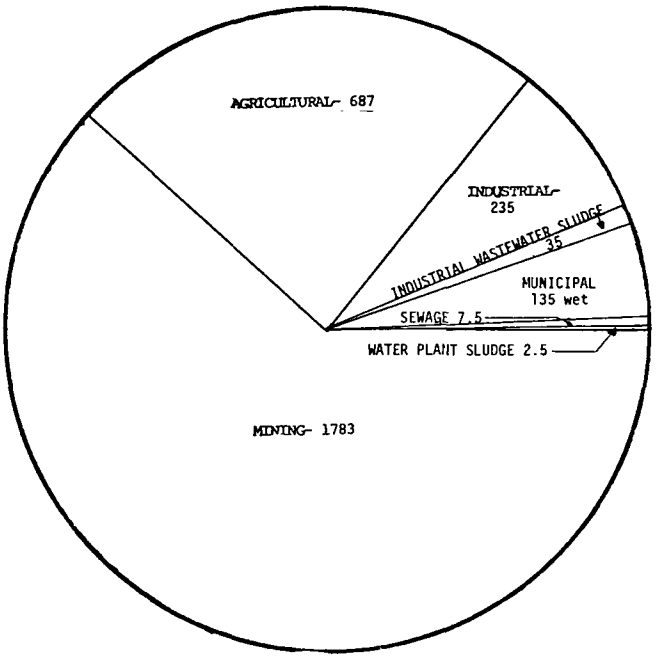

Figure 2: Estimated Industrial Versus Other Residual (August, 1970–1974) (Dry Weight in Million Tons per Year)

Nitrogen

One of the limiting factors to unlimited application of residues onto the land is nitrogen; its uptake by humans and animals can constitute a potential hazard. Consequently, the mass distribution of all forms of nitrogen applied to the land is an important facet of residue disposal that must be known or accounted for. The factors affecting the fate of nitrogen are shown in Table I.

Table I: Factors Affecting Fate of Nitrogen

AVAILABILITY OF OXYGEN
FORM OF NITROGEN
BIODEGRADABILITY OF CARBON (OGRANIC) SOURCES
WATER
TEMPERATURE
pH

The various sources of nitrogen applied to the land are precipitation, rain out, biologically fixed nitrogen, and synthetic and natural fertilizers applied to the soil. The forms of nitrogen are determined by the micro-environment surrounding the nitrogen. The transport phenomena is closely associated with the amount and rate of movement of soil water. The factors affecting nitrogen uptake and movement are the characteristics of the nitrogen in the residue, its fate in and through the soil, and the utilization of the end-product as shown in Figure 3.

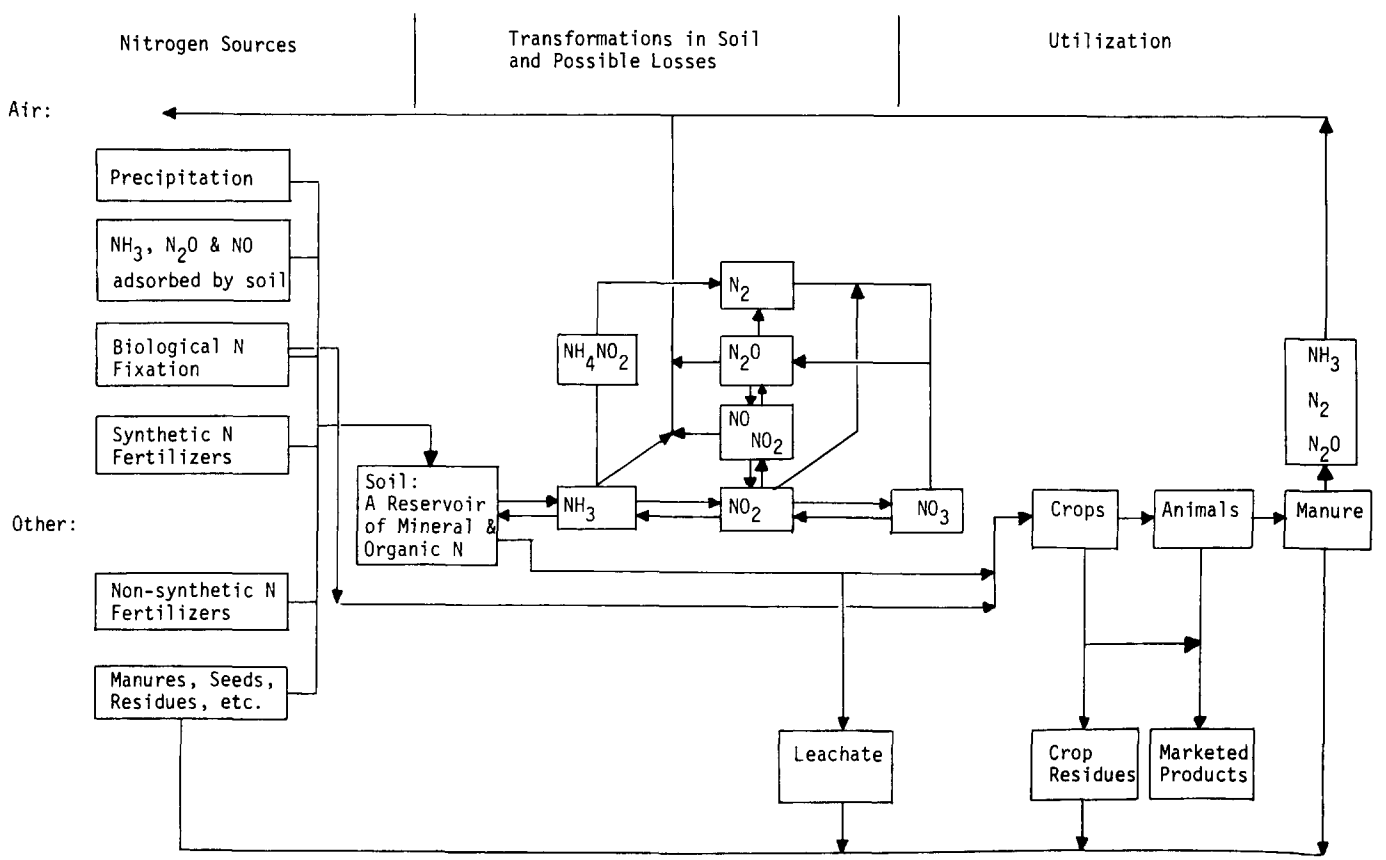

Figure 3: Soil Nitrogen Sources and Transformations and Fate of the End Products

Rain has about a 50% efficiency for scrubbing or scavenging pollutants from the air. Figure 4 shows a substantial amount of NH_4 and NO_3 nitrogen in rainout. A significant fraction of this source of nitrogen is immediately available. For example, I have a small 24-foot diameter swimming pool in my yard. I live in the suburbs of Washington, DC, a relatively industrial-free environment, and yet every time it rains, the swimming pool shows an instant algal bloom, unless it is predoused with extra chlorine to prevent the algal bloom. I also noticed that when I am caught in the first 10 minutes of any rainfall, my scalp begins to itch like crazy (my personal variation of litmus paper). This is due to the acidity of rainfall as it washes the industrial pollutants from the air. Figure 5 shows the variation of rainfall pH in the eastern part of the country, ranging from about 4.4 to about 5.5

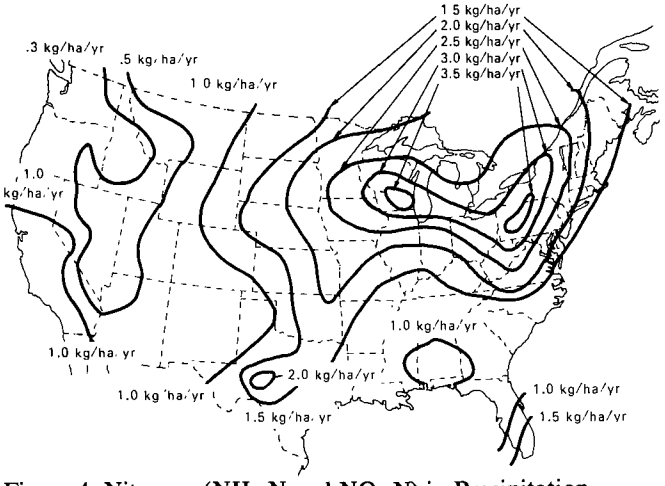

Figure 4: Nitrogen (NH_4-N and NO_3-N) in Precipitation

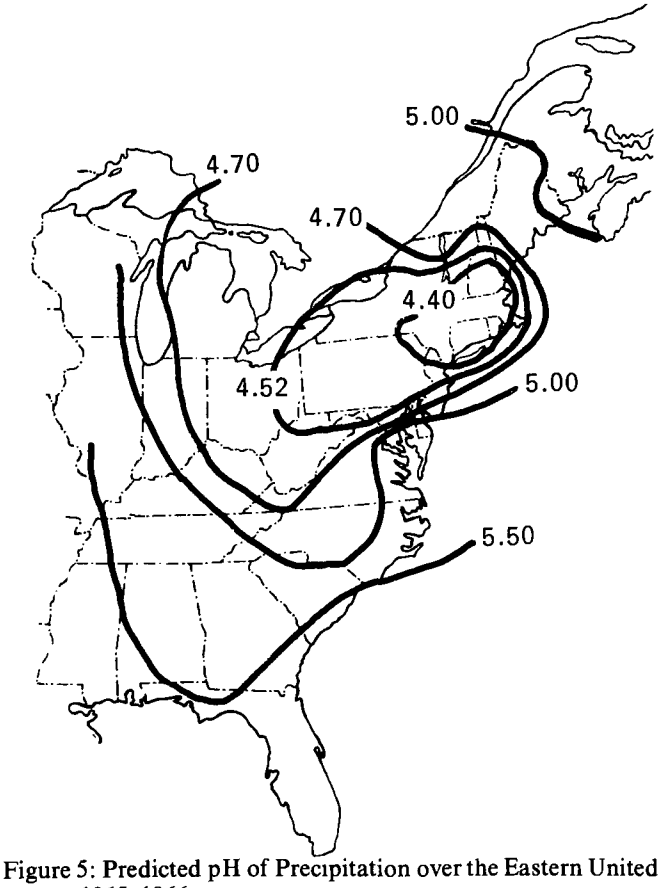

Figure 5: Predicted pH of Precipitation over the Eastern United States, 1965–1966

Rainfall is a significant source of pollution in industrial communities and should not be overlooked either as a source of nitrogen or as a vector for moving constituents through the soil column. Not all residues deleteriously affect soils. Fertilizer, nitrogen and heavy metals are applied to the land on purpose; crops need them for growth. Table II indicates the tonnage of these elements annually applied to the soil. Residues can have a beneficial effect on the soil and crops if applied and managed judiciously. Please utilize the tonnages as an indication of values, not as absolute values. They are presented to indicate an overview.

Table II: Plant Nutrients Applied to the Land from Fertilizers

NITROGEN	9 MILLION TONS/YEAR
PHOSPHATE	2.5 MILLION TONS/YEAR
POTASSIUM	3.5 MILLION TONS/YEAR
COPPER	2500 TONS/YEAR
IRON	3300 TONS/YEAR
MANGANESE	11,000 TONS/YEAR
ZINC	15,000 TONS/YEAR
MOLYBDENUM	80 TONS/YEAR

Phosphate

The factors affecting the uptake of phosphate are shown in Table III. Phosphate is a peculiar sort of a compound in that most of our soils already have appreciable quantities of phosphate associated with them; however, very little phosphate is available to the plants. Farmers annually apply an excess of phosphate onto the land to make up the deficiency, but the plant has only a relatively small percentage of the phosphate that is applied available for utilization. Apparently the needs of the soil must first be satisfied before the phosphate is available to the crops. A detailed treatment of phosphates is included in Mr. Enfield's paper, "Phosphate Transport Through Soil", which is included in these proceedings.

Heavy Metals

Table IV indicates the numerous factors affecting the fate and uptake of heavy metals applied to soils. Type and form of heavy metals are extremely important. The pH of the soil and sludge have a tremendous impact on fate of heavy metals in residues. A low pH will generally release heavy metals to the terrestrial environment. The micro and macro geology is likewise important. Whether the soil has an ion exchange capacity of one mili equivalent per 100 grams or 60 mili equivalents per 100 grams of soil makes a tremendous difference on the amount of heavy metals that can be adsorbed by the soil, the type of crops harvested, the rate and total quantity of metals applied yearly and the transport phenomena that can be expected.

Table III: Factors Affecting Fate of Phosphates

FORM OF PHOSPHOROUS
pH OF SOIL
TYPE OF SOIL
CLAY FRACTIONS
PERMEABILITY
PRIOR HISTORY OF PHOSPHATE APPLICATIONS
PLANT
CROPPING PRACTICES
PLANT TYPE

Table IV: Factors Affecting Uptake of Heavy Metals

TYPE AND FORM OF HEAVY METAL
pH OF SOIL AND SLUDGE
CLAY FRACTIONS IN SOIL
EXCHANGE CAPACITY OF SOIL
ORGANIC FRACTIONS IN SOIL
PERMEABILITY OF SOIL
CLIMATE
SOIL TEMPERATURE
SOIL MOISTURE
PLANT TYPE
PLANT AGE
TOTAL QUANTITY OF HEAVY METALS
INTERFERENCE OF OTHER HEAVY METALS
PAST HISTORY OF APPLICATION
AGE OF HEAVY METAL (FORM?)
PRESENCE OF HYDROUS OXIDES

Though the Conference will deal with heavy metals in residues, similar constituents already abound in soils. Table V indicates the various elements that are both inherently found in soil and in plants, and which are necessary for the satisfactory growth of particular crops.

Table VI shows the range of heavy metals in extracts actually taken from municipal sludges and California soils. Note the similarity of the ranges of these elements found in sludges and in soils. One could ask the question, "If this is a reality then why is there so much concern for the application of residues to the soil?" Is it the application rate or dose, or is it the chemical form of the constituent, or the end-product of the crop, or all of these?

Table V: Total Concentrations of Trace Elements Typically Found in Soils and Plants

Element	Conc. in Soils (μg/g) Common	Range	Conc. in Plants (μg/g) Normal	Toxic 1/
As	6	0.1 -40	0.1 -5	-
B	10	2 -100	30 -75	>75
Cd	0.06	0.01-7	0.2 -0.8	
Cr	100	5 -3000	0.2 -1.0	-
Co	8	1 -40	0.05-0.5	
Cu	20	2 -100	4 -15	>20
Pb	10	2 -200	0.1 -10	
Mn	850	100 -4000	15 -100	-
Mo	2	0.2 -5	1 -100	
Ni	40	10 -1000	1	>50
Se	0.5	0.1 -2.0	0.02-2.0	50-100
V	100	20 -500	0.1 -10	>10
Zn	50	10 -300	15 -200	>200

1/ Toxicities listed do not apply to certain accumulator plant species

Table VI: Range of Heavy Metals in Extracts from Sludges and California Soils (milligrams per liter)

Element	Range Sludges	Range Soils	Median Sludges	Median Soils
Molybdenum	0.10 - 0.37	0.01 - 22.0	0.18	0.01
Copper	0.14 - 6.0	0.01 0.20	1.30	0.03
Zinc	0.5 2.5	0.01 0.40	1.25	0.04
Nickel	0.6 18	0.01 0.09	1.15	0.01
Cobalt	0.04 - 0.35	0.01 0.14	0.16	0.01
Lead	0.3 - 2.0	0.01 0.30	0.35	0.01
Vanadium	0.04 - 0.25	0.01 1.20	0.05	0.01
Boron	2.7 - 17.0	0.10 - 26.0	6.80	0.1
Cadmium	0.05 - 2.0	0.01	0.12	0.01
Silver	0.01 - 0.30	0.01	0.20	0.01

a) Derived from Bradford (1973), and Bradford, Bair, and Hunsaker (1971).
b) Data for soils represent 68 soil samples obtained from 30 soil series. Data for sludges are obtained from six metropolitan Southern California sludges.
c) From Page 1974.

In addition to concern for the heavy metals and elements as they are applied to the soil, there is also concern for the magnification of these constituents in biological vectors. When there is direct uptake by biological factions, there is generally subsequent biological magnification of these constituents by each species that is higher in trophic level due to its feeding on lower trophic level species, therefore ingesting the heavy metals incorporated in the lower trophic level prey. Since the feeder generally absorbs much more quantity than its prey, it magnifies manyfold the heavy metal in its own metabolic processes, as

indicated in Table VII. If you've ever eaten a metallically-tasting oyster, it's probably due to the concentration in the oyster of the zinc extracted from the local waters. Usually the zinc doesn't do much for the oyster, but does galvanize you for action.

Organic Constituents

Organic residues is the most difficult category to consider. Besides the (literally) thousands of commercially available organic compounds and the variability of these compounds, industry annually develops some 5000 new organic compounds. Many of these, like their predecessor compounds, eventually terminate as a residue requiring disposal. The organic contents of municipal residues are indicated in Table VIII.

Table VIII: Content of Municipal Residues

CELLULOSE
LIGNINS
PROTEINS
CARBOHYDRATES
FATS
GREASES
METALS

Leachate analyses of refuse disposed onto land indicates that there is a significant fraction of organic compounds that are released to the surrounding soil. Table IX indicates the percent of the leachate emanating from a refuse pile that is organic.

Public Health Aspects of Land Disposal

An important aspect of land disposal of residues that have contained pathogens is the potential effect on public health. Sewage sludge carrying products of human metabolic waste are suspect as vectors of pathogenic organisms (Table X). Industrial and chemical sludges also contain large microbial populations which may affect the environment (Table XI).

Questions that must be answered are: are pathogens present, what are the species, what are their survival times and under what conditions? Tables X and XII indicate the survival times of various bacteria and pathogens in sludges and in various environments. Table XII also indicates the travel distance and time for various species of bacteria. With this information one can possibly utilize site selection such that travel times offsite are in excess of survival times of the various species of concern.

Groundwater

Once the contaminants have penetrated the soil and have passed the root zone, one must become concerned about any impact on the receiving groundwater, the travel time and pathway of a contaminant in the groundwater regime and the eventual resurfacing either in a stream or from extraction via a pumped or artesian well, as shown in Figure 6.

The variables that affect movement and fate of pollutants in an unsaturated or saturated soil column are (1) depth to zone of saturation, (2) frequency and amount of precipitation or water application, (3) nature of zone of aeration, (4) nature of quality of groundwater, (5) physical and chemical nature of aquifer, (6) physical and chemical nature of pollutant, and (7) uses of groundwater.

Table VII: Concentration Factors of Various Elements in the Marine Environment. The Factors were Based on the Live Weight of the Organisms.

Element	Form in Sea Water	Concentration in Sea Water µg/liter)	Algae (noncalcareous)	Invertebrates		Vertebrates	
				Soft	Skeletal	Soft	Skeletal
Na	Ionic	10^7	1	0.5	0	0.07	1
K	Ionic	3.8×10^5	25	10	0	5	20
Cs	Ionic	0.5	1	10		10	
Ca	Ionic	4×10^5	10	10	1,000	1	200
Sr	Ionic	7×10^3	20	10	1,000	1	50
Zn	Ionic	10	100	5,000	1,000	1,000	30,000
Cu	Ionic	3	100	5,000	5,000	1,000	1,000
Fe	Particulate	10	20,000	10,000	100,000	1,000	5,000
Ni	Ionic	2	500	200	200	100	0
Mo	Ionic-particulate	10	10	100		20	
V	not given	2	1,000	100		20	
Ti	not given	1	1,000	1,000		40	
Cr	not given	0.05	300				
P	Ionic	70	10,000	10,000	10,000	40,000	2,000,000
S	Ionic	9×10^5	10	5	1	2	
I	Ionic	50	10,000	100	50	10	

Table IX: % Leachate from Refuse and Ash

Material leached	Percentage leached under given conditions* 1	2
Permanganate value.....30 min.....	0.039	.....
Do..... 4 hr	.060	0.037
Chloride.....	.105	.127
Ammonia nitrogen.....	.055	.037
Biochemical oxygen demand.....	.515	.249
Organic carbon.....	.285	.163
Sulfate.....	.130	.084
Sulfide.....	.011	.....
Albumin nitrogen.....	.005	.....
Alkalinity (as $CaCO_3$).....		
Calcium.....		
Magnesium.....		
Sodium.....		
Potassium.....		
Total iron.....		
Inorganic phosphate.....		
Nitrate.....		
Organic nitrogen.....	.0075	.0072

*Conditions of leaching:
1. Analyses of leachate from domestic refuse deposited in standing water.
2. Analyses of leachate from domestic refuse deposited in unsaturated environment and leached only by natural precipitation.

Table X: Survival Times of Organisms

Organism	Medium	Type of application	Survival time
Ascaris ova [b]	Soil	Sewage	up to 7 years
	Vegetables	AC [c]	27 - 35 days
B. Typhosa	Soil	AC	29 - 70 days
	Vegetables	AC	31 days
Cholera vibrios	Spinach, lettuce	AC	22 - 29 days
	Non-acid vegetables	AC	2 days
Coliform	Grass	Sewage	14 days
	Tomatoes	Sewage	35 days
Endamoeba histolytica [b]	Vegetables	AC	3 days
	Soil	AC	8 days
Hookworm larvae [b]	Soil	Infected feces	6 weeks
Leptospira	Soil	AC	15 - 43 days
Polio virus	Polluted water		20 days
Salmonella typhi	Radishes	Infected feces	53 days
	Soil	Infected feces	74 days
Shigella	Tomatoes	AC	2 - 7 days
Tubercle bacilli	Soil	AC	6 months
Typhoid bacilli	Soil	AC	7 - 40 days

a) After Pound and Crites 1973
b) Unlikely to move in the unsaturated zone
c) Artificial Contamination

Table XI: Densities of Various Bacteria in Different Chemical Sewage Sludges[2]

Sampling Date	Heterotrophic Bacteria (20°C)	Coliform MF	Fecal Coliform MF	Fecal Streptococcus MF
		Alum Sludge (Point Edward)		
6- 5-73	8.8×10^9	1.1×10^6	7×10^4	4×10^4
7-27-73	7.5×10^9	8.7×10^5	1×10^5	2×10^4
9- 5-73	2.7×10^{10}	1.5×10^6	5×10^5	5×10^4
Mean:	1.4×10^{10}	1.2×10^6	2.2×10^5	3.7×10^4
		Iron Sludge (North Toronto)		
6- 5-73	2.7×10^{10}	2×10^4	1×10^4	2×10^4
7-27-73	2.2×10^{10}	9×10^4	3×10^4	1×10^4
9- 5-73	4.1×10^{10}	6×10^5	8×10^4	3×10^3
Mean:	3×10^{10}	2.4×10^5	4×10^4	1.1×10^4
		Lime Sludge (Newmarket)		
6- 5-73	1.2×10^{10}	2.5×10^6	4.5×10^5	3.4×10^5
7-27-73	3.2×10^{10}	7.5×10^5	1×10^4	5×10^4
9- 5-73	1.1×10^{10}	3×10^5		3×10^3
Mean:	1.8×10^{10}	1.2×10^6	2.3×10^5	1.3×10^5

a) Expressed as number of bacteria per 100 ml of sludge.

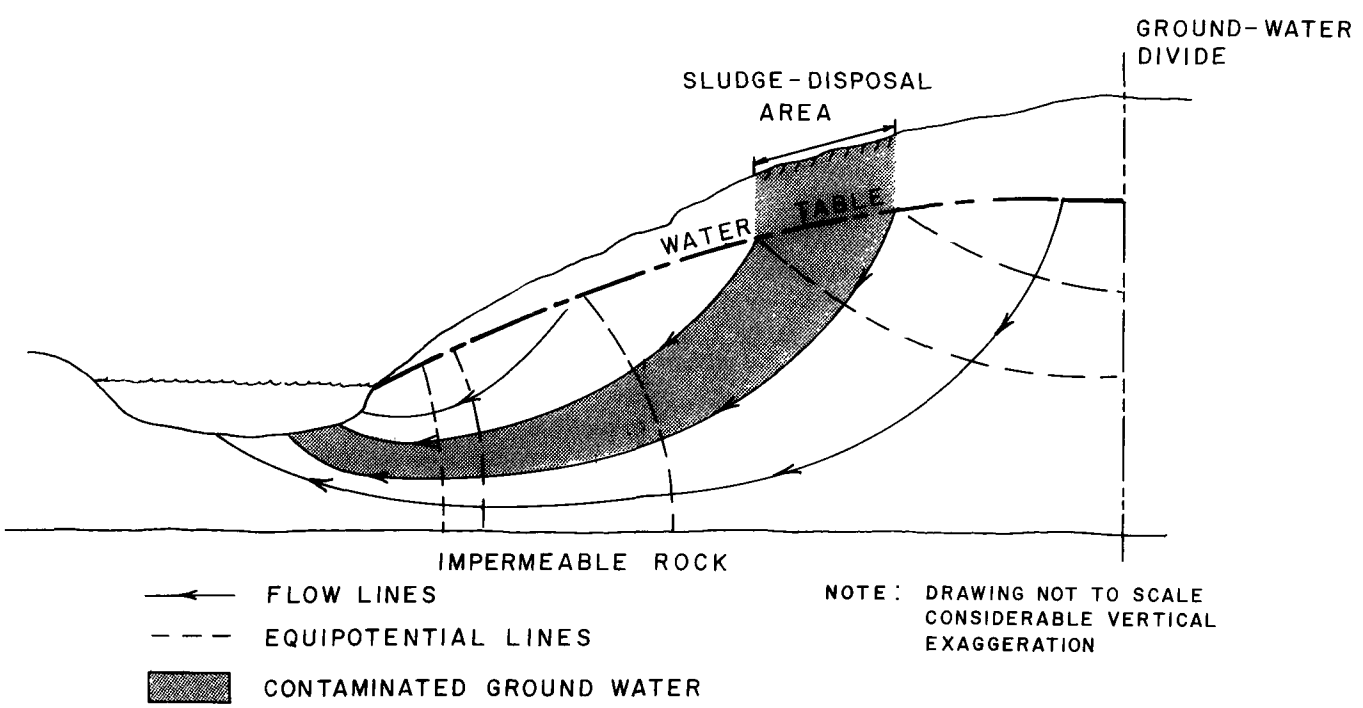

Figure 6: Flow in a Water-Table Aquifer (Humid Region)

Table XII: Summary of Reported Distances of Travel of Pollution in Soil and Ground Water[2]

Nature of Pollution	Pollutant	Observed distance of travel [b]	Time of travel
Sewage polluted trenches intersecting ground water	Coliform bacteria	65 feet	27 weeks
Polluted trenches intersecting ground water	Coliform bacteria	232 feet	
Sewage in bored latrines intersecting ground water	Coliform bacteria Anaerobic bacteria	10 feet 50 feet	
Sewage in bored latrines lined with fine soil	Coliform bacteria	10 feet	
Sewage in bored latrines intersecting ground water	Coliform bacteria	35 feet	
Sewage in bored latrines intersecting ground water	Coliform bacteria	80 feet regressed to 20 feet	
Coliform organisms introduced into soil	Coliform bacteria	50 meters	37 days
Sewage effluents on percolation beds	Coliform bacteria	400 feet	
Sewage effluents on percolation beds	Bacteria	150 feet	
Sewage polluted ground water	Bacteria	a few meters	
Introduced bacteria	Bacillus prodigiosus	69 feet	9 days
Chlorinated sewage	Fungi	300 feet	

a) After U. S. Environmental Protection Agency (1973).
b) For bacteria, the distance observed was the extent of travel.

The total depth from the root zone to the water table, the physical and chemical nature of the soil column and the amount of carrier water that is applied to the land determine the spatial distribution of the constituent species and their respective time of travel to the aquifer. Similarly, the physical-chemical nature of an aquifer and its hydraulic parameters will determine the fate and travel times of the various constituents to the points of resurface (Figure 6). Obviously, any artificial extractions will have to be superimposed onto the natural phenomenon.

A classical example of a discharge and its spatial distribution is a disposal operation concerning the discharge of low-level radioactive wastes shown in Figure 7. Following some initial testing and field monitoring, the transport and distribution of the hydraulic plume sphere of the discharged liquid and contaminants were predicted. Another example of the "detention" capability of the soil is the operation at the National Reactor Testing Station near Idaho Falls, Idaho. In that operation, radioactive wastes have been injected into the ground since 1953. Other than tritium, radioactive metal isotopes have been detected only a distance of less than one mile from the injection well.

In other words, though heavy metals may eventually leach into an aquifer, they may never become available. On the other hand, organic, chelated, anionic, etc., wastes, may be insignificantly detained and therefore can be predicted to be available by similitude to that determined for the water in the aquifer.

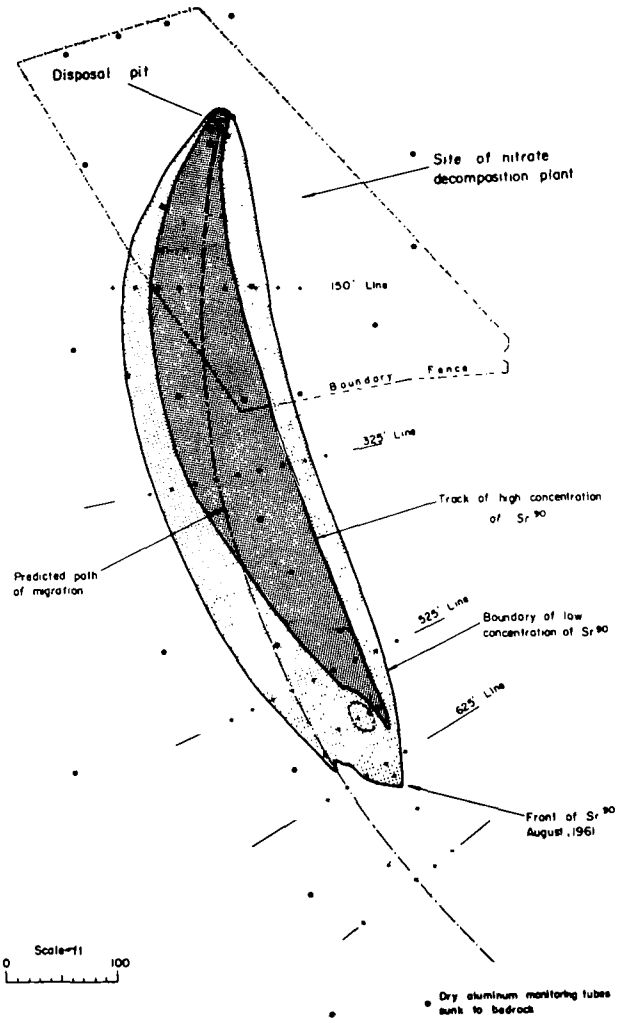

Figure 7: Migration of Radionuclides from Ground Disposal Operations at Chalk River, Canada (Initiated in 1951)

NOTE:

The papers following this overview paper will provide the answers to the following questions: what do we know, what is the confidence level, what information can we use now, how should we use the information in the real world, and what needs more research.

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2. *Report to the National Commission on Water Quality on the Environmental Impact of the Disposal of Wastewater Residuals*, Environmental Quality Systems, Inc., March 1976.

Current EPA Guidance on Land Application of Municipal Sewage Sludges

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INTRODUCTION

No matter what technologies are applied, there is nearly always something left over as a result of wastewater treatment. While treating sewage to acceptable discharge quality levels, various residual byproducts are inevitably produced, be it sewage sludges from conventional physical/chemical and biological treatment plants, algae in pond systems, or crops from land treatment systems.

The management of the conventional wastewater treatment residuals (sewage sludges) is a twofold problem. The sludge must be disposed of to complete the wastewater treatment efforts and it must be done in an environmentally acceptable manner.

The requirements of the Federal Water Pollution Control Act Amendments of 1972 (P.L. 92-500) emphasize the need to employ cost-effective and environmentally sound waste management technology. At the same time its requirements for improved wastewater treatment will result in a nationwide increase in the production of greater quantities of sewage sludges. The current estimated 5 million dry tons of sewage sludge produced each year will more than double as a result of upgrading the nation's publicly owned treatment works to meet secondary treatment standards.

The "Sludge Bulletin"

Since as much as 40% of the construction costs for individual treatment plants may be required to build adequate sludge management facilities and EPA may provide as much as 75% of the capital funding required for these facilities under the Construction Grants Program, the Office of Water Program Operations (OWPO) which manages the EPA Construction Grants Program has prepared the proposed technical bulletin, "Municipal Sludge Management: Environmental Factors." This bulletin was published for public comment in the June 3, 1976 Federal Register to assist the EPA Regional Administrators and their staffs in evaluating grant applications for construction of publicly owned sewage treatment works under Section 203(a) of P.L. 92-500. The document also will provide designers and municipal engineers with information for selecting optimal sludge management options, but should not be construed to be a regulatory document.

The sludge technical bulletin, as it is commonly referred to, was developed over a three year period (that involved at least three versions of the document) by an Agency workgroup with substantial assistance provided by individuals from CEQ, USDA, FDA and the Department of the Army. The bulletin addresses only factors important to the environmental acceptability of a particular sludge management option and does so in a general manner to allow a maximum flexibility in its interpretation to meet varying Regional needs and site-by-site evaluation considerations. Detailed information on costs and cost-effectiveness analysis procedures, environmental assessment and environmental impact statement procedures, pretreatment guidelines and regulations, sample collection/preservation/analysis procedures, as well as in depth reviews of the somewhat controversial potential impacts of land application are or will be covered in additional supporting documents.

The sludge technical bulletin is based on current knowledge and will be modified from time to time as any new regulations are developed and additional information becomes available from current and future research, development and demonstration projects. The document emphasizes land application alternatives since no Agency guidance has been issued on this option in the past, and Agency guidance (and in some cases regulations) is already available on the other major options—incineration, landfill, and ocean disposal.

The proposed bulletin is divided into two distinct parts, one including methods in which the sludge is utilized as a resource and the second including those methods not utilizing the sludge for any beneficial purpose. Appendixes are also available that cover the preparation of environmental impact statements, groundwater requirements of BPT, guidelines for the land disposal of solid wastes, incinerator emission and performance standards, and criteria established for ocean dumping of municipal sewage sludges. Requirements for implementation plans to reduce toxic materials and interim continuation permits are discussed in light of established ocean dumping criteria. Discussion of incineration alternatives includes information on pretreatment programs, new source performance standards, destruction of organic compounds, adequate ash disposal, and monitoring plans. Discussion of sanitary landfill criteria covers information on stabilization, EPA guidance for Federal facilities, groundwater protection and monitoring plans. Land application information includes discussions and suggestions for acceptable stabilization techniques, application methods, application rates, crops and monitoring plans, as well as precautions for protection of public health, groundwater and surface waters.

During the development of the technical bulletin, considerable disagreement surfaced on the topic of utilizing sewage sludges by application to agricultural lands. Although utilization of sewage sludges as a resource to recover nutrients and other benefits has been encouraged by P.L. 92-500 and various advisory groups, the workgroup members and others involved in developing the technical bulletin identified conflicting opinions concerning the overall merits *vs.* potential hazards of applying sludges to cropland. Possible adverse effects upon the human food chain (e.g., the potential for increasing human cad-

mium intake) has remained a major concern expressed whenever this practice is considered. The relative risks of applying sewage sludges to croplands, when compared to other routes through which these contaminants enter the human diet, have yet to be determined. In addition, detailed trade-off analyses comparing environmental impacts of land application *vs.* incineration *vs.* landfill *vs.* ocean disposal have rarely been undertaken in a manner that provided meaningful results.

The proposed bulletin placed primary reliance on FDA and USDA to establish recommendations for acceptable levels of heavy metals in food crops and best agricultural practices for sludge application to agricultural lands. Until the necessary food quality standards are established, strict regulation of food crop production on sludge amended soils and required design criteria necessarily will have to be based upon rather arbitrary values. There are currently no basic standards for control of most contaminants in sludges when traced through water, soil, and plants, possibly to livestock, or ultimately to foods grown on sludge amended soils. The proposed technical bulletin will apply some control to the design and proper management of this practice—at least to the extent that eligibility for capital funds from the Construction Grants Program is concerned. However, the new toxics substances and hazardous waste legislation may encourage new regulatory efforts in the sludge management area.

Land application of sludge remains a controversial area, but most of the discussion centers around application to agricultural lands, especially for food crop production. However, the use of sludges on non-agricultural lands (strip mine reclamation, parks, construction sites, etc.) or non-food chain crop production (thus allowing for sod production, etc.) can be used without much controversy to recover the nutrient and soil building value of municipal sewage sludge.

Our experience shows that public acceptance and health effects concerns are two of the major impediments to the use of sludge in agriculture. Many of the concerns relate to possible or potential problems that might occur under adverse situations, rather than known dangers or hazards that can be dealt with directly. Improved dissemination of information to the public and governmental officials may help improve the picture, but certainly will not remove all opposition or concern to the practice.

One area of current comment is the need for increased pretreatment activities to improve the quality of many sludges that could be applied to the land. Several studies have indicated that industrial dischargers to publicly owned treatment works are a significant source of sewage sludge contamination of heavy metals and other toxic chemicals. However, both residential wastes and stormwater runoff are known to contribute toxics to municipal sewage and sewage sludges. It is also important to recognize that pretreatment of toxic substances is not equal to destruction of these materials. Toxic substances removed by industry must be disposed of in sludges resulting from pretreatment by those industries. In this regard, it is necessary to weigh the potential impacts of discharge of toxics into the environment (i.e., in sludge or effluents whether from municipalities or industries).

In accordance with the rquirements of P.L. 92-500 and several recent court rulings, EPA has embarked on an accelerated program to develop (1) pretreatment standards for the most significant polluting industries, and (2) standards pertaining to the discharge of designated toxic pollutants. A concentrated effort has been initiated to implement an effective Federal Pretreatment program to achieve compliance with the provisions of P.L. 92-500. Additionally, the Agency has revised and is preparing to issue pretreatment guidelines to assist municipalities in developing local pretreatment requirements.

Work Needed

Major technical needs to support the Construction Grants Program involvement in municipal sewage sludge management activities actually boil down to developing the best design criteria and cost information for the available technology and the development of innovative technologies for future implementation. With the current phase-out attitude toward ocean dumping, we are dealing with providing guidance to the Regions on the best available land-based technologies for sludge management rather than developing regulatory programs.

From our viewpoint, the work most urgently needed in the municipal sewage sludge management field includes:

- Resolution of health effects issues
- Continued emphasis on innovative technology leading to beneficial use and resource recovery
- Breakthrough in public acceptance
- Information dissemination to both design engineers/operators and elected and government officials.

Runoff and Movement of Soil Particles

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INTRODUCTION

The process of soil particle movement by raindrop impact and runoff is soil erosion. An end-product of erosion is sediment. Unabated erosion of agricultural lands destroys an essential and irreplaceable natural resource. The U.S. Department of Agriculture has been active in research of soil-erosion processes and control for more than 40 years.

Sediment is the solid material, both mineral and organic, that has been moved from its original location by the erosive agents. Sediment impairs the quality of water resources in which it is entrained and often degrades the location where it is deposited. It may also carry pesticides, toxic metals, and plant nutrients absorbed on the soil particles.[4]

Amount and Sources of Sediment

Sediment concentrations in rivers of the United States range from 200 to 50,000 ppm, with occasional much higher concentrations.[3] The amount of sediment moved by flowing water has been estimated to average at least 4 billion tons per year, with about 1 billion tons reaching major streams. A ton of sediment is roughly one cubic yard in volume.

Estimates ascribe about 30% of this country's total sediment to geological erosion—the erosion that occurs under natural conditions of climate and vegetation, undisturbed by man and machines.

About 20% of the total sediment comes from non-agricultural sources like construction and mining activities, streambank and channel erosion, and mass wasting from landslides. Per-acre sediment production from these conditions may be more than 100 times as great as from cropland.

However, because of the large area involved, our 438 million acres of cropland as a whole produce about 50% of our country's total sediment. About half of our cropland is estimated to average between 3 and 8 tons of soil loss per acre per year. About 30% of it averages less than this, and about 20% averages more.

These soil-loss figures are amounts of soil moved from its general position on the field slopes by runoff. The major portion of this eroded soil may be deposited in places like fence rows, the toe of field slopes, depressional areas, and elsewhere along the path of the runoff before it reaches a major stream. On the average, less than one-fourth of the eroded soil reaches a river.

The Erosion Process

Soil erosion is a mechanical process that requires energy. Much of this energy is supplied by falling raindrops. The impact energy of the billions of raindrops falling in 30 minutes of a Midwest thunderstorm may exceed 1,000 foot-tons per acre. When raindrops strike bare soil at a high velocity, they shatter soil granules and clods and detach particles from the soil mass. Splash action moves the detached particles only short distances, but shallow overland flow transports some of them directly downslope and others to small depressions where the flow is more concentrated and provides better transportation for them.

This type of soil movement is referred to as *sheet erosion.* Very shallow sheet flow transports soil material that has been detached by raindrop impact. When the runoff is impeded by an obstruction, such as an across-slope strip of plant residues, its flow velocity is reduced and deposition is likely to occur. Since sheet erosion occurs rather uniformly over the field, it can remove considerable soil without becoming readily evident, but it cannot be ignored as a source of sediment.

Rill erosion is a process in which numerous small channels only several inches deep are formed. In rill erosion soil particles are detached by the shearing action of the flowing water and by slumping of undercut sidewalls. The detached particles are transported by a combination of suspension, saltation and rolling. Suspended particles, which are mostly clay and fine silt, may travel long distances before being deposited on the earth's surface. The erosive potential of flowing water depends on its velocity, depth, turbulence and type and amount of material being transported. Rill erosion increases rapidly as longer or steeper slopes increase runoff flow depth and velocity. Under continued rainfall, sheet erosion continues between the rills and feeds additional sediment to the rill flow.

A surface cover of plant residues or close-growing vegetation like grass reduces erosion by protecting the soil from raindrop impact and by reducing the flow velocity of the runoff and thereby decreasing its capacity to detach and transport soil material. However, small pieces of residue that are not anchored may be carried away by the runoff as sediment.

Field and construction-site soil losses are usually from a combination of sheet and rill erosion. Since sediment from these two types of erosion comes from near the surface, it is more likely to contain nutrient and pesticide contaminants than sediment deriving from gully, streambank or channel erosion, although the amount of sediment from the latter sources may be much greater.

The average-annual sheet and rill erosion from a particular site, under given conditions, can be predicted by the universal soil loss equation. This equation is a very helpful tool for evaluating the severity of sheet and rill erosion hazards and determining the control practices needed to hold average-annual erosion losses within some prescribed limit. It was designed for cropland and construction areas, but can also be adapted for other conditions.

The Universal Soil Loss Equation (USLE)

The universal soil loss equation computes average annual soil loss from sheet and rill erosion on a particular tract of land as a function of rainstorm characteristics, soil properties, topographic features, land use, and management practices. The equation is

$$A = R\ K\ L\ S\ C\ P, \text{ where}$$

A is soil loss in tons per acre,
R is a measure of the erosive forces of the rainfall and associated runoff,
K is a measure of the inherent susceptibility of the particular soil to erosion,
L and S define the effects of length and steepness of slope on soil loss per unit area,
C is the cover and management factor, and
P is the factor for supplemental erosion-control practices like contouring and stripcropping.

The product of the first four factors (R,K,L and S) is the inherent erosion potential at the site; that is, the soil loss that would occur in the absence of any surface cover or management practices. The last two factors reduce this potential loss to compensate for effects of land use, management, and special practices.

Values of the six factors at a particular site can be obtained from maps, graphs and tables published in Agriculture Handbook No. 282[14] and several more recent supplemental reports available from the Agriculture Research Service at Purdue University.[2,8,9,20,12] Updating of AH-282 to include the more recent material is under way and scheduled for completion in 1977.

The individual USLE factors are briefly discussed below to give a concept of their significance, range of values, and sources of specific-site values. Details on the derivation and limitations of the equation and published factor-value sources have been published.[5,7,11]

Factor R.

The capability of a rainstorm to erode soil depends on both the total energy of the raindrops and the associated runoff. The impact energy of a unit of rainfall increases with increasing drop size, and dropsize generally increases with rainfall intensity up to about 3 inches per hour. The total energy of a rainstorm can be computed from recording-raingage data. The most accurate available index of rainfall erosive potential is the EI parameter. For a given storm, this parameter equals the product of the storm's raindrop energy and its maximum 30-minute intensity. Storm EI values can be summed to obtain seasonal or annual values of the erosivity of a rainfall pattern.

Figure 1 shows average annual EI values computed from 22-year location rainfall records. The appropriate R value for the USLE can generally be taken directly from this map, but in the Northwest a factor for runoff from thaw and snowmelt must be added to the EI. The EI lines on this map are the same as those on the more detailed map given in Agriculture Handbook No. 282 except in the Coastal Plains of the Southeast and in the eleven western states.

Factor K.

Some soils erode much more rapidly than others under identical conditions. Those high in silt or very fine sand erode most readily. Erodibility decreases as the content of either clay or sand particles (other than very fine) becomes greater. Soil organic matter improves structure, infiltration, and aggregation and decreases erodibility, but fairly large soil aggregates may be transported by high-velocity runoff. Profile permeability is important because it influences runoff.

Factor K for a given soil is the expected soil loss per acre per unit of EI on a unit plot (a 9% slope 72.6 feet long, continuously in clean-tilled fallow with tillage operations up-and-down slope). Known values of this soil factor range from 0.03 to 0.69.

Table I indicates the general relation of K to soil texture, but texture-class alone does not determine a soil's erodibility. More accurate K values can be obtained from the Soil Conservation Service or by use of a published soil-erodibility nomograph.[12] The nomograph graphically computes K for a given soil as a function of the particle-size distribution, organic-matter content, structure, and profile permeability.

Table I: Indications of the General Magnitude of the Soil-Erodibility Factor, K_1

Texture class	Organic matter content		
	<0.5%	2%	4%
	K	K	K
Sand	0.05	0.03	0.02
Fine sand	.16	.14	.10
Very fine sand	.42	.36	.28
Loamy sand	.12	.10	.08
Loamy fine sand	.24	.20	.16
Loamy very fine sand	.44	.38	.30
Sandy loam	.27	.24	.19
Fine sandy loam	.35	.30	.24
Very fine sandy loam	.47	.41	.33
Loam	.38	.34	.29
Silt loam	.48	.42	.33
Silt	.60	.52	.42
Sandy clay loam	.27	.25	.21
Clay loam	.28	.25	.21
Silty clay loam	.37	.32	.26
Sandy clay	.14	.13	.12
Silty clay	.25	.23	.19

[1]The values shown are estimated averages of broad ranges of specific-soil values. When a texture is near the borderline of two texture classes use the average of the two K values. For specific soils, use of the nomograph or Soil Conservation Service K-value tables will provide much greater accuracy.

Factor L.

As runoff accumulates from a long slope, its detachment and transport capabilities increase. On gradients of 5% or more, factor $L = (\lambda / 72.6)^{0.5}$, where λ = slope length in feet. On gradients of 3% or less, the exponent is 0.3, and for 4% slopes it is 0.4.

Factor S.

For slopes not exceeding 20 percent, slope-steepness effect is expressed by

$$S = \frac{430 \sin^2 \theta + 30 \sin \theta + 0.43}{6.574}$$

where θ is the angle of slope.

Factors L and S are usually combined in a single topographic factor, LS. Values of LS for various combinations of slope length and uniform steepness are given in Table II.

When a slope is appreciably concave, convex, or irregular, it is evaluated in segments that for practical purposes can be assumed uniform. If the segments are taken at equal length, the gradient of each segment is used with the overall slope length to enter the slope-effect chart or Table II, and the segmental values are weighted by the factors given in Table III to obtain an LS value for the entire slope length.[10]

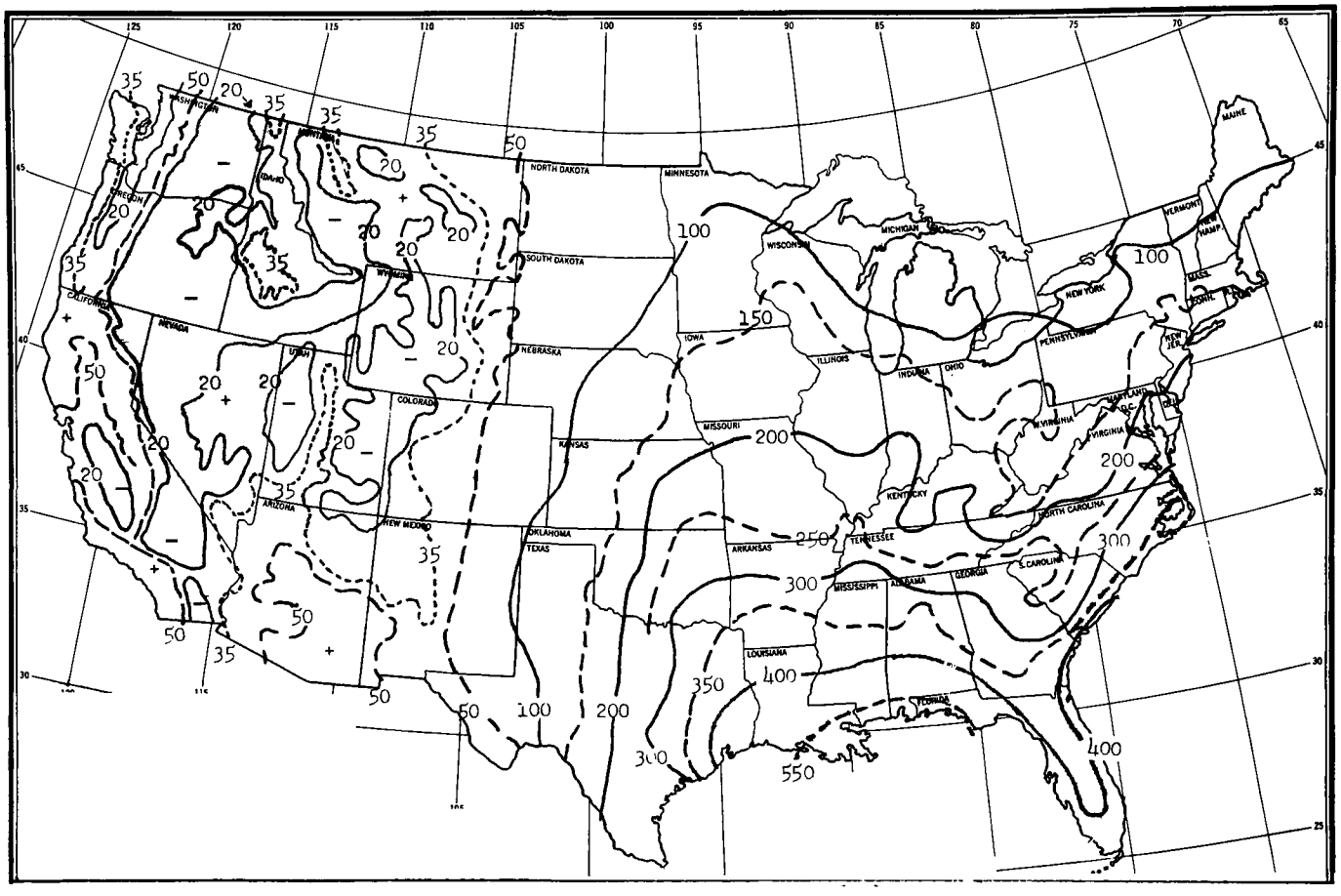

Figure 1: Average-Annual EI Values

Table II: Values of the Topographic Factor, LS, for Specific Combinations of Slope Length and Steepness

% Slope	Slope Length (Feet)											
	25	50	75	100	150	200	300	400	500	600	800	1000
0.5	.065	.080	.091	.099	.112	.122	.138	.150	.160	.169	.185	.197
1	.085	.105	.119	.129	.146	.159	.180	.196	.210	.222	.242	.258
2	.133	.163	.185	.201	.227	.248	.280	.305	.326	.344	.376	.402
3	.190	.233	.264	.287	.325	.354	.400	.437	.466	.492	.536	.573
4	.230	.303	.357	.400	.471	.528	.621	.697	.762	.820	.920	1.01
5	.268	.379	.464	.536	.656	.758	.928	1.07	1.20	1.31	1.52	1.69
6	.336	.476	.583	.673	.824	.952	1.17	1.35	1.50	1.65	1.90	2.13
8	.496	.701	.859	.992	1.21	1.40	1.72	1.98	2.22	2.43	2.81	3.14
10	.685	.968	1.19	1.37	1.68	1.94	2.37	2.74	3.06	3.36	3.87	4.33
12	.903	1.28	1.56	1.80	2.21	2.55	3.13	3.61	4.04	4.42	5.11	5.71
14	1.15	1.62	1.99	2.30	2.81	3.25	3.98	4.59	5.13	5.62	6.49	7.26
16	1.42	2.01	2.46	2.84	3.48	4.01	4.92	5.68	6.35	6.95	8.03	8.98
18	1.72	2.43	2.97	3.43	4.21	4.86	5.95	6.87	7.68	8.41	9.71	10.9
20	2.04	2.88	3.53	4.08	5.00	5.77	7.07	8.16	9.12	10.0	11.5	12.9

Factor C.

The greatest deterrent to erosion is soil cover, but a host of other crop-system and management variables also greatly influence the ability of the soil surface to resist erosion. All of these are combined in the cover-and-management factor, C. Agriculture Handbook 282 presents a procedure for computing C for a given cropping and management system in relation to the local rainfall pattern. Regional tables of C values derived by this procedure are available from state offices of the Soil Conservation Service. C values are also available for construction-site conditions[13] and for range, idle, and woodland conditions.[8]

The sample segment of a C-value table given in Table III illustrates the wide range of this factor and how much it can be influenced by management decisions. This is extremely important to planners because if any of the equation's factors is reduced without changing the other factors, soil loss is reduced by the same percentage. The table shows, for instance, that factor C for continuous corn can range from 0.54 to as low as 0.03 as a result of management differences. A good grass-and-legume meadow may at times allow substantial runoff, but sediment in the runoff will be extremely low as indicated by the C-value of 0.004.

Table III: Factors to Adjust the LS-Chart Values for Successive Segments of a Slope When Gradient is $\leq 5\%$

Segment No. (from top)	No. of equal-length segments: 5	4	3	2
1.	0.45	0.50	0.58	0.71
2.	.82	.91	1.06	1.29
3.	1.06	1.18	1.37	-
4.	1.25	1.40	-	-
5.	1.42	-	-	-

Factor P.

This factor accounts for effects of supplemental practices like contouring or stripcropping. Its value depends on the land slope and can be obtained from handbook tables.[5,14] For estimating off-site sediment contributions, terrace systems are given a P-value of 0.2 to compensate for deposition in the terrace channels and outlet.

Application of USLE.

Soil-loss computation with the USLE is a process of factor selection and direct multiplication. To illustrate, assume a location for which the EI map shows that R=175, the erodibility nomograph shows that K=0.32, and the slope-effect table gives an LS value of 1.2. If the field is cropped continuously to corn, with the residues plowed-under in spring and use of conventional planting methods, C=0.38. If the slope is less than 8% and tillage and rows are on the contour, P=0.5.

The predicted average-annual soil loss is then the product of these five values, or 13 tons per acre. Without contouring, it would have been 26 tons. If the corn had been no-till planted in a 70% cover of shredded cornstalks, C would have been about 0.11 and the predicted soil loss with contouring would be less than 4 tons per acre.

If a tolerance limit of T tons per acre has been prescribed and the equation is written in the form C=T/RKLSP, the solution will be the maximum value of C that can be tolerated on the field. In the foregoing example, if T=5 T/A, the maximum acceptable C would be 5/175 (0.32)(1.2)(.5) = 5/33.6 = 0.15.

Limitations of the USLE

The capabilities and limitations of the USLE were recently reported in considerable detail.[11] Several qualities of the USLE factors are highly important if the equation is used for prescribing or monitoring sediment-control standards:

1. The USLE predicts *long-time average* soil losses for specified physical and management conditions. In any specific season or year, soil loss may be much more or less than this average—because of fluctuations in rainfall, planting dates, or any of a host of uncontrolled random variables which the equation takes at their average values.

2. The USLE solutions are estimates, subject to usual experimental and extrapolation error.

3. The USLE was developed for field-size areas. If it is used to estimate sediment yield from a larger watershed, the drainage area should be subdivided into relatively homogeneous subareas for which representative values of the USLE can be defined. This not only facilitates use of the equation; it also shows which segments of the watershed require the most attention. Sediment from gully, streambank, and channel erosion must be estimated separately and added to the USLE estimate to compute the gross erosion.

4. The amount of sediment discharged to large rivers is usually less than one-fourth of that eroded from the land surface. The fraction of soil loss from specific farm fields that is discharged to a river varies widely with distance and with soil and watershed parameters. The erosion equation does not credit deposition by overland flow, and a dependable equation has not become available. The gross-erosion estimate must be multiplied by an appropriate sediment-delivery ratio to compensate for deposition. The best available guides for estimating watershed sediment-delivery ratios are given in Section 3 of the Soil Conservation Service National Engineering Handbook. However, inability to predict delivery ratios for specific subareas with desirable precision is presently perhaps the greatest weakness in sediment estimation.

Planning on Large-Area Basis

For section 208 area planning, nonpoint pollution hazards must to some extent be assessed on a large drainage-area basis, and some helpful guides are pointed out below. Planners must bear in mind, however, that the factors that cause erosion are highly localized and erosion hazards are site specific. Most of the sediment from a watershed may come from only a small portion of the drainage area. For effective sediment control, the subareas that are the major sediment contributors must be identified, and control-practice requirements must be so stated that they apply to specific soil and topographic features within the watershed rather than to the entire area.

Sources of information for broad-area appraisal of problems and control planning include several methods of land classification and a recently published manual.

The best source of information on soil characteristics and associated land features is soil survey maps. These maps usually include erosion class and slope class, but they cannot provide detailed information on slope lengths, gradients and shapes because these characteristics are extremely localized.

All land is also classified in one of eight capability classes, with generally four subclasses in each.[6] A capability unit is a grouping of soils that are suited to the same kinds of cultivated crops and have about the same responses to systems of management. Capability subclasses recognize four kinds of limitations or hazards: erosion, wetness, root zone, and climate. Acreage data for each capability class and subclass are available by states, land resource areas, and several land-use classifications.[1]

The conterminous 48 states have also been mapped as 156 major Land Resource Areas (LRA's). Each LRA consists of geographically associated land units that are characterized by particular patterns of soil, climate, water resources, land use, and type of farming. The map and major characteristics of each of the 156 LRA's are given in Agriculture Handbook No. 296.

In 1974, a panel of five Agricultural Research Service specialists was assigned the responsibility of compiling a two-volume manual for control of water pollution from cropland.[5] The first volume presents systematic procedures to aid the user in identifying specific potential problems and appropriate control measures. The second volume reviews the basic principles on which the instructions in Volume I are founded and provides documentation of the information presented. Volume I was

printed in 1975 and copies are available from ARS and EPA. The second volume is now at the printers and will be available from the same sources.

Forty maps and charts and 21 tables included in the manual summarize source data for pollution-control planning. The runoff percolation, and erosion-hazard maps show relative data for each of the 156 major land resource areas.

Neither actual nor potential erosion rates have been quantitatively mapped nationally because they are extremely localized. The important soil, topographic, and cultural-practice details are generally available only on a local basis. However, geographic trends in the levels of these parameters and in rainfall pattern were estimated in relative terms and used to prepare a map of "relative potential contributions of cropland to watershed sediment yields." The mapped cropland-sediment potentials reflect a combination of potential erosion and cropland density. A second map shows cropland acreage as the percentage of total land area for each of the 156 major land resource areas. A third map shows the distribution of cropland on which soil erosion is the dominant limitation for agricultural use, and a fourth shows percentages of rangeland. Since these maps were published in color and are readily available,[5] I shall not reproduce them for this paper but shall refer to the four maps by number to illustrate their utility.

If the first map ranks the LRA in question as "low" but samplings show excessive sediment in a stream, the fourth map is consulted for likely contributions from rangeland. If that is also low, non-agricultural sources should be suspected. Noncropland conditions indicative of high sediment-yield potential that can be identified by observation include: gullies, residential or commercial construction, highway construction, unstabilized roadbanks or streambanks, surface mine spoils, and bare areas.

A rating of "moderate" on the first map combined with a "high" rating on the third map would suggest widespread need of relatively minor control practices. But a rating of "moderate" on the first map combined with a relatively low rating on the third map would suggest that only a small portion of the area needs attention and that treatments on that portion may need to be substantial. Conditions of high cropland-sediment yield that can be visually observed include:

Long slopes farmed without terrace systems or diversions,
Runoff from upslope pasture or rangeland flowing across cropland,
Rows and tillage up-and-down moderate or steep slopes,
No crop residues on the surface after new crop seeding,
Poor stands or poor quality of vegetation,
Intensively farmed land adjacent to a stream without an intervening strip of vegetation.

The universal soil loss equation can be applied to sub-areas suspected of being high sediment contributors, to obtain numerical evaluations of the erosion hazards and to determine the specific combinations of control practices that would meet the specified goals.

Runoff from long rains at high intensities cannot be prevented. But runoff can be reduced, and sediment content of the runoff can be controlled by practices that have low values of the USLE factors C and P. These practices rely largely on five means of achieving erosion control: vegetation, plant residues, improved tillage methods, residual effects of crops in rotation, and mechanical support practices. The principal types of erosion-control practices are described in the manual. They are also listed in tabular form together with the highlights, merits, and limitations of each.

Other tables list the major types of practices for control of direct runoff, nutrient losses in runoff, and pesticide losses and summarize the highlights, merits, and limitations of these practices.

Determining whether a nonpoint pollution problem may exist and, if so, what measures may be taken to alleviate it most effectively, involves a logical sequence of decisions. This sequence is illustrated schematically in the manual by a series of flow charts. The flow charts are designed as guides for assessing potential erosion, nutrient, and pesticide problems and selecting physically feasible control practices for them. They are keyed to the source-data maps and tables.

Sediment-Control Standards

Sediment-control standards that coincide with the soil-loss tolerances already established for soil conservation have the distinct advantage that a farmer is in compliance if he follows a conservation plan approved by his Soil Conservation District. They are probably the most feasible starting points. But if the initial standards fail to attain the desired level of water-quality control, the next step should be variable standards that suit the requirements of various local conditions rather than successive lowerings of uniform soil-loss limits.

For controlling water pollution from nonpoint sources, a limit on the potential amount of off-farm sediment may be more appropriate than a limit on soil movement within field areas. Sediment filters and traps would then also be possible options as control measures. Soil texture and the locations of the cropland relative to streams, lakes, reservoirs, or critical areas are also important in determining how much field soil loss could be tolerated. Texture is important because collodial materials remain in suspension longer than larger particles and are probably the primary carriers of chemical compounds. Short-time peak sediment loads may be more important in pollution control than they are in preservation of the land resource. Merits and limitations of possible standards based on other than longtime-average field soil loss are discussed at length in the manual on control of water pollution from cropland.[5]

SUMMARY

About 30 percent of our country's total sediment is ascribed to geological erosion, 20 percent to accelerated erosion on nonagricultural lands, and about 50 percent to our 438 million acres of cropland.

Soil-particles are detached by both raindrop impact and runoff, but transportation of the detached particles is primarily by runoff. Sediment from sheet and rill erosion comes from near the surface and is more likely to contain nutrient and pesticide contaminants than that from gully, streambank, or channel erosion. Average annual soil loss from sheet and rill erosion on specific land areas can be predicted by the universal soil loss equation as a function of rainfall characteristics, soil properties, topographic features, land-use, cultural management, and erosion-control practices. The equation's factors and sources of specific-location values of the factors are discussed, and use of the equation is demonstrated.

The universal soil loss equation is designed to predict longtime average soil losses, not specific events. It does not predict or credit sediment deposition by overland flow and does not compute gully, streambank or channel erosion. It was designed for field-size areas but can be adapted for use in estimating watershed sediment yields.

Helpful guides for Section 208 area planning on a drainage-area basis are given in a recently published manual, "Control of Water Pollution from Cropland." Flow charts have been developed to guide methodical assessment of potential erosion, nutrient, and pesticide problems and selection of physically feasible control practices for them.

For controlling water pollution from nonpoint sources, limits on the potential amount of off-farm sediment may be more appropriate than uniform limits on soil-loss rates from field slopes.

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Heavy Metals Contained in Runoff From Land Receiving Wastes*

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INTRODUCTION

Heavy metals were measured in runoff waters and eroded sediments on a sewage sludge treated area. The soils on the 8-ha area are largely Typic Hapludolls on up to 10% slopes, on which tile-outlet terraces were constructed. The domestic sludge was low in metals and 28.5 mt/ha was applied over a 2-year period.

Concentrations of Zn, Cu, Cd, Pb, Ni, and Cr in the runoff water were low and usually near detection limits with the procedures used. Quantities of Zn and Cu were much greater in sediment than in waters, except during snowmelt runoff and during a storm after sludge application.

Heavy metals contained in waters from sludge-amended soils are of concern because of possible deleterious effects on human, animal, or plant life, from water ingested directly or from plants grown on soils or sediments contaminated with these elements. Because sewage sludge often contains significant quantities of heavy metals, possible transport of metals by surface waters from sludge-amended land is an important consideration.

Runoff water and the sediment from land areas are influenced by many factors, especially: (a) rainfall characteristics (amount, duration, intensity, and frequency); (b) watershed characteristics (area, shape, slope gradient, length and orientation, and type of drainage network); (c) ease of soil erodibility; (d) cropping practice; and (e) land management and conservation practices.

Proximity of the runoff-producing rainfall event to chemical application date is a major influence on their concentrations in runoff water (Leonard, Bailey, and Swank[14]). High concentrations of chemicals contained in sludge may occur in runoff water if the rainfall event occurs before surface-applied liquid sludge dries on the soil surface.

Thus, to guard against direct runoff occurring from land receiving sludge, an engineering system for temporarily retaining the runoff water and sediment may be desirable. A backslope terrace system with pipe drains has been used to slowly release surface waters and to retain most of the sediments within agricultural watersheds. Laflen, Johnson, and Reeve[12] found that average annual soil loss from four tile-outlet terrace systems in Iowa was less than 840 kg/ha with less than 5% of soil erosion between terraces. Sediment concentrations averaged between 800 and 3850 mg/l. Annual average inorganic P concentrations in surface runoff varied from 0.013 to 0.204 mg/l P and average annual inorganic N concentrations in surface runoff were 4 mg/l N or less at three of four sites and 11 mg/l N at one site (Hanway and Laflen[10]).

Plan of Experiment

Physical Setup:

Eleven grassed backslope terraces with separate surface tile inlets were constructed on a 16-ha watershed at the Rosemount Agricultural Experiment Station of the University of Minnesota near Rosemount, Minnesota (Figure 1) (Larson et al.,[13]). Port Byron (Typic Hapludolls), Bold (Typic Udorthents), and Tallula (Typic Hapludolls) are the dominant soil types. The soils consist of 60 to 240 cm of a silt loam loess cap overlaying compact glacial till. Slopes, after terracing, range from 2 to 10%.

The parallel terraces were constructed by a cut-and-fill technique leaving a 2:1 backslope that was seeded to bluegrass. The terrace ridges were spaced 40 m apart and were designed to impound a maximum runoff of 6.4 cm. Terrace channels were graded to the inlet pipes, which were placed in natural depressions (Figure 2). Solid PVC pipe individually connected each inlet to sampling stations located below the bottom terraces. At the sampling station flow from runoff water was measured and sampled by automatic sample collectors.

Water drainage from the terraced area was stored in a reservoir designed to impound a 100-year storm runoff (11.2 cm). Water stored in the reservoir is periodically used to irrigate a 2-ha area designated for this purpose.

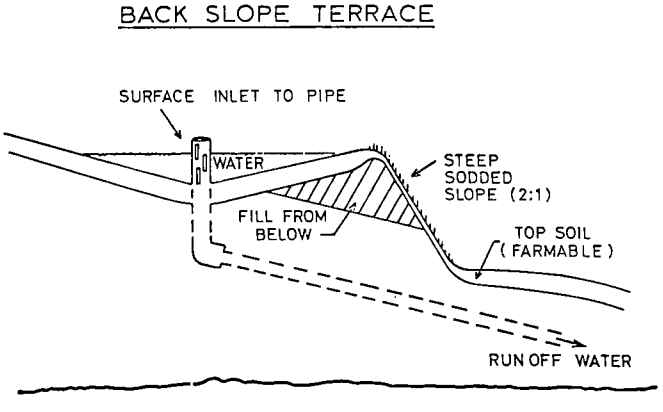

Figure 2: Terrace and Surface Inlet

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Cooperation and financial support from the Metropolitan Waste Control Commission, St. Paul, MN, is gratefully acknowledged.

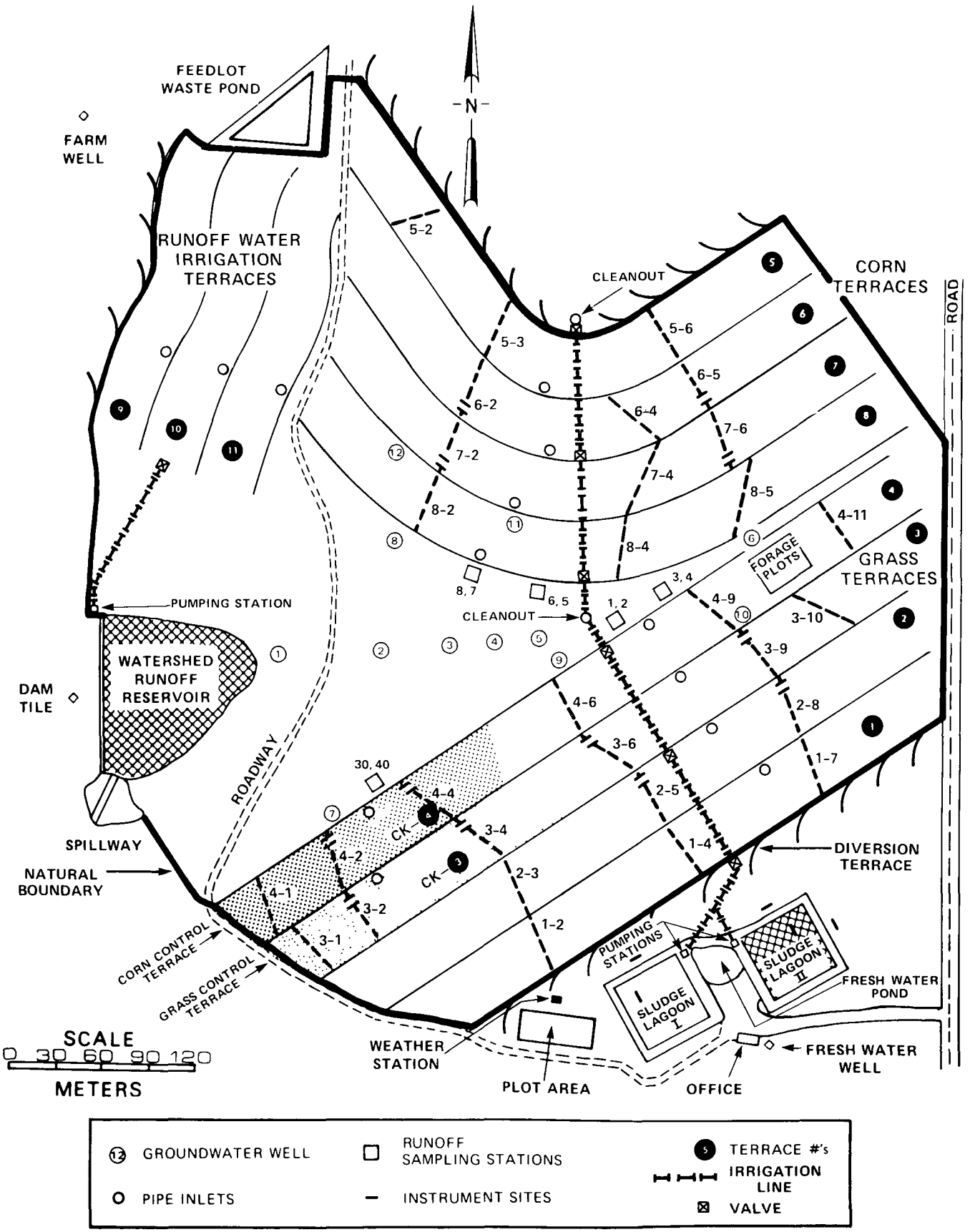

Figure 1: Rosemount Sewage Sludge Watershed (engineering design and sample collection locations)

Sludge Storage and Application:

Liquid digested sludge (approximately 2 to 5% solids) from four metropolitan wastewater treatment plants was hauled to the watershed by tank truck and stored in two lagoons. The combined capacity of the lagoons was 11,400 m^3 (3,000,000 gal), which will store approximately one-half of the annual sludge production of the four treatment plants it served.

An underground pipeline extended from the sludge lagoons across the watershed in the approximate midline of the terraces for sludge application. At appropriate intervals riser pipes and outlet valves were installed (Figure 1) to which a traveling irrigation gun or subsurface injector could be connected by flexible hose. A 1700-l/min (450-gal/min) positive displacement electric pump was used for pumping sludge and runoff water to the traveling gun. The traveling gun capacity was 1230 l/min (325 gal/min) with 7.0 kg/cm^2 (100 psi) pressure and a 2.7-cm (1.05-in) nozzle covering a 45-m arc, which can cover a 0.8-ha area with 1.3 cm of sludge in 1 hr.

About 1 to 1.5 cm sludge per application was applied to the soil surface during 1974 and spring of 1975. In the fall of 1975, sludge was applied on the corn area using a subsurface injector mounted on a wide-tracked tractor. Spring-loaded shanks applied approximately 5-cm sludge/pass pass at 2.1 to 2.8 kg/cm^2 (30 to 40 psi) pressure with a flow rate of 2400 l/min (640 gal/min). Runoff, soil loss, and metal concentrations are reported for the corn area of the watershed, since grass was not established until the summer of 1975. A control area not receiving sludge was also included in the watershed (Figure 1).

Before application, sludge in the lagoon was mixed using a tractor-driven pump with a flexible outlet hose connected to a floating, movable raft. The intake of the sludge irrigation pump was connected to another movable raft by a flexible suction hose. The suction hose inlet was mounted on a movable boom, which could be lowered from the raft to the bottom of the lagoon.

During periods of sludge application, tile inlets were covered to prevent sludge from entering the runoff drainage system. For protection from aerosols, irrigations were carried out when the wind speed was less than 8 km/hr (5 mph).

Table I presents the times of application, amounts, and metal contents of sludge applied to corn in 1974 and 1975. The concentration of metals in the sludge at the four application times varied depending on their solids content which varied depending upon the degree of mixing in the lagoon. Low metal concentrations reflect low solids content from liquid in the upper part of the lagoon, while higher solids contents and higher metal concentrations occurred in the lower levels of the lagoon. In all cases the concentrations of metals in the sludge were relatively low, reflecting the domestic source of the sewage. The total amount of metals applied to the corn area is given in Table II.

Runoff samples were collected during peak flow for any given runoff event. The sediment fraction was removed immediately by centrifugation and dried at 105 C. The water was acidified to pH = 1 with distilled HNO_3 and stored for analyses.

Water samples were prepared for analyses as follows: i) 100 ml of solution were evaporated to dryness in Vycor† glass crucibles, ii) ashed at 450 C for 24 hr, and iii) extracted with 2*N* distilled HCl. Sediment samples were: i) extracted with 4*N* distilled HNO_3 (1:8 solid to liquid), ii) evaporated to dryness, and iii) extracted with 1.1*N* distilled HCl. All water and sediment extracts had a pH < 1. Glass-distilled deionized water was used in all procedures. Metal concentrations of final extracts were determined by atomic absorption spectroscopy utilizing a deuterium lamp background corrector.

Results and Discussion

Runoff water during 1975 totaled 2.1 cm for the control and 11.0 cm for the sludge-treated areas, and sediment loss totaled 130 kg/ha for the control and 700 kg/ha for the sludge-treated areas. The amount of runoff from the control was smaller because of differences in snowmelt runoff which reflects differences in snow cover.

The concentrations of trace metals in storm water runoff was very low (Table III) and was usually lower than the concentrations in surface waters found in rivers and lakes in selected basins during the period 1962–1967 (Table IV; Kopp and Kroner[11]). Except for the 6/11/75 runoff event, Zn levels in runoff waters from the sludge-treated areas were no greater than those from

† Mention of trade products or companies in this paper does not imply that they are recommended or endorsed by the U.S. Department of Agriculture over similar products of other companies not mentioned. Trade names are used here for convenience in reference only.

Table I: Time, Amounts, and Metal Concentrations of Sludge Applied to the Corn Area.

	Maximum permissible[1]	Mean, of all surface waters[2]	Upper Mississippi[2]	Northeast[2]	Southeast[2]	California[2]	Lake Erie[2]
	µg/l						
Zinc	5000	64	45	96	52	16	205
Copper	1000	15	14	15	14	12	11
Nickel	----	19	15	8	4	10	56
Lead	50	23	33	17	8	4	39
Chromium	50	9.7	7	14	4	15	12
Cadmium	10	9.5	6	5	5	--	50

[1] Maximum Permissible in Public Water Supplies (Report of the Committee on Water Quality Criteria, Federal Water Pollution Control Administration, U.S. Department of the Interior, Washington, D.C., April (1968))

[2] Kopp and Kroner (1967)

the control area. However, the Zn level was four times higher (125 μg/l) in runoff water from the sludge-treated land versus the control area for the 6/11/75 storm, which followed a 3.6-mt/ha sludge application on the soil surface the previous month. Several workers have shown that the concentration of pesticides in runoff increased as the time between applications and a runoff event decreased (Leonard, Bailey, and Swank[14]). Chaney and Giordano[6] described this phenomenon as "reversion," where metals added to soil slowly become bound in an insoluble form.

Copper and Cr concentrations in runoff water were the same for control and sludge-amended areas (Table III), although 3.2 kg of Cu and 1.38 kg Cr/ha had been applied. Dowdy and Larson[9] added sludge containing 610 and 4550 μg/g of Cu and Cr, respectively, to a soil, found they were not appreciably taken up by plants and presumably insoluble. Levels of Cd, Pb, and Ni in runoff were usually below our detection limits of 1.0, 6.5, and 3.5 μg/l, respectively.

Table III: Metal Content of Selected Storm Runoff and Sediment from the Corn Area.

Date	Metal					
	Zn	Cu	Cd	Ni	Pb	Cr
	kg/ha					
1974	4.15	2.39	0.04	0.11	2.27	8.96
Spring 1975	1.37	0.79	0.02	0.05	0.43	4.86
Total	5.52	3.18	0.06	0.16	2.70	13.82

The low sediment yields (Table V) limited metal analyses to Zn, Cu, and Cd. The 4*N* HNO_3 extractable metals from sediment, which approximates total metal content (Bradford et al.[3]), were always higher from the sludge-treated areas than from the control areas (Table IV). However, differences in sediment Zn and Cu levels were much less (control versus sludge terraces) for the major 4/27/75 storm of 9.3 cm rainfall, which suggests that small, frequent periods of precipitation cause proportionally larger losses of sludge-borne metals per unit weight of sediment. During small runoff events, the less dense sludge-derived organic colloids and associated metals are probably preferentially eroded. Also, a proportionally higher Zn concentration was observed in sediment from sludge-amended areas after sludge had been applied 1 mo (6/11/75 storm) than was observed for longer time intervals after application. This observation is consistent with the runoff-water data and suggested that Zn losses are more-highly dependent on application/precipitation timing than are the loss of other metals. Cadmium losses in sediment followed the same general trends as those for Zn and Cu, but absolute losses were generally two orders of magnitude less.

Table IV: Permissible and Mean Concentrations of Metals in Surface Waters from Selected Basins in the United States.

Terrace	Date	Metal					
		Zn	Cu	Cd	Pb	Ni	Cr
		Runoff					
		µg/l					
Control*	4/18/75	7.0	4.5	<0.8	<6.5	<3.5	6.5
Sludge		4.5	5.0	<0.8	<6.5	<3.5	11.0
Control	4/23/75	6.5	4.5	<0.8	<6.5	<3.5	5.5
Sludge		5.0	2.5	<0.8	<6.5	<3.5	7.0
Control	4/27/75	5.0	5.0	<0.8	<6.5	<3.5	<4.5
Sludge		6.0	<2.5	<0.8	<6.5	<3.5	<4.5
Control	6/11/75	36	7.5	1.0	<6.5	<3.5	<4.5
Sludge		125	8.0	1.0	<6.5	4.0	5.5
Control*	3/15/76	22	36	<1.0	<6.5	<6.0	9.0
Sludge		25	41	<1.0	<6.5	<6.0	10.7
		Sediment					
		µg/g					
Control	4/18/75	32	12	0.35			
Sludge		57	36	0.48			
Control	4/23/75	30	11	0.18			
Sludge		53	18	0.90			
Control	4/27/75	30	11	0.15			
Sludge		36	14	0.53			
Control	6/11/75	60	12	0.18			
Sludge		320	38	1.01			

*Snowmelt

Table V: Heavy Metals Removed in Selected Stormwater and Sediment Losses from the Corn Area.

Terrace	Date	Sample	Runoff		Metal		
			Water	Sediment	Zn	Cu	Cd
			cm	kg/ha	mg/ha		
Control	4/18/75+	Water	0.10		70	45	—
		Sediment		22	260	700	—
Sludge	4/18/75+	Water	7.40		3330	3700	—
		Sediment		18	990	625	
Control	4/23/75	Water	0.05		35	20	—
		Sediment		5	145	55	—
Sludge	4/23/75	Water	0.04		15	10	—
		Sediment		4	215	70	—
Control	4/27/75	Water	1.70		850	810	—
		Sediment		—	(3400)*	—	—
Sludge	4/27/75	Water	3.10		1860	—	—
		Sediment		640	22,970	9000	—
Control	6/11/75	Water	0.25		925	190	27
		Sediment		16	960	190	3
Sludge	6/11/75	Water	0.48		6,000	375	48
		Sediment		30	9,525	1140	30

+Represents cumulative snowmelt.

*Sediment yield missing. Value estimated by assuming that partitioning of Zn loss between water and sediment was the same for this runoff event as it was for previous events.

Table II: Metal Applied to Corn Through Spring 1975.

Season	Applications number	Sludge		Metal					
		cm	Solids	Zn	Cu	Ni	Pb	Cr	Cd
			mt/ha	ppm					
Spring 1974*	2	2.6	1.8	542	374	15	219	500	5
Fall 1974+	3	2.9	5.2	610	330	15	360	1550	6
Spring 1975+	3	4.5	3.6	380	220	14	120	1350	4
Fall 1975‡	2	6.4	17.9	1200	840	16	325	4360	9
Total	10	16.4	28.5						

*Applied with tank wagon on soil surface

+Applied with traveling gun on soil surface

‡Applied with subsurface injector

Zinc and Cu losses were calculated for selected runoff events for the spring of 1975 (Table V). Most of the eroded metals were associated with the sediment from the sludge-treated areas during the major storm of 4/27/75 where ~8% of the Zn losses were attributable to runoff waters. Curnoe[8] noted similar findings for runoff from poorly drained sandy clay loam soils with a 2 to 6% slope. However, for snowmelt (4/18/75) and storms closely following sludge applications (6/11/75) proportionally more Zn was associated with the solution phase.

Runoff losses of sludge-borne metals closely paralleled phosphorus (P) runoff findings. Burwell, Timmons, and Holt[4] reported that <6% of the total P loss in surface runoff was associated with the solution phase from a continuous corn cropping system. In contrast, total pesticide losses were generally greatest in the aqueous phase as compared with sediment losses, although pesticide concentrations may be greater in the sediment phase (Leonard et al.[14]).

The total metal losses for the first four storms (Table V) represent an approximation of total metal losses in the spring of 1975 as a result of sludge applications of 6 mt/ha the previous years. By performing these calculations for Zn and comparing this value with that of total Zn applied (Table II), <1.0% of the applied Zn was lost by surface runoff. Curnoe[8] also reported very small metal losses by surface runoff, when using an Fe-precipitated sewage sludge. However, as Leonard et al.[14] so aptly indicated, caution must be exercised when assessing the potential impact of metal losses based on percent loss of that applied. Generally, it is the concentration of metals in runoff water and sediment that determines impact.

Our data are limited in scope and preliminary in nature. Metal concentrations were low and often close to detection limits. Also, sediment yields and storm runoff were quite low.

Although most of the sludge-borne metals eroded from the landscape are associated with soil particles, the mechanisms by which sludge-borne metals are sorbed on, or associated with, soil particles are very complex and numerous, and definitive experimental findings are essentially lacking as Chaney and Giordano[6] reviewed and discussed.

Soil pH has been shown to be highly correlated with plant-available metals. However, Cheng, Patterson, and Minear[7] have shown that soluble metal levels in sludge-water mixtures exceeded levels that can exist in tap water systems. Hence, theoretical solubility considerations may yield very little insight into the processes associated with metal losses by surface runoff. Andersson and Nilsson[1] found wide variations in the amount of Cd sorbed on various soil materials at different pH's (Figure 3). However, for all soil materials, the quantities of Cd sorbed increased as pH increased (reduced solution concentration). By knowing soil pH and estimating the partitioning of soil components within sediments, it may be possible to predict metal runoff associated with sediments.

Predicting metal losses in the aqueous phase of surface runoff will be difficult. It is complicated by the fact that only a very small percentage of the total metals are in the soluble form in sludge. Busman[4] found 1.5% of the Cd in digested sludge was in the soluble form, while Cheng[6] observed that a synthetic activated sludge sorbed 84% of added soluble Cd.

Perhaps, soluble-metal runoff potential can be best estimated from water-extraction data of sludge-amended soil. Silviera and Sommers[14] incubated soil-sludge suspensions (23.75-g soil + 1.25-g sludge in 75-ml volume) and observed that < 2% of the total Zn and Cu was soluble in water or 1*N* KNO_3. Water-soluble Cd and Pb were below their detection limits. Bloomfield and Pruden[2] aerobically incubated moistened mixtures of sludge andsoil (2-g sludge + 10-g soil) for 4 mo. The sludge originally contained 3900, 1400, 6500, 1200, 3300, and 64 μg/g of Cu, Ni, Zn, Pb, Cr, and Cd, respectively. After incubation, approximately 0.35, 3.2 0.8, 0.65, and 2.9% of Cu, Ni, Zn, Pb, Cr, and Cd, respectively, was water extractable. The presence of soil reduced the water-soluble fraction of all metals, except Cd and Cr where solubility was increased. Adding lime to the soil-sludge mixtures enhanced the water-soluble Cu, Pb, and Cr, and decreased the water solubility of Zn, Cd, and Ni. Any conclusions, drawn from the preceding data, must be considered as "worst-possible" situations. Bloomfield and Pruden[2] applied sludge at a rate of ~450 mt/ha, which is at least an order of magnitude higher than sludge-utilization rates used in agricultural crop production. At lower rates of sludge application, proportionally less water-soluble metals would be anticipated, as demonstrated by Cheng et al.[9] for sludge alone.

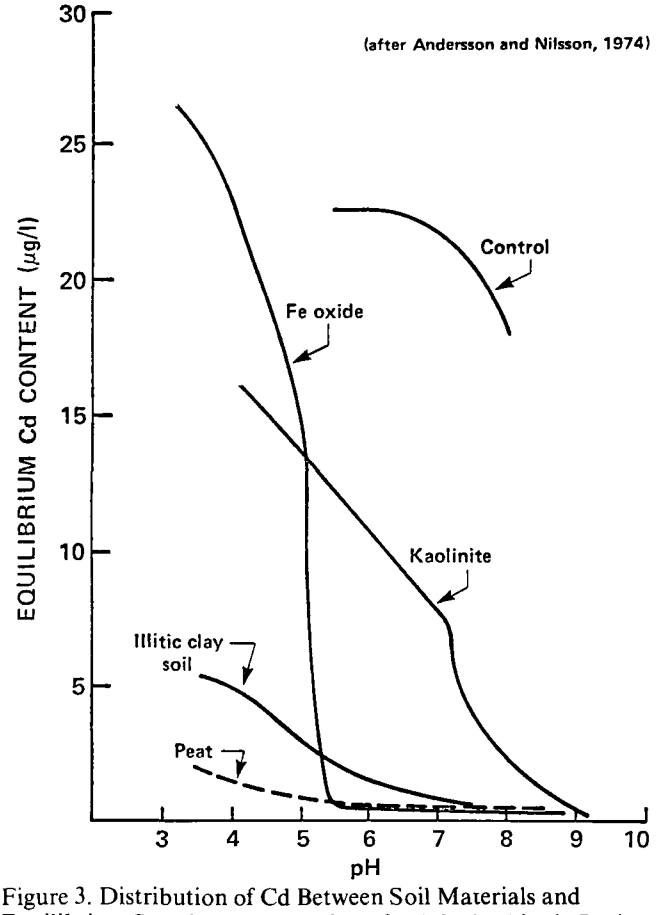

Figure 3. Distribution of Cd Between Soil Materials and Equilibrium Solution as a Function of pH. Solid/Liquid Ratio was 1/50, and 20 μ eq. of Cd was Added/g Soil Material (after Andersson and Nilsson[2]).

The terraces and underground drain system reported herein were designed to minimize runoff and sediment loss on this sloping permeable soil landscape. Our preliminary data (Table V) indicated the engineering design has limited sediment movement to the drainage way to less than 700 kg/ha. Because the metals are highly sorbed on the sediment, limiting sediment movement off the land effectively limits total metal loss. The terrace outlet tile perforated-entrance retains the heavier runoff events and distributes them over longer time periods, which increases total infiltration. An engineering design to control sediment movement and slow runoff is desirable on all sloping lands.

Management of the soil and crop are important aspects of controlling sediment and water loss. By using established conservation practices, these losses can be held to acceptable levels. We used a chisel as the primary tillage tool and kept the soil surface rough with some residue cover at all times when there was no crop canopy. Sludge was applied only during periods of dry weather.

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Heavy Metal Contents in Runoff and Drainage Waters from Sludge-Treated Field Lysimeter Plots

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INTRODUCTION

Beginning in 1969, sludge from high-rate anaerobic digesters at the Calumet and Stickney wastewater treatment plants near Chicago was applied by ridge and furrow irrigation on 44 lysimeter plots measuring 3.05 by 15.25 m. Plots were arranged in two banks of 22 plots each, referred to below as north and south series. The lysimeter installation was located on a small watershed on the Northeast Agronomy Research Center near Elwood, Illinois. Each sludge treatment was replicated three times on the native Blount silt loam soil occupying the small watershed. Elliott silt loam soil was simulated in 10 lysimeters by removing the surface one-foot depth of Blount silt loam and replacing it with an equivalent depth of surface soil from Elliott silt loam sites. Also, 10 lysimeter plots were constructed by excavating the complete plot to a depth of 1.52 m and filling with Plainfield sand. Tile drains were installed through the center of each lysimeter plot and at the downslope end of each plot a fiberglass trough was installed to collect runoff water. Both drainage water and runoff water were conveyed separately through PVC pipes from the plots by gravity to the basement of an instrument house. Tipping bucket equipment was provided to measure rates and total volume of flows from each of the PVC pipes through which either runoff or drainage water was delivered from the plots to the instrument house basement. Automated sampling equipment was provided for each of the PVC pipes and, for the most part, a 400ml sample was collected from the second tip of a tipping bucket and again on each sequential 42nd tip of a bucket thereafter for the duration of a flow event. Thus, except for some special studies, a sample represented the instantaneous water flow that occurred between each 42 volumes of sequential flow. The equipment was designed to take samples at more frequent volumes of flow if desired, but the number of water samples collected at the selected flow volume increments were all that could be conveniently analyzed for heavy metals and several other parameters not discussed here. Multiple-channel event recorders were used to record rates and total flow volume of runoff and drainage waters relative to clock time. Detailed descriptions of all the flow volume measuring, recording, and sampling equipment, as well as the construction of lysimeter plots were presented in an earlier report (Hinesly et al.[5]) and therefore were not discussed in detail here.

Sludge loading rates and some constituents of sludge

During the first two years of operations, the north series were planted to soybeans and the south series to corn each year. Each year sludge was applied as often as weather conditions permitted, at rates of 2.54, 1.27, and 0.64 cm during and after the growing season. All plots received an annual application of KCl at a rate to supply 111kg K/ha. Control plots received further additions of inorganic fertilizer to supply 333kg N/ha and 111kg P/ha. Except for maximum sludge-treated plots of simulated Elliott silt loam and Plainfield sand, sludge applications were terminated on the north 22 lysimeter plots after November, 1973, at which time total sludge applications on a dry weight basis were 223.8, 111.9, and 56.0 mt/ha on maximum, one-half maximum, and one-fourth maximum sludge-treated plots, respectively. On the south 22 lysimeter plots where applications were continued, total sludge applications at the end of the 1975 application period amounted to 374.3, 187.2, and 93.6 mt/ha of dry solids on maximum, one-half maximum, and one-fourth maximum sludge-treated plots, respectively. Sludge loading rates as well as quantities of several heavy metals applied annually on lysimeter plots as constituents of the sludge are presented in Table I. Although, numerous data have been collected with regard to the accumulations of heavy metals in soils and plant tissues, the discussion here is limited to the effect of maximum sludge loading rates, that is, those plots receiving incremental applications of 2.54 cm, on concentrations of Fe, Mn, Zn, Cu, and Cd in runoff and drainage waters.

Procedures and methods of analysis

As water samples were removed from automated sample collection equipment they were sealed with a clean cap, labeled to identify the date, plot number, kind of water (runoff or drainage) and sequence of sampling, after which they were placed in specially prepared shipping crates for transfer to the laboratories within a period of 30 hours after collection. All of the elements, Fe, Mn, Zn, Cu and Cd, were determined from a water sample volume of 150 ml to which 2 ml of 6 *N* HCl (redistilled) was added before evaporating to dryness on a steam-heated sand bath, whereupon an additional 2 ml of 6 *N* HCl was added to samples before evaporating to dryness for a second time. To the dry residues, 10 ml of 1.0 *N* HCl (redistilled) was added and refluxed with a watch glass cover for one hour (on a sand bath). Samples were then diluted to 25 ml with deionized water, filtered and analyzed by atomic absorption spectroscopy.

Data Handling

The scheme by which water data were collected and treated is conceptually depicted in Figure 1. The physical aspects of collecting water samples were briefly discussed above, but it should be recognized that the samples were collected by a systematic sampling plan, as contrasted to random and stratified random sampling plans. That is to say, the first sample to be collected during any runoff or drainage event was chosen and then a sam-

ple was collected each time an amount of flow equal to 77.87 l from the lysimeter surface and 26.04 l from the lysimeter drainage tiles was delivered to tipping buckets. To our knowledge, this is the first and may still be the only field lysimeter equipped to provide observations on discrete volumes of flow. In the past, most sampling of lysimeter waters was conducted by a more or less random sampling plan since all or some of the water from a flow event was collected in containers from which subsamples were withdrawn. In other cases, lysimeter flows were automatically sampled on a unit time basis. Neither of these methods of sampling provide opportunities for observing changes in water quality parameters which change with flow rates or volumes of flow.

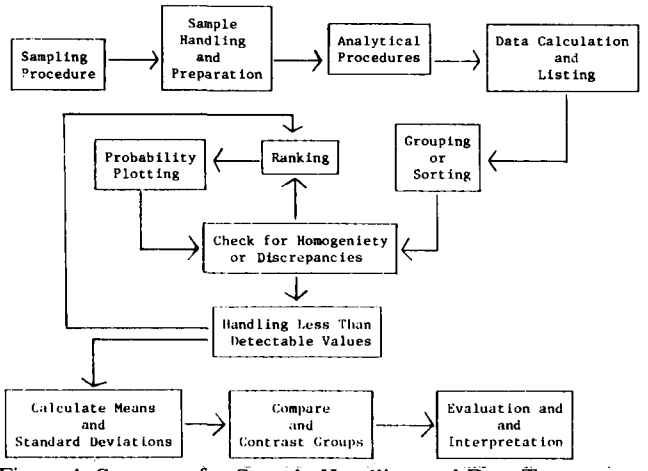

Figure 1: Sequence for Sample Handling and Data Treatment.

Following the preparation and analysis of water samples, all raw data required some calculations to transform them to standard reportable units. Most of the calulations were performed on an electronic desk calculator. After the data were converted to reportable units, they were punched on cards for storage on disks. Then an IBM sort-merge routine was used to group data stored on disks according to kind of water (runoff or drainage), soil type, soil treatment, and period of time (an observation year began on May 1 and continued to April 30). After checking for discrepancies, the data were sorted again to arrange them in order of lowest to the highest value of a measured metal concentration (data ranking), where below detectable level values were entered as one magnitude less than the lowest detectable level. For example, Cd concentrations could not be detected below 0.001 ppm in water samples, but were entered as concentrations of 0.0001 ppm as a means of including them in the total number, N, observations. From the number of ranked data points, N, the cumulative percent groups were calculated from lowest to highest utilizing the equation cumulative percent = $^{n_i}/_{N}$ 100 where n_i is the "i"th rank in a group of N data. Following the ranking of data within groups and assignment of cumulative percentiles to each datum, log-normal probability graphs were generated using a computer program developed in FORTRAN language and an IBM calcomp plotter. Where the number of observations were equal or greater than 100, only a representative portion of the plotted points were depicted on the graphs. That is, symbols were not drawn for all plotted values but all data were included in the graph. Less than detectable values were included in the calculation of percentile distributions, but were not shown in graphs. Data are log-normally distributed when their logarithms fit a normal (Gaussian) distribution. For the log-normal probability plots presented here, the ordinate is a logarithmic scale of measured values and the abscissa is the probability scale where the frequency of a measured value x is expressed as a percent of occurrences equal to or less than the specified value.

Table I: Annual digested sludge loading rates and quantities of heavy metals applied as constituents of sludge on maximum sludge-treated Blount silt loam, Elliott silt loam, and Plainfield loamy sand lysimeter plots before and after the growing seasons of 1969 through 1974. Maximum sludge-treated plots were located in north and south series of plots. Sludge quantities are expressed as mt/ha dry weight and constituents are kg/ha dry weight.

Sludge or Constituent	Location	Year	Soil Type: Blount silt loam	Elliott silt loam	Plainfield loamy sand
			mt/ha		
Sludge	South	1969	19.33	same	same
		1970	36.15	"	"
		1971	104.69	"	"
		1972	32.19	"	"
		1973	58.75	"	"
		1974	70.73	"	"
	North	1969	16.37	same	same
		1970	52.78	"	44.60
		1971	57.83	"	49.56
		1972	44.38	"	52.23
		1973	61.08	"	same
		1974	terminated	69.80	"
			kg/ha		
Fe	South	1969	455	same	same
		1970	1723	"	"
		1971	3967	"	"
		1972	1239	"	"
		1973	2041	"	"
		1974	3339	"	"
	North	1969	860	same	same
		1970	2734	"	2187
		1971	2526	"	2112
		1972	1825	"	2401
		1973	2067	"	same
		1974	terminated	3190	"
Mn	South	1969	4	same	same
		1970	10	"	"
		1971	25	"	"
		1972	14	"	"
		1973	31	"	"
		1974	37	"	"
	North	1969	5	same	same
		1970	17	"	13
		1971	17	"	15
		1972	21	"	25
		1973	32	"	same
		1974	terminated	30	"
Zn	South	1969	122	same	same
		1970	312	"	"
		1971	464	"	"
		1972	135	"	"
		1973	224	"	"
		1974	350	"	"
	North	1969	158	same	same
		1970	427	"	341
		1971	265	"	224
		1972	192	"	229
		1973	248	"	same
		1974	terminated	359	"
Cu	South	1969	27	same	same
		1970	69	"	"
		1971	114	"	"
		1972	22	"	"
		1973	38	"	"
		1974	114	"	"
	North	1969	36	same	same
		1970	101	"	81
		1971	69	"	57
		1972	33	"	39
		1973	41	"	same
		1974	terminated	117	"
Cd	South	1969	5.2	same	same
		1970	22.2	"	"
		1971	24.0	"	"
		1972	5.8	"	"
		1973	6.7	"	"
		1974	21.7	"	"
	North	1969	7.9	same	same
		1970	22.6	"	18.1
		1971	13.2	"	10.7
		1972	7.8	"	9.3
		1973	6.8	"	same
		1974	terminated	21.8	"

Many kinds of data exhibit log-normally distributed concentrations and can be collectively described as members of a homogenous group by a single central value and a variance (Aitchison and Brown,[1]). when log x concentrations or other appropriate units of measured water quality parameters are plotted versus the percent of the population of observations having values $\leq x$, on log-probability paper, a straight line is the best fit to the plotted points when the distribution of the population of values is log-normal. From this straight line, the estimated geometric mean $\hat{\mu}$ is given by the fiftieth cumulative percent intercept while the estimated standard geometric deviation is indicated by the slope of the line. The estimated standard geometric deviation $\hat{\sigma}$ is often calculated as the ratio between values for cumulative percent intercepts of either 84.13 and 50 or 50 and 15.87, where either of the ratios corresponds to a whole unit of standard deviation. More exactly, the estimated standard geometric deviation $\hat{\sigma}$ is obtained from

$$\log \hat{\sigma} = \log x_{0.8413} - \log x_{0.50} = \log \frac{x_{0.8413}}{x_{0.50}}$$

or

$$\log \hat{\sigma} = \log x_{0.50} - \log x_{0.1587} = \log \frac{x_{0.50}}{x_{0.1587}}$$

In the same way that 68.3, 95.5, and 99.7 percent of the area under a normal distribution curve are located, respectively, in the ranges x + s, x + 2s, and x + 3s (where "s" is the standard deviation), confidence intervals for the estimation of the true value of x can be calculated when the frequency distribution of log x is presumed to be a normal "error" distribution. The difference in calculating confidence limits is that the estimated standard deviation for a normally distributed population is an added and subtracted factor, whereas the antilog of the estimated geometric standard deviation is a multiplying and dividing factor applied to the antilog of the estimated geometric mean. More specifically, the intervals between $\mu \times \hat{\sigma}$ and $\mu \div \hat{\sigma}$, $\mu \times \hat{\sigma}^2$ and $\mu \div \hat{\sigma}^2$, and $\mu \times \hat{\sigma}^3$ and $\mu \div \hat{\sigma}^3$ are estimates of boundaries containing 84.1, 97.5, and 99.9 percent, respectively, of the total number of observations from a log-normal distributed population.

Rather than fit a straight line to all the log-normal probability graphs, it was more convenient to compute both the estimated geometric mean and geometric standard deviation values for the several measured water quality parameters. The estimated geometric means were calculated by the formula:

$$\log \hat{\mu} = \frac{\log x_1 + \log x_2 + \log x_3 \ldots \log x_n}{N}$$

where $x_1, x_2, x_3 \ldots x_n$ are values of individual observations, or are values one magnitude less than the lowest detectable concentration level. Using the computer generated estimated geometric mean values, estimated geometric standard deviations were computer calculated by the formula:

$$\log \hat{\sigma} = \sqrt{\sum_{i=1}^{n} (\log x_i - \log \hat{\mu})^2 / N - 1}$$

where x_i, i = 1, 2, 3 . . . n are the values determined from N observations.

For purposes of comparison, other measurements of central tendency, such as the median, arithmetic mean, and the standard deviation associated with arithmetic mean values for metal concentrations were also calculated. It may be noted that in the majority of cases, the arithmetic average or mean values are larger than either the geometric mean or median values. Although the geometric mean, like the arithmetic mean, is a mathematical rather than a positional average, the way in which individual measured values enter into the calculation of the geometric mean causes less weight to be given to extreme values. Thus, unless the numbers being averaged all have the same value, the geometric mean will always be less than the arithmetic mean. The median value is often an appropriate measure of central tendency for random variables which are not symmetrically distributed. Like the geometric mean, the median is not as sensitive to a small number of extreme values as is the arithmetic mean. The median is the mid-point value that divides in exactly one half the random variable values that are higher or lower values than itself.

Total numbers of observations, N, for each of the metal concentrations measured during each of the data years from water samples collected from the various lysimeter plots were presented in Table II. Thus, with the availability of total number of observations in Table II and estimated standard deviations for metal concentrations presented later in this section, all the information is provided for calculating standard error of means for each of the measured water quality parameters.

Comparisons of geometric means of data from sludge-treated plots to those from control plots were made to determine possible significant differences in metal concentrations due to treatment. Data were prepared according to sampling year, kind of water (runoff or drainage), soil type, and location of plots in north or south series. Tests for significant differences between two treatments within each group were based on the t-distribution. Values of t for a log-normal distribution were calculated and significant differences in geometric means due to treatment were determined from a table of the distribution of t for two-tailed tests (Snedecor and Cochran,[11] p. 549).

Discussion of Results

Relating the metal concentrations in runoff and drainage waters to water quality criteria for public water supplies seemed to be the most appropriate method for interpreting the findings presented here. More specifically, metal concentrations were compared to water quality recommendations for public water sources published in *Water Quality Criteria 1972,* Ecological Research Series, EPA-R3-73-0003, March, 1973.

Concentrations of Fe and Mn in Runoff Waters

Iron and Mn concentrations in runoff water were plotted as log-normal frequency distribution graphs. As examples of such graphs, Figure 2 for Fe and Figure 3 for Mn concentrations in runoff water samples collected in 1972–73 from Blount silt loam plots were presented. Since most of the concentration levels plotted as frequency distribution graphs could have been represented fairly well by a straight line, the population was interpreted as being log-normally distributed. Thus, geometric means and geometric standard deviations for Fe and Mn concentrations in runoff waters, as presented in Tables III through VIII, were most useful in assessing results obtained from the study. In runoff waters from control and sludge-treated Blount plots mean Fe contents ranged from 7.90 to 17.05 ppm and 5.73 to 10.86 ppm, respectively (Table III). Sludge treatments did not significantly affect mean concentration of Fe and Mn in runoff waters from Blount silt loam plots during the three years of collecting samples. However, 1972–73 runoff waters from the

sludge-treated Elliott silt loam plot, located in the north series, had significantly ($Pr<0.05$) higher mean levels of Mn than were found in runoff waters from control plots (Table IV). Both Fe and Mn concentrations in runoff waters from the sludge-treated Plainfield loamy sand plot, located in the north series, were higher than levels in comparable waters from control plots during 1972-73 ($Pr<0.05$) and 1973-74 ($Pr<0.01$) (Tables V and VIII, respectively). Mean levels of Fe and Mn were also increased in 1971-72 runoff waters from the Plainfield loamy sand plot in the south series by sludge applications ($Pr<0.01$).

If Fe and Mn concentrations have been determined in runoff waters by others, reported results were not discovered. Since waters in streams are composed to varying degrees of watershed runoff and drainage waters these kinds of reported data may be the best available for comparison with results reported here. Kopp and Kroner[9] pointed out that Fe may occur in stream waters in both bivalent and trivalent forms, but in natural streams most of the ferrous-Fe is readily oxidized to ferric-Fe to form insoluble $Fe(OH)_3$. Precipitates of $Fe(OH)_3$ tend to agglomerate, flocculate, and settle or be absorbed so that, in well-aerated waters, soluble Fe concentrations seldom exceed 0.2 ppm. Like Fe, bivalent and trivalent Nn may be present in surface waters but in natural streams most of it exists in the latter oxidized state and concentrations are generally less than 0.02 ppm as a result of precipitate settling. Probably appreciable amounts of Fe and Mn applied as constituents of digested sludge were in more soluble bivalent states and pronounced differences in mean concentrations of both elements in runoff waters from control and sludge-treated plots might have been expected. Perhaps the reason why differences in concentration levels were not greater is the same as that for the relatively low NO_3-N contents in runoff waters; that is, the more soluble forms were probably carried into the soil with infiltrating water before runoff occurred.

Table II: Number of observations, N, for heavy metal concentrations in runoff and drainage water samples collected from Blount silt loam, Elliott silt loam and Plainfield loamy sand lysimeter plots during the period May 1 to April 30 for the data years 1971-72, 1972-73, and 1973-74. Water samples were collected from fertilized and irrigated control or check plots, 1, and maximum, 4, sludge-treated plots located in either a north, N, or south, S, series from an instrument house.

Water Quality Parameter	Year	Location and Treatment	Runoff Water			Drainage Water		
			Soil Type					
			Blount silt loam	Elliott silt loam	Plainfield loamy sand	Blount silt loam	Elliott silt loam	Plainfield loamy sand
Fe	71-72	S1	40	46	12	41	24	96
		N1	52	32	16	15	31	50
		S4	62	16	9	85	35	3
		N4	42	13	13	51	16	14
	72-73	S1	108	88	54	126	43	392
		N1	107	64	37	57	216	214
		S4	124	33	30	167	93	31
		N4	66	37	36	314	24	140
	73-74	S1	52	52	28	183	51	209
		N1	34	70	22	147	259	177
		S4	59	17	19	268	111	43
		N4	21	21	22	336	33	126
Mn	71-72	S1	38	44	9	37	20	91
		N1	48	30	13	14	28	49
		S4	54	14	9	47	17	3
		N4	38	13	12	45	13	18
	72-73	S1	103	86	49	127	44	406
		N1	103	58	37	57	221	230
		S4	118	35	28	166	91	31
		N4	66	35	34	321	24	140
	73-74	S1	53	51	27	181	51	203
		N1	35	70	22	147	257	171
		S4	57	18	20	269	110	43
		N4	21	23	22	330	32	123
Zn	71-72	S1	40	46	12	42	24	99
		N1	52	30	16	14	30	50
		S4	62	16	9	91	33	3
		N4	42	13	13	52	15	21
	72-73	S1	109	91	54	124	43	403
		N1	106	65	39	53	221	233
		S4	123	35	30	167	92	31
		N4	68	38	37	324	24	143
	73-74	S1	53	52	28	179	48	208
		N1	34	71	22	134	250	170
		S4	59	18	20	265	107	43
		N4	21	21	21	321	30	124

Table II (Cont.)

Water Quality Parameter	Year	Location and Treatment	Runoff Water, Soil Type: Blount silt loam	Runoff Water, Soil Type: Elliott silt loam	Runoff Water, Soil Type: Plainfield loamy sand	Drainage Water, Soil Type: Blount silt loam	Drainage Water, Soil Type: Elliott silt loam	Drainage Water, Soil Type: Plainfield loamy sand
Cd	71-72	S1	26	27	6	36	16	56
		N1	32	18	13	14	28	19
		S4	44	13	8	83	31	3
		N4	20	9	7	43	14	10
	72-73	S1	109	90	54	128	44	398
		N1	100	63	36	57	222	219
		S4	124	35	30	167	93	31
		N4	66	37	34	324	24	145
	73-74	S1	54	52	28	184	51	210
		N1	34	71	22	147	261	177
		S4	59	18	20	269	111	44
		N4	21	22	22	337	33	127
Cu	71-72	S1	40	45	12	40	24	97
		N1	52	32	16	14	30	48
		S4	63	16	9	91	37	3
		N4	42	13	13	53	16	21
	72-73	S1	108	91	53	126	44	407
		N1	105	64	39	57	222	225
		S4	124	35	30	168	94	31
		N4	68	37	37	321	24	144
	73-74	S1	54	52	28	180	51	211
		N1	34	71	22	147	261	176
		S4	59	18	20	270	111	44
		N4	21	23	22	332	33	127

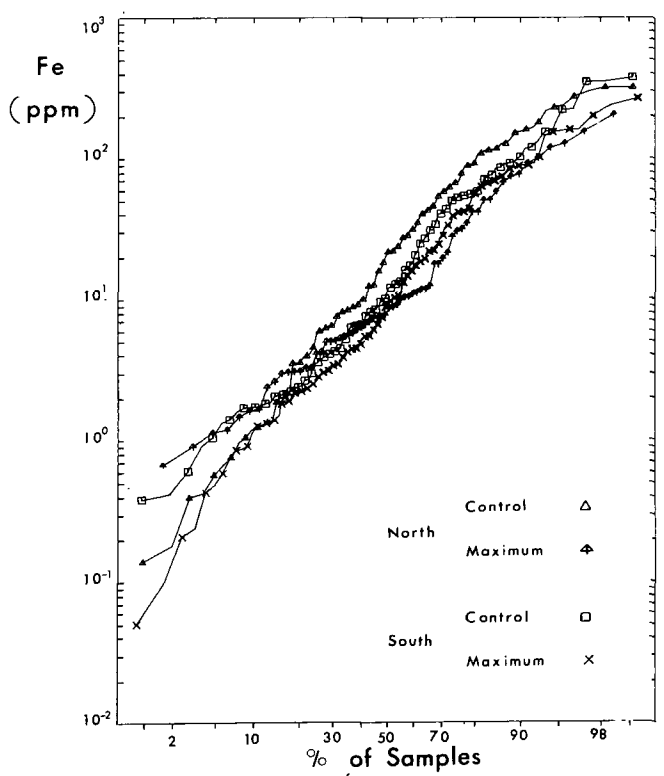

Figure 2: Frequency distribution of Fe concentrations during the period May 1, 1972 to April 30, 1973, in runoff water samples collected from field lysimeter plots containing Blount silt loam soil. Distributions of Fe concentrations are percent of samples containing less than amounts shown on the vertical axis. Median concentrations and standard deviations are presented in Table III.

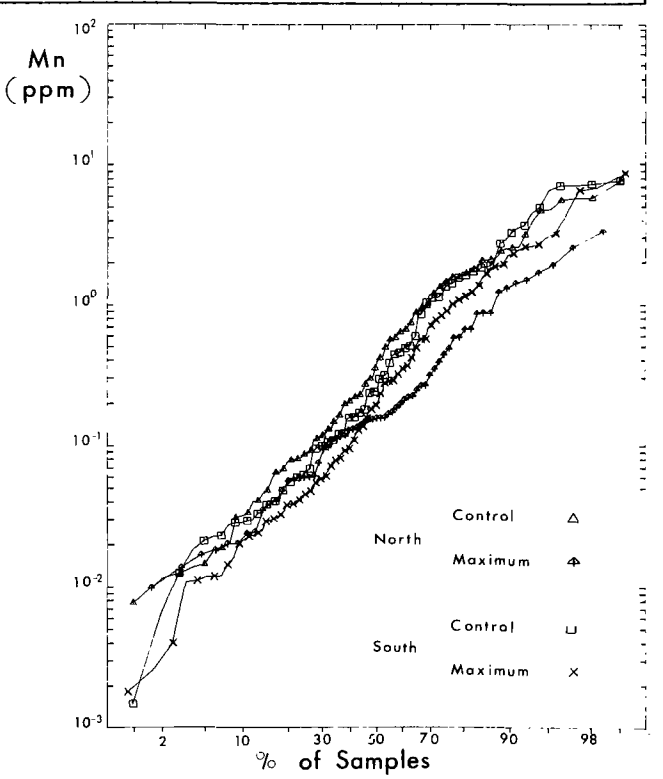

Figure 3: Frequency distribution of Mn concentrations during the period May 1, 1972 to April 30, 1973, in runoff water samples collected from field lysimeter plots containing Blount silt loam soil. Distributions of Mn concentrations are percent of samples containing less than amounts shown on the vertical axis. Median concentrations and standard deviations are presented in Table VI.

Table III: Arithmetic mean, $\bar{X}$, standard deviation, s, median, M, geometric mean, $\hat{\mu}$, and geometric standard deviation, $\hat{\sigma}$, for Fe concentrations as ppm in runoff and drainage water samples collected from Blount silt loam lysimeter plots during the period May 1 to April 30 during each of the data years 1971-1972, 1972-73, and 1973-1974. Water samples were collected from fertilized and irrigated control or check plots, 1, and maximum, 4, sluge-treated plots located in either a north, N, or south, S, series of plots adjacent to an instrument house. Summary measurements include data from three replications in each of two series.

Year	Location and Treatment	Runoff Water					Drainage Water				
		$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$	$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$
71-72	S1	32.81	54.09	10.47	12.43	4.25	3.49	7.08	0.73	0.52	9.63
	N1	67.28	162.12	8.95	12.91	6.52	1.75	5.56	0.18	0.23	5.52
	S4	16.21	24.04	5.98	6.45	3.99	1.47	2.70	0.19	0.26	8.50
	N4	27.17	65.83	4.10	5.73	5.70	3.15	8.88	0.13	0.24	8.67
72-73	S1	45.49	85.54	12.04	13.15	5.24	3.23	9.13	0.77	0.54	15.30
	N1	55.38	77.21	21.52	17.05	6.26	1.34	2.08	0.48	0.29	13.90
	S4	35.28	66.30	9.63	9.63	5.96	1.15	1.54	0.55	0.46	5.87
	N4	29.74	50.00	8.53	10.86	4.14	1.18	2.97	0.31	0.22	12.00
73-74	S1	24.95	49.83	7.57	7.90	4.76	5.85	19.35	0.67	0.66	11.83
	N1	68.93	119.41	11.17	12.72	8.18	4.57	24.56	0.35	0.30	17.50
	S4	32.71	46.96	10.91	10.17	5.65	1.06	2.12	0.37	0.37	5.81
	N4	16.23	17.13	10.40	9.36	3.41	0.56	1.91	0.21	0.12	12.67

In *Water Quality Criteria 1972*[2] it was recommended that soluble Fe should not exceed 0.3 ppm and soluble Mn should not exceed 0.05 ppm in public water sources. Both of these metals are undesirable at higher soluble concentrations because of their effect on taste, staining of plumbing fixtures and laundered clothes, and accumulation of deposits in distribution systems. To compare runoff water quality with these recommendations, the soluble proportion of the total Fe and Mn concentration would need to be determined. Although much less than in drainage waters, runoff waters from lysimeter plots generally contained NO_3-N at some concentration level indicating that high levels of reduced or soluble forms of Fe and Mn could not have existed in the same water samples. Thus, the major portion of the Fe and Mn transported by runoff water from lysimeter plots was probably constituents of settleable suspended solids. If true, most of the Fe and Mn in runoff water could be maintained at very low levels by soil conservation structures and practices. In the same way, sediment basins, as employed in connection with the use of digested sludge to reclaim strip-mined lands, will probably reduce Fe and Mn contents in surface runoff waters to levels acceptable for discharge to streams used as public water sources.

Concentrations of Fe and Mn in Drainage Waters

Typical log-normal frequency distribution plots for both Fe and Mn concentrations in drainage water were presented in Figures 4 and 5. Since these plots of data could be represented fairly well by a straight line, Fe and Mn concentrations in drainage waters were discussed in terms of geometric mean concentrations and associated geometric standard deviations. First, data reported in Tables III through VIII show that both Fe and Mn geometric mean concentrations are severalfold less than levels found in runoff water. As was the case for runoff waters, geometric standard deviations associated with mean concentrations of Fe and Mn in drainage waters indicate a considerable range of contents. Geometric mean concentrations of total Fe ranging from 0.12 to 0.66 ppm in drainage waters from Blount silt loam frequently exceeded maximum recommended levels of soluble Fe in public water sources, regardless of treatment. Concentrations of total Mn ranging from 0.009 to 0.027 ppm in drainage water from Blount silt loam (Table VI) were seldom higher than recommended maximum soluble concentrations for public water sources. Sludge treatments apparently affected Mn levels in drainage waters in Blount silt loam soils only in 1971-72. During this one year, drainage waters from the maximum sludge-treated Blount silt loam plots in the north series had higher Mn concentrations ($Pr<.05$) than waters from control plots. Sludge treatments apparently did not affect Fe and Mn levels in drainage waters from Elliott silt loam plots if allowances are made for levels identified in Tables IV and CII as plot S4. This plot was known to produce contaminated drainage water during the early years of operations. Sludge treatments significantly ($Pr<0.01$) increased Fe concentrations in drainage waters from this particular Elliott silt loam plot in the south series in 1971-72. But concentrations of Fe in drainage water from Elliott silt loam plots were not significantly different for any other annual comparisons. Also in drainage waters from Elliott silt loam plots located in the south series, sludge treatments caused increased concentrations of Mn in all three years ($Pr<0.01$). Drainage waters from the Elliott silt loam plot in the north series had increased Mn concentrations attributable to the maximum sludge application only in 1972-73 ($Pr<0.05$). contrary to expectations, drainage waters had lower Fe contents where samples originated from maximum sludge-treated Plainfield loamy sand plots in the north series in 1971-72 and 1973-74 ($Pr<0.01$) and in the south series in 1973-74 ($Pr<0.01$). Similar to Fe concentrations, Mn levels in drainage waters from Plainfield loamy sand plots located in the north series were decreased by sludge applications during all three years ($Pr<0.01$). Sludge applications also caused significantly lower Mn concentrations in drainage water during 1973-74 ($Pr<0.01$) from the Plainfield loamy sand plot located in the south series.

Because of the rapid rate at which sludge organic matter is decomposed in soils and the relatively large annual loading rates applied on maximum sludge-treated plots it had been anticipated that a major proportion of the Fe and Mn applied as a constituent of sludge would be transported through the soil profile in a chelated form by percolating waters. Evidently this did not happen. It seemed likely that chelated Fe^{+2} and Mn^{+2} forms do exist in anaerobically digested sludge or would be formed during microbial decomposition of sludge organic matter. But if true, they must be converted to inorganic or ionic

forms and absorbed on soil particle surfaces before they reach drainage tiles. This speculation has not been verified by results from analyses of samples from several soil depths because amounts of Fe and Mn supplied by sludge applications, although sizable in comparison to amounts of other metals, are relatively low in comparison to native amounts of Fe and Mn in soils. In their native state, surface horizons of Blount and Elliott silt loam soils contain about 2 percent and Plainfield loamy sand about 0.8 percent Fe. Additions to the surface of these soils (Table I, Fe and Mn) through 1974 amounted to 10 percent or less of the native Fe contents and less than 5 percent of native Mn contents.

Hem[4] discussed the stability of solids and solutes and solubility of Mn as functions of pH and redox potential. He pointed out that within the water stability region the three oxidation states of +2, +3, and +4 must be considered for Mn. From his discussion it seems probable that the Mn supplied on the soil surface as a constituent of anaerobically digested sludge was present as Mn^{+2} but was readily oxidized to the Mn^{+4} state soon after the sludge dried on the well aerated Plainfield sand plot surface. Evidently, once Mn^{+2} is precipitated the Mn^{+2} to Mn^{+4} reaction goes very readily (Jenne[6]. As soon as Mn oxides are present they act as a catalyst for the oxidation of sorbed Mn^{+2} causing Mn concretions to grow. Perhaps because of better aeration these kinds of processes occurred more readily on the sandy textured soil than on the heavier textured silt loam soils. Such reactions must also occur to a lesser extent in the artificially drained, finer textured soils as evidenced by the fact than Mn in drainage water was maintained at an unexpectedly low level.

Table IV: Arithmetic mean, $\bar{X}$, standard deviation, s, median, M, geometric mean, $\hat{\mu}$, and geometric standard deviation, $\hat{\sigma}$, for Fe concentrations as ppm in runoff and drainage water samples collected from Elliott silt loam lysimeter plots during the period May 1 to April 30 during each of the data years 1971-1972, 1972-1973, and 1973-1974. Water samples were collected from fertilized and irrigated control or check plots, 1, and maximum, 4, sludge-treated plots located in either a north, N, or south, S, series of plots adjacent to an instrument house. Summary measurements include data from two control plots and one maximum sludge-treated plot in each of two series of plots.

Year	Location and Treatment	Runoff Water					Drainage Water				
		$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$	$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$
71-72	S1	22.20	35.61	6.18	7.56	4.76	0.80	1.04	0.21	0.29	5.14
	N1	50.86	79.52	16.05	15.11	6.30	1.77	3.77	0.10	0.20	9.10
	S4	17.06	33.82	4.47	5.92	4.06	10.43	20.44	2.39	2.00	7.72
	N4	36.06	49.42	16.21	15.19	4.47	0.51	0.52	0.26	0.21	6.14
72-73	S1	24.53	42.81	8.45	9.00	4.59	1.94	2.22	1.10	1.04	3.50
	N1	45.83	70.69	15.99	14.30	5.49	1.50	3.24	0.36	0.32	10.16
	S4	21.32	29.71	12.55	9.03	4.41	1.38	3.14	0.51	0.43	7.42
	N4	51.70	58.11	26.35	23.00	4.42	2.70	7.95	0.51	0.46	10.39
73-74	S1	24.44	51.33	7.39	8.43	4.13	1.23	1.48	0.70	0.42	11.02
	N1	50.53	76.32	11.89	14.54	8.76	5.69	21.09	0.42	0.40	17.37
	S4	10.06	7.43	9.29	5.52	4.58	1.39	3.71	0.31	0.37	6.68
	N4	63.95	102.32	20.72	17.10	6.48	3.04	6.03	0.44	0.29	30.34

Table V: Arithmetic mean, $\bar{X}$, standard deviation, s, median, M, geometric mean, $\hat{\mu}$, and geometric standard deviation, $\hat{\sigma}$, for Fe concentrations as ppm in runoff and drainage water samples collected from Plainfield loamy sand lysimeter plots during the period May 1 to April 30 during each of the data years 1971-1972, 1972-1973, and 1973-1974. Water samples were collected from fertilized and irrigated control or check plots, 1, and maximum, 4, sludge-treated plots located in either a north, N, or south, S, series of plots adjacent to an instrument house. Summary measurements include data from two control plots and one maximum sludged-treated plot in each of two series of plots.

Year	Location and Treatment	Runoff Water					Drainage Water				
		$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$	$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$
71-72	S1	3.92	3.65	1.74	2.13	4.21	5.64	11.07	0.56	0.56	11.23
	N1	23.37	41.16	5.59	7.23	4.74	1.52	1.74	0.72	0.80	3.38
	S4	46.46	43.82	28.08	22.91	4.57	0.31	0.48	0.04	0.10	6.50
	N4	25.21	46.73	3.52	5.13	6.95	1.25	3.93	0.07	0.09	8.11
72-73	S1	33.09	42.76	15.40	11.40	6.03	1.27	3.05	0.20	0.28	7.04
	N1	46.21	85.53	15.74	11.29	7.27	2.65	7.57	0.41	0.32	13.41
	S4	44.28	49.51	23.50	23.01	3.69	1.34	3.05	0.47	0.46	6.67
	N4	70.53	56.84	74.60	33.62	4.86	0.98	2.04	0.18	0.20	8.10
73-74	S1	36.23	96.69	7.70	9.66	5.10	1.80	3.87	0.58	0.51	9.14
	N1	24.01	50.52	4.72	6.92	4.53	4.43	7.84	1.78	1.81	4.43
	S4	24.47	36.38	9.91	7.63	5.84	3.05	16.88	0.17	0.05	37.00
	N4	105.86	75.67	90.96	64.09	3.93	1.12	5.23	0.20	0.16	10.31

Although drainage water from sludge-treated plots contained total Fe contents which generally exceeded maximum soluble Fe contents recommended for public water supplies, it seems probable that only a small proportion of the total Fe was in soluble form. At any rate, total Fe contents in drainage water were not higher than soluble contents in many ground water sources not considered to be a problem by users (Miller et al.[10]). Like total Fe it seems probable that only a small fraction of the total Mn measured in drainage water was in soluble form. Nevertheless, even mean total concentrations of Mn in drainage waters did not generally exceed maximum recommended levels for soluble Mn in public water supplies.

Table VI: Arithmetic mean, $\bar{X}$, standard deviation, s, median, M, geometric mean, $\hat{\mu}$, and geometric standard deviation, $\hat{\sigma}$, for Mn concentrations as ppm in runoff and drainage water samples collected from Blount silt loam lysimeter plots during the period May 1 to April 30 during each of the data years 1971-1972, 1972-1973, and 1973-1974. Water samples were collected from fertilized and irrigated control or check plots, 1, and maximum, 4, sludge-treated plots located in either a north, N, or south, S, series of plots adjacent to an instrument house. Summary measurements include data from three replications in each of two series of plots.

Year	Location and Treatment	Runoff Water					Drainage Water				
		$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$	$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$
71-72	S1	0.67	1.12	0.21	0.24	4.38	0.050	0.096	0.008	0.014	5.00
	N1	1.48	3.84	0.15	0.25	6.53	0.038	0.064	0.007	0.014	4.07
	S4	0.34	0.54	0.09	0.13	4.10	0.019	0.034	0.008	0.009	3.00
	N4	0.40	0.83	0.09	0.12	4.45	0.039	0.053	0.015	0.018	3.67
72-73	S1	1.20	2.32	0.25	0.30	6.24	0.035	0.067	0.013	0.015	3.73
	N1	1.09	1.68	0.41	0.35	5.52	0.020	0.021	0.014	0.012	3.17
	S4	0.90	2.09	0.19	0.20	6.47	0.022	0.022	0.015	0.015	2.40
	N4	0.47	0.78	0.16	0.18	4.19	0.041	0.054	0.015	0.018	2.83
73-74	S1	0.95	2.09	0.16	0.21	6.10	0.228	0.803	0.016	0.027	5.59
	N1	2.14	3.88	0.35	0.40	7.81	0.071	0.267	0.016	0.015	4.27
	S4	0.92	1.29	0.24	0.24	6.81	0.069	0.308	0.013	0.017	3.06
	N4	0.71	2.03	0.21	0.19	4.48	0.083	0.442	0.013	0.017	3.41

Table VII: Arithmetic mean, $\bar{X}$, standard deviation, s, median, M, geometric mean, $\hat{\mu}$, and geometric standard deviation, $\hat{\sigma}$, for Mn concentrations as ppm in runoff and drainage water samples collected from Elliott silt loam lysimeter plots during the period May 1 to April 30 during each of the data years 1971-1972, 1972-1973, and 1973-1974. Water samples were collected from fertilized and irrigated control or check plots, 1, and maximum, 4, sludge-treated plots located in either a north, N, or south, S, series of plots adjacent to an instrument house. Summary measurements include data from two control plots and one maximum sludge-treated plot in each of two series of plots.

Year	Location and Treatment	Runoff Water					Drainage Water				
		$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$	$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$
71-72	S1	0.55	0.93	0.18	0.19	4.40	.014	.017	.007	.008	3.38
	N1	1.23	1.84	0.26	0.40	5.16	.032	.055	.006	.010	5.10
	S4	0.52	0.86	0.16	0.20	4.23	.045	.053	.024	.030	2.33
	N4	0.83	0.91	0.36	0.43	3.78	.026	.035	.014	.019	1.95
72-73	S1	0.68	1.28	0.23	0.22	4.82	.027	.034	.014	.013	4.15
	N1	0.95	1.65	0.26	0.22	6.75	.018	.026	.009	.009	3.67
	S4	0.57	0.77	0.75	0.25	4.22	.133	.233	.038	.051	3.82
	N4	1.00	1.10	0.42	0.52	3.56	.032	.057	.014	.017	2.65
73-74	S1	1.04	2.46	0.19	0.21	7.05	.018	.018	.012	.012	2.42
	N1	1.85	2.94	0.47	0.47	6.71	.234	.738	.017	.027	6.04
	S4	0.25	0.19	0.23	0.11	8.06	.091	.270	.015	.025	3.28
	N4	2.56	5.75	0.52	0.57	6.45	.052	.086	.013	.022	3.50

Table VIII: Arithmetic mean, $\bar{X}$, standard deviation, s, median, M, geometric mean, $\hat{\mu}$, and geometric standard deviation, $\hat{\sigma}$, for Mn concentrations as ppm in runoff and drainage water samples collected from Plainfield loamy sand lysimeter plots during the period May 1 to April 30 during each of the data years 1971-1972, 1972-1973, and 1973-1974. Water samples were collected from fertilized and irrigated control or check plots, 1, and maximum, 4, sludge-treated plots located in either a north, N, or south, S, series of plots adjacent to an instrument house. Summary measurements include data from two control plots and one maximum sludge-treated plot in each of two series of plots.

Year	Location and Treatment	Runoff Water					Drainage Water				
		$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$	$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$
71-72	S1	0.07	0.05	0.04	0.05	1.98	0.119	0.225	0.014	0.018	7.61
	N1	0.53	0.82	0.12	0.17	4.98	0.041	0.045	0.017	0.021	3.57
	S4	1.01	1.04	0.87	0.59	3.25	0.013	0.017	0.006	0.005	6.60
	N4	0.42	0.67	0.07	0.10	7.40	0.012	0.035	0.002	0.003	4.00
72-73	S1	0.79	0.94	0.38	0.25	6.81	0.022	0.061	0.007	0.007	4.00
	N1	0.99	2.00	0.19	0.26	2.71	0.054	0.158	0.012	0.016	4.06
	S4	0.73	0.90	0.33	0.33	4.02	0.011	0.014	0.006	0.006	4.50
	N4	1.35	1.17	0.60	0.64	4.67	0.009	0.010	0.005	0.005	3.20
73-74	S1	1.23	3.39	0.16	0.26	5.42	0.070	0.196	0.018	0.023	3.61
	N1	1.01	2.02	0.19	0.29	4.55	0.105	0.199	0.043	0.046	3.46
	S4	0.80	1.55	0.18	0.17	7.03	0.086	0.486	0.007	0.008	3.63
	N4	2.68	1.74	3.06	1.56	4.61	0.029	0.148	0.007	0.008	2.75

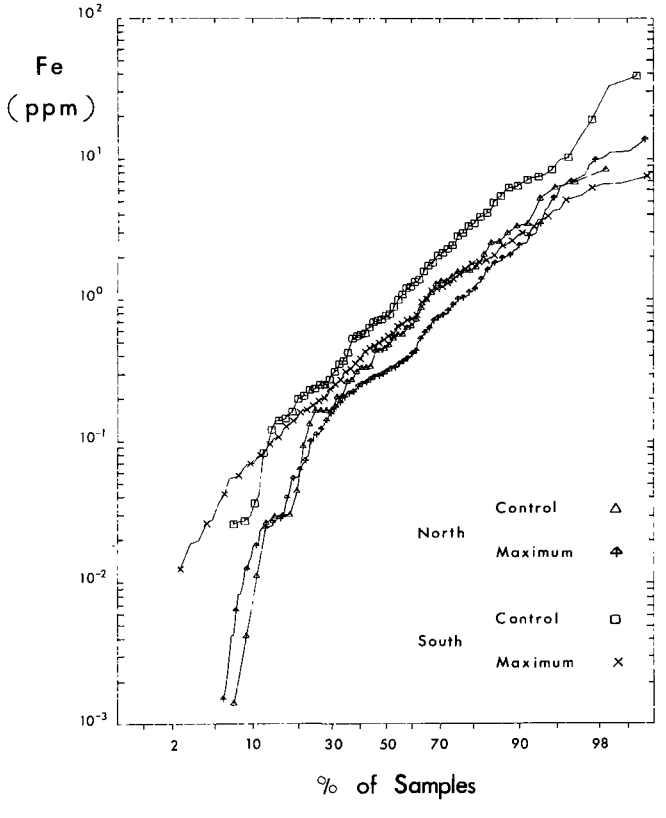

Figure 4: Frequency distribution of Fe concentrations during the period May 1, 1972 to April 30, 1973, in drainage water samples collected from field lysimeter plots containing Blount silt loam soil. Distributions of Fe concentrations are percent of samples containing less than amounts shown on the vertical axis. Median concentrations and standard deviations are presented in Table III.

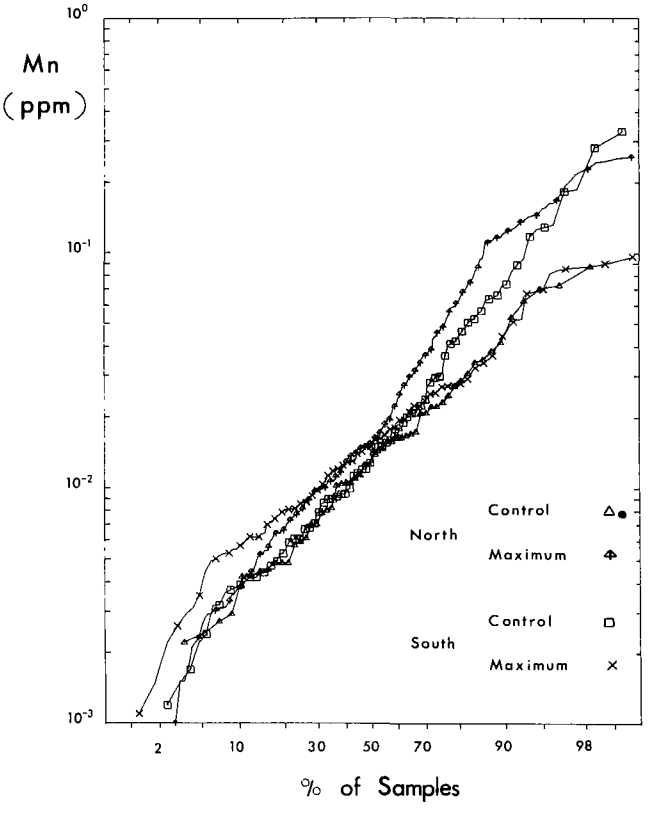

Figure 5: Frequency distribution of Mn concentrations during the period May 1, 1972 to April 30, 1973, in drainage water samples collected from field lysimeter plots containing Blount silt loam soil. Distributions of Mn concentrations are percent of samples containing less than amounts shown on the vertical axis. Median concentrations and standard deviations are presented in Table VI.

Concentrations of Zn, Cu, and Cd in Runoff Water

Like the Fe and Mn data previously discussed, frequency distribution graphs for concentrations of Zn, Cu, and Cd (Figures 6, 7, and 8, respectively) indicated that the results were best described in terms of geometric mean concentrations and their corresponding geometric standard deviations.

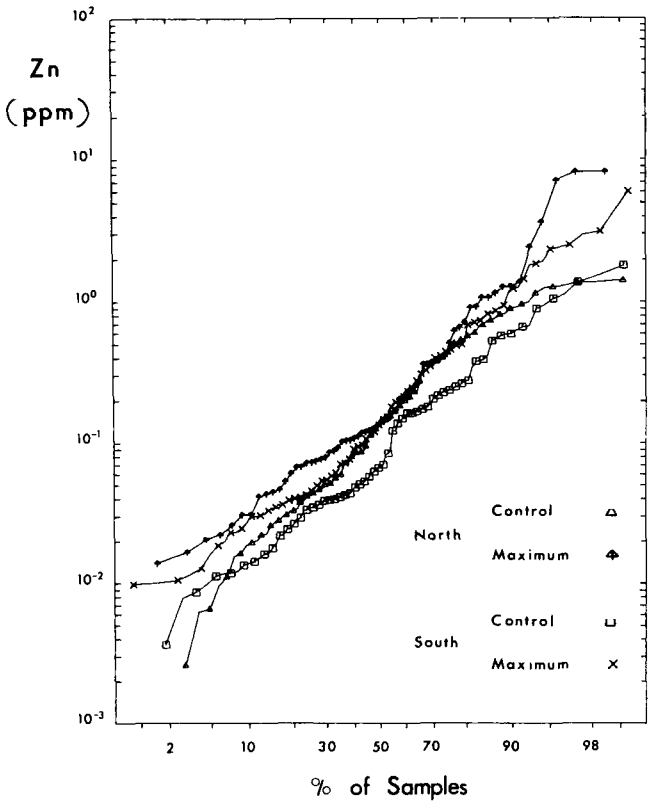

Figure 6: Frequency distribution of Zn concentrations during the period May 1, 1972 to April 30, 1973, in runoff water samples collected from field lysimeter plots containing Blount silt loam soil. Distributions of Zn concentrations are percent of samples containing less than amounts shown on the vertical axis. Median concentrations and standard deviations are presented in Table IX.

Inspection of results reported in Tables IX through XVII show that runoff water from lysimeter plots subjected to more or less normal agricultural management practices had mean concentrations in the range of 0.05- to 0.15- ppm Zn, 0.016- to 0.038- ppm Cu, and 0.003- to 0.008- ppm Cd. Where sludge was applied at rates several times amounts required to supply N and P fertility, mean levels ranged from 0.10- to 0.63- ppm Zn, 0.036- to 0.170- ppm Cu, and 0.003- to 0.027- ppm Cd. Compared with control plots, runoff waters from sludge-treated Blount silt loam plots, located in the south series, had higher total Zn contents during 1971-72 ($Pr<0.05$), 1972-73 ($Pr<0.01$). and 1973-74 ($Pr<0.01$), while those located in the north series had higher levels only in 1972-73 ($Pr<0.05$). Maximum sludge applications caused increased levels of Zn in runoff waters from Elliott silt loam plots during 1971-72 ($Pr<0.05$) and 1972-73 ($Pr<0.01$) for the one located in the south series and 1971-72 ($Pr<0.05$), 1972-73 ($Pr<0.01$), and 1973-74 ($Pr<0.05$) for the one located in the north series. Mean Zn contents of runoff waters from Plainfield loamy sand were significantly increased in 1971-72 and 1972-73 ($Pr<0.01$) by sludge applications on the plot in the south series and in 1972-73 and 1973-74 ($Pr<0.01$) by sludge applications on the plot in the north series. Copper contents were increased in runoff waters by sludge applications on Blount silt loam during all three years ($Pr<0.01$) for plots in the south series and in 1971-72 ($Pr<0.05$) and in 1972-73 ($Pr<0.01$) for plots in the north series. Except for those waters collected in 1973-74 from plots in the south series, runoff waters from Elliott silt loam and Plainfield loamy sand plots had higher Cu contents attributable to maximum sludge application during every year, regardless of location in a particular series ($Pr<0.01$). Significant increases in mean Cd concentrations ($Pr<0.01$) due to maximum sludge applications were found in runoff waters from Blount silt loam plots in 1972-73 and 1973-74 for those located in the north series. Sludge application on Elliott silt loam plots resulted in higher mean Cd levels during 1971-72 ($Pr<0.05$) and 1972-73 ($Pr<0.01$) in runoff waters from the plot in the south series and during 1971-72 ($Pr<0.05$), 1972-73 ($Pr<0.01$), and 1973-74 ($Pr<0.01$) in runoff waters from the plot located in the north series. Runoff waters collected from Plainfield loamy sand plots located in the south series had higher Cd contents as a result of sludge application only in 1972-72 ($Pr<0.01$). On the other hand, runoff waters from the same soil type, but a plot located in the north series, had higher mean Cd contents that were significantly higher in 1972-73 ($Pr<0.01$) and 1973-74 ($Pr<0.05$) where sludge was applied.

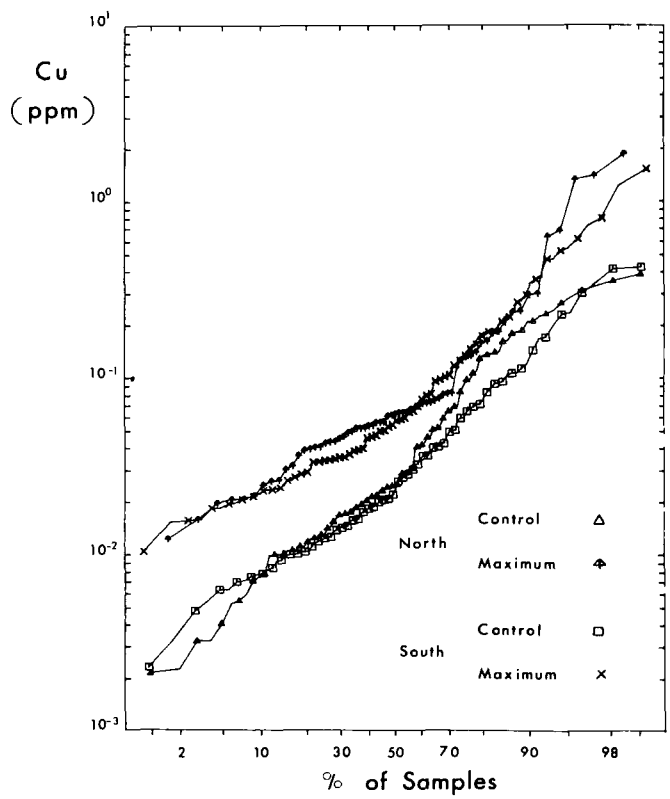

Figure 7: Frequency distribution of Cu concentrations during the period May 1, 1972 to April 30, 1973, in runoff water samples collected from field lysimeter plots containing Blount silt loam soil. Distributions of Cu concentrations are percent of samples containing less than amounts shown on the vertical axis. Median concentrations and standard deviations are presented in Table XII.

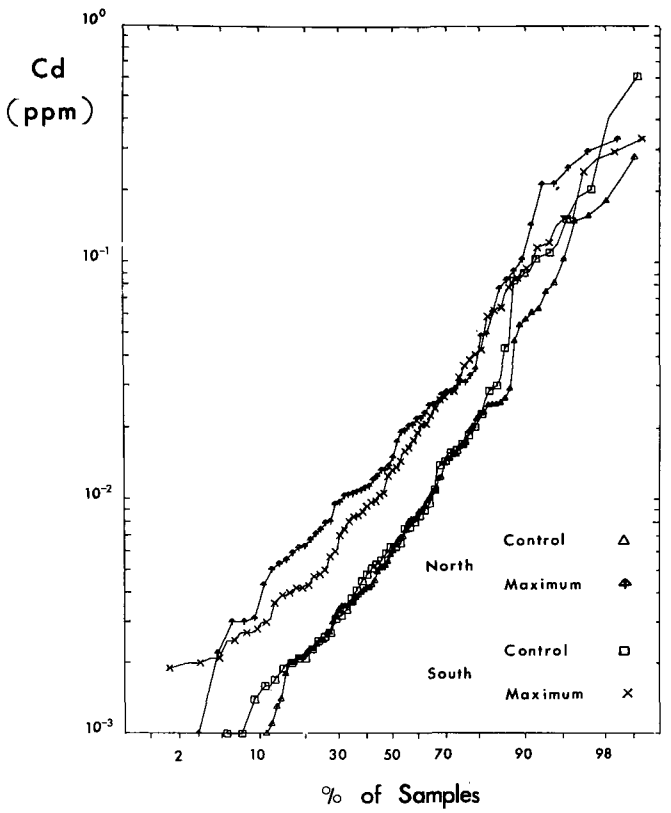

Figure 8: Frequency distribution of Cd concentrations during the period May 1, 1972 to April 30, 1973, in runoff water samples collected from field lysimeter plots containing Bount silt loam soil. Distributions of Cd concentrations are percent of samples containing less than amounts shown on the vertical axis. Median concentrations and standard deviations are presented in Table XV.

These data for total Zn, Cu, and Cd contents in runoff waters from lysimeter plots may be the only ones compiled, since none were found in the literature. However, concentrations of these metals have been measured in urban runoff waters by Klein et al. (1974). They found average concentrations of 1.6-, 0.46-, and 0.025- ppm Zn, Cu, and Cd, respectively, in 35 grab samples of runoff water collected at several areas in New York. Sampled runoff events were produced by rains of various intensities following a variety of antecedent dry weather periods. With these limited numbers of data it appears that urban runoff water can be expected to contain much higher levels of Zn and Cu and about the same concentration of Cd as runoff waters from agricultural lands amended with digested sludge at rates which far exceeded requirements of crop plants for supplementary N. Acid extractable contents of Zn, Cu, Cd, Pb, Ni, and Hg in runoff waters from plots treated with various rates of sludge from the north Toronto sewage treatment plant were measured during several events in 1972 and 1973 (Environment Canada[3]). Unfortunately acid extractable metals in runoff waters were reported only in terms of kg/ha total losses from lands with different slopes and concentrations of metals for comparison with data presented here were not included. Nevertheless, heavy metal losses were not noticeably increased by sludge application except where sludge was eroded immediately following an application. They concluded that "Heavy metal losses tend to be small particularly where sludge of low metal content is used; the mobility of metals when at higher concentrations cannot be predicted from the present work" (Environment Canada[3] p. 23).

On the basis of consumer taste preference and because water treatment processes may not remove appreciable amounts of Zn and Cu it was recommended in *Water Quality Criteria 1972*[2] that levels in public water supply sources should not exceed 5 ppm of Zn and 1 ppm of Cu. It was further recommended, on the basis of adverse physiological effects, that Cd levels should not exceed 0.010 ppm. At the maximum recommended level for Cd, human intake of the element from water would amount to about one-third of the Cd intake as a constituent of foods. According to these recommendations mean total concentrations of both Zn

Table IX: Arithmetic mean, $\bar{X}$, standard deviation, s, median, M, geometric mean, $\hat{\mu}$, and geometric standard deviation, $\hat{\sigma}$, for Zn concentrations as ppm in runoff and drainage water samples collected from Blount silt loam lysimeter plots during the period May 1 to April 30 during each of the data years 1971-1972, 1972-1973, and 1973-1974. Water samples were collected from fertilized and irrigated control or check plots, 1, and maximum, 4, sludge-treated plots located in either a north, N, or south, S, series of plots adjacent to an instrument house. Summary measurements include data from three replications in each of two series of plots.

Year	Location and Treatment	Runoff Water					Drainage Water				
		X	s	M	$\hat{\mu}$	$\hat{\sigma}$	X	s	M	$\hat{\mu}$	$\hat{\sigma}$
71-72	S1	0.14	0.19	.066	0.08	2.96	0.028	0.026	0.019	0.019	2.47
	N1	0.25	0.51	.103	0.10	4.07	0.031	0.034	0.016	0.021	2.43
	S4	0.17	0.16	.107	0.12	2.30	0.052	0.043	0.035	0.037	2.41
	N4	0.28	0.54	.101	0.12	3.57	0.047	0.059	0.022	0.021	4.05
72-73	S1	0.24	0.42	.068	0.09	4.44	0.026	0.028	0.016	0.016	3.06
	N1	0.32	0.41	.141	0.12	5.28	0.027	0.035	0.016	0.015	3.80
	S4	0.51	1.10	.147	0.16	4.46	0.085	0.307	0.035	0.038	2.92
	N4	0.89	2.19	.137	0.21	4.76	0.026	0.028	0.018	0.018	2.50
73-74	S1	0.13	0.25	.047	0.05	4.49	0.041	0.085	0.018	0.016	4.50
	N1	0.32	0.60	.070	0.07	7.93	0.038	0.087	0.017	0.016	4.06
	S4	0.31	0.40	.131	0.14	4.19	0.048	0.043	0.035	0.033	2.58
	N4	0.18	0.16	.141	0.13	2.61	0.025	0.047	0.015	0.015	2.93

and Cu were well within the tolerances for public water sources, even in runoff water from maximum sludge-treated plots. However, mean total Cd concentrations in runoff waters from sludge-treated plots may sometimes exceed allowable limits. Results from several studies in the literature suggest that recommended maximum Cd levels in public water sources were established at levels just slightly above those existing in many streams. Furthermore, it can be seen from the results reported here that the agreement between maximum recommended levels and the upper range of mean total Cd concentrations observed in runoff water from control plots were rather remarkable. Thus, if a major proportion of Cd in runoff waters exists in soluble forms, no increase over background levels would be acceptable in water discharged directly to public sources. However, if sludge applications were limited to rates that supply N at optimum amounts for crop production and insoluble fractions of total Cd present in runoff waters were retained on the field or farm by erosion control practices or sediment basins, soluble contents in runoff water reaching streams may not exceed recommended maximum levels.

Table X: Arithmetic mean, $\bar{X}$, standard deviation, s, median, M, geometric mean, $\hat{\mu}$, and geometric standard deviation, $\hat{\sigma}$, for Zn concentrations as ppm in runoff and drainage water samples collected from Elliott silt loam lysimeter plots during the period May 1 to April 30 during each of the data years 1971-1972, 1972-1973, and 1973-1974. Water samples were collected from fertilized and irrigated control or check plots, 1, and maximum, 4, sludge-treated plots located in either a north, N, or south, S, series of plots adjacent to an instrument house. Summary measurements include data from two control plots and one maximum sludge-treated plot in each of the two series of plots.

Year	Location and Treatment	Runoff Water					Drainage Water				
		$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$	$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$
71-72	S1	0.10	0.12	0.06	0.06	3.49	.027	.028	.018	.018	2.67
	N1	0.24	0.26	0.16	0.15	2.75	.025	.027	.011	.015	2.73
	S4	0.17	0.19	0.09	0.12	2.31	1.837	3.155	.675	.688	3.91
	N4	0.54	0.55	0.40	0.34	2.90	.049	.037	.038	.040	1.92
72-73	S1	0.15	0.24	0.06	0.06	4.30	.037	.037	.022	.022	3.00
	N1	0.25	0.35	0.11	0.09	5.30	.018	.063	.010	.008	3.75
	S4	0.29	0.39	0.15	0.15	3.07	.418	.444	.243	.271	2.48
	N4	0.60	0.60	0.39	0.34	3.18	.029	.031	.023	.021	2.33
73-74	S1	0.13	0.19	0.06	0.07	3.26	.031	.036	.020	.019	3.11
	N1	0.27	0.33	0.10	0.11	4.10	.046	.135	.015	.014	4.71
	S4	0.13	0.11	0.10	0.10	4.39	.197	.263	.134	.151	1.87
	N4	0.58	0.79	0.29	0.25	4.00	.083	.100	.032	.047	3.00

Table XI: Arithmetic mean, $\bar{X}$, standard deviation, s, median, M, geometric mean, $\hat{\mu}$, and geometric standard deviation, $\hat{\sigma}$, for Zn concentrations as ppm in runoff and drainage water sample collected from Plainfield loamy sand lysimeter plots during the period May 1 to April 30 during each of the data years 1971-1972, 1972-1973, and 1973-1974. Water samples were collected from fertilized and irrigated control or check plots, 1, and maximum, 4, sludge-treated plots located in either a north, N, or south, S, series of plots adjacent to an instrument house. Summary measurements include data from two control plots and one maximum sludge-treated plot in each of two series of plots.

Year	Location and Treatment	Runoff Water					Drainage Water				
		$\bar{X}$	s	M		$\hat{\sigma}$	$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$
71-72	S1	0.07	0.06	0.05	0.06	2.07	0.032	0.034	0.016	0.016	3.69
	N1	0.15	0.18	0.07	0.09	2.88	0.020	0.017	0.013	0.013	2.92
	S4	0.45	0.49	0.26	0.31	2.37	0.016	0.013	0.015	0.012	2.67
	N4	0.35	0.41	0.10	0.18	3.54	0.019	0.018	0.013	0.015	1.93
72-73	S1	0.21	0.25	0.12	0.10	4.21	0.036	0.175	0.009	0.008	4.25
	N1	0.26	0.32	0.13	0.13	3.27	0.047	0.247	0.018	0.018	2.78
	S4	0.37	0.42	0.22	0.22	2.96	0.019	0.011	0.019	0.015	2.20
	N4	0.95	1.21	0.51	0.44	4.14	0.039	0.154	0.020	0.022	2.09
73-74	S1	0.27	0.73	0.07	0.08	3.91	0.022	0.030	0.015	0.013	3.08
	N1	0.15	0.20	0.08	0.09	2.60	0.038	0.043	0.026	0.026	2.31
	S4	0.20	0.27	0.10	0.10	3.73	0.029	0.087	0.016	0.011	4.09
	N4	1.26	1.82	0.94	0.63	4.14	0.023	0.043	0.015	0.014	3.00

Table XII: Arithmetic mean, $\bar{X}$, standard deviation, s, median, M, geometric mean, $\hat{\mu}$, and geometric standard deviation, $\hat{\sigma}$, for Cu concentrations as ppm in runoff and drainage water samples collected from Blount silt loam lysimeter plots during the period May 1 to April 30 during each of the data years 1971-1972, 1972-1973, and 1973-1974. Water samples were collected from fertilized and irrigated control or check plots, 1, and maximum, 4, sludge-treated plots located in either a north, N, or south, S, series of plots adjacent to an instrument house. Summary measurements include data from three replications in each of two series of plots.

Year	Location and Treatment	Runoff Water					Drainage Water				
		$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$	$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$
71-72	S1	0.032	0.032	0.021	0.022	2.36	0.011	0.020	0.005	0.007	2.43
	N1	0.061	0.133	0.022	0.025	3.28	0.006	0.005	0.003	0.004	2.25
	S4	0.053	0.027	0.049	0.047	1.70	0.022	0.019	0.014	0.016	2.31
	N4	0.069	0.096	0.039	0.043	2.47	0.014	0.017	0.006	0.007	3.29
72-73	S1	0.059	0.093	0.022	0.028	3.46	0.013	0.013	0.010	0.009	2.56
	N1	0.081	0.159	0.025	0.034	3.65	0.015	0.025	0.008	0.008	3.25
	S4	0.145	0.253	0.055	0.072	2.88	0.104	0.834	0.028	0.026	3.00
	N4	0.204	0.468	0.063	0.080	3.07	0.016	0.016	0.012	0.011	2.73
73-74	S1	0.046	0.073	0.019	0.024	2.83	0.019	0.026	0.011	0.012	2.67
	N1	0.099	0.174	0.031	0.033	4.48	0.023	0.051	0.011	0.012	2.67
	S4	0.099	0.099	0.058	0.063	2.67	0.040	0.059	0.027	0.029	2.17
	N4	0.060	0.032	0.051	0.054	1.57	0.017	0.018	0.013	0.013	2.31

Concentrations of Zn, Cu and Cd in Drainage Water

As may be seen in example Figures 9, 10, 11 concentrations of Zn, Cu, and Cd found in drainage water could have been represented fairly well by a straight line when they were plotted in a log-normal frequency distribution array. Therefore, results were most appropriately interpreted in terms of estimated geometric mean concentrations and geometric standard deviation. These statistical measurements are presented in Tables IX through XVII along with values for other methods of expressing central tendenices and variations of data. As previously mentioned, a great deal more confidence was placed on the results from the Blount silt loam than on results from other soil types. Mean concentrations of metals in drainage water from Blount silt loam plots were compilations of results from three replications of each treatment in each series, whereas sludge-treated plots of the other 2 soil types were not replicated. It was also mentioned earlier that during the early years of operations the Elliott silt loam sludge-treated plot, located in the south series of plots (S4, Table X), often leaked sludge into the tile system following an irrigation. Thus very little significance is attached to the fact than Zn and other heavy metal elements appeared in relatively high levels in drainage waters from this particular plot.

Geometric mean concentrations of total Zn in drainage waters from Blount silt loam control plots varied from 0.015 to 0.021 ppm and from 0.015 to 0.038 ppm in samples from sludge-treated plots on the same soil type. Drainage waters from Elliott silt loam had mean Zn contents that ranged from 0.008 to 0.022 ppm in samples from control plots and from 0.021 to 0.047 ppm in samples from the sludge-treated plot in the north series. Mean Zn contents in drainage waters from the sludge-treated Elliott silt loam plot in the south series were 0.688, 0.271, and 0.151 ppm in successive years from 1971 to 1974. These values indicated that the amount of direct contamination of drainage water by sludge decreased with the succeeding years, but nevertheless remained at levels too high to have occurred by simple leaching processes. Plainfield loamy sand discharged drainage water from control plots having mean Zn concentrations ranging from 0.008 to 0.026 ppm as compared to mean Zn concentrations ranging from 0.011 to 0.022 ppm in similar waters from sludge-treated plots. Levels of Zn in drainage waters from sludge-treated Blount plots in the south series were significantly higher (Pr 0.01) during all three years as compared to levels in similar water samples from control plots, whereas, Zn contents of waters from plots in the north series did not differ with treatment. Differences in Zn contents of drainage waters from Elliott silt loam plots were similar to those from Blount silt loam plots. Maximum sludge treatments increase Zn contents in drainage waters from the Elliott silt loam plot in the south series (Pr 0.01) during all three years, but not in the north series. Only in 1972-73 did sludge treatments on Plainfield loamy sand cause increased Zn levels in drainage waters (Pr 0.05). During this one year waters from Plainfield loamy sand plots in both the north and south series were similarly affected by sludge treatments.

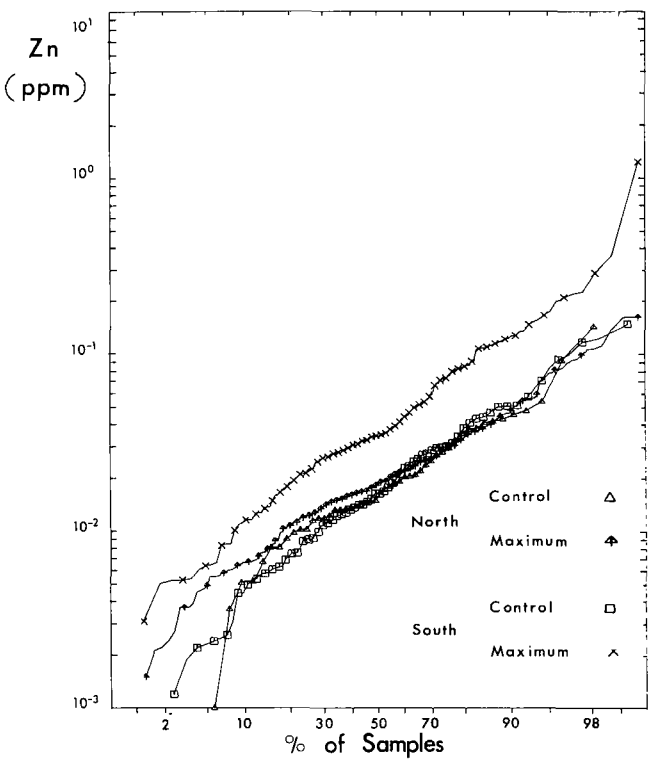

Figure 9: Frequency distribution of Zn concentrations during the period May 1, 1972 to April 30, 1973, in drainage water samples collected from field lysimeter plots containing Blount silt loam soil. Distributions of Zn concentrations are percent of samples containing less than amounts shown on the vertical axis. Median concentrations and standard deviations are presented in Table IX.

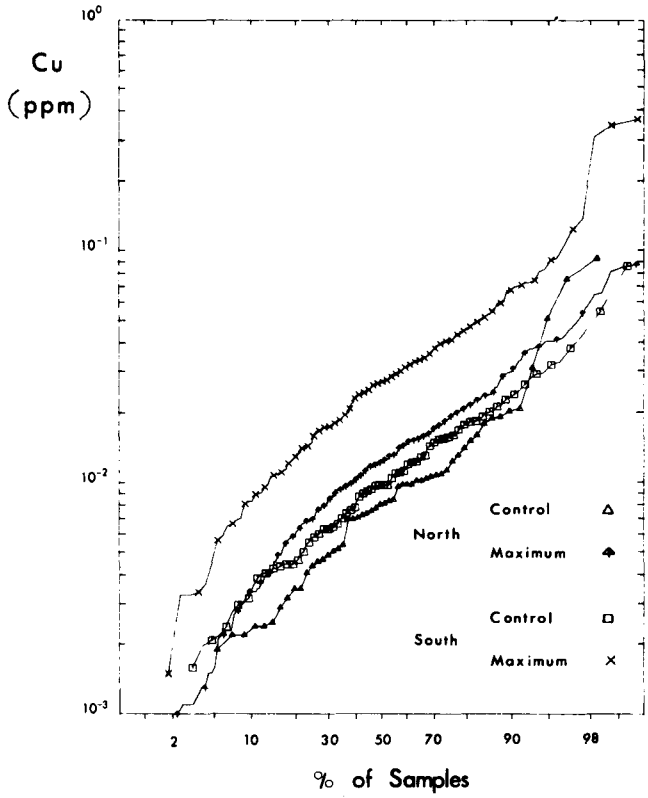

Figure 10: Frequency distribution of Cu concentrations during the period May 1, 1972 to April 30, 1973, in drainage water samples collected from field lysimeter plots containing Blount silt loam soil. Distributions of Cu concentrations are percent of samples containing less than amounts shown on the vertical axis. Median concentrations and standard deviations are presented in Table XII.

During the three years, mean Cu concentrations in D drainage waters from Blount silt loam control plots ranged from 0.007 to 0.012 ppm in samples from the south series and from 0.004 to 0.012 ppm in samples from the north series. Drainage waters from sludge-treated Blount silt loam plots had mean Cu concentrations that ranged from 0.016 to 0.029 ppm in those collected from plots in the south series and from 0.007 to 0.013 ppm in samples from the north series. Mean Cu contents of drainage waters from Elliott silt loam control plots (Table XIII) ranged from 0.007 to 0.010 ppm in samples from the south series and from 0.005 to 0.010 ppm in samples from the north series. During successive years mean Cu contents were 0.074, 0.044, and 0.039 ppm in drainage waters from the sludge-treated Elliott plot in the south series which initially produced water directly contaminated with sludge as was discussed earlier. On the other hand, drainage waters from the sludge-treated Elliott silt loam plot in the north series contained mean Cu concentrations ranging from 0.013 to 0.022 ppm. Thus, in the absence of direct contamination Cu levels in drainage water from sludge-treated Elliott silt loam were similar to those observed in samples from Blount silt loam. Regardless of location in north or south series, Plainfield loamy sands (Table XIV) produced drainage waters having mean Cu contents ranging from 0.005 to 0.007 ppm in samples from control plots and from 0.007 to 0.015 ppm in samples from sludge-treated plots. Sludge applications significantly ($Pr \leq 0.01$) increased mean Cu levels in drainage waters from Blount silt loam plots located in the south series during all years and during the 1972–73 data year ($Pr < 0.05$) in samples from plots located in the north series. Sludge treatments caused higher levels of Cu in drainage water from Elliott plots during all years ($Pr \leq 0.01$), but for reasons mentioned above evidence is uncertain with regard to the data collection from the sludge-treated plot in the south series. Mean Cu levels were significantly ($Pr \leq 0.01$) increased by sludge applications in drainage waters from Plainfield loamy sand plots in the south series during 1972–73 and 1973–74 and north series during 1971–72 and 1972–73.

Table XIII: Arithmetic mean, $\bar{X}$, standard deviation, s, median, M, geometric mean, $\hat{\mu}$, and geometric standard deviation, $\hat{\sigma}$, for Cu concentrations as ppm in runoff and drainage water samples collected from Elliott silt loam lysimeter plots during the period May 1 to April 30 during each of the data years 1971–1972, 1972–1973, and 1973–1974. Water samples were collected from fertilized and irrigated control or check plots, 1, and maximum, 4, sludge-treated plots located in either a north, N, or south, S, series of plots adjacent to an instrument house. Summary measurements include data from two control plots and one maximum sludge-treated plot in each of two series of plots.

Year	Location and Treatment	Runoff Water					Drainage Water				
		$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$	$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$
71-72	S1	0.027	0.026	0.019	0.018	2.44	0.009	0.007	0.007	0.007	2.14
	N1	0.041	0.040	0.026	0.026	2.73	0.006	0.005	0.005	0.005	2.20
	S4	0.054	0.046	0.037	0.043	1.91	0.378	0.819	0.048	0.074	5.20
	N4	0.123	0.120	0.090	0.081	2.72	0.019	0.017	0.011	0.013	2.38
72-73	S1	0.030	0.042	0.018	0.017	3.29	0.013	0.011	0.009	0.010	2.00
	N1	0.055	0.078	0.023	0.027	3.26	0.010	0.023	0.007	0.005	4.00
	S4	0.071	0.082	0.042	0.048	2.26	0.073	0.141	0.036	0.044	2.25
	N4	0.160	0.160	0.097	0.098	2.81	0.022	0.014	0.018	0.018	1.89
73-74	S1			0.024	0.034	3.68	0.011	0.007	0.011	0.008	3.00
	N1	0.068	0.080	0.031	0.038	2.92	0.022	0.083	0.010	0.010	3.30
	S4	0.043	0.029	0.038	0.036	1.86	0.054	0.093	0.033	0.039	1.85
	N4	0.157	0.196	0.073	0.085	3.07	0.025	0.015	0.023	0.022	1.73

Table XIV: Arithmetic mean, $\bar{X}$, standard deviation, s, median, M, geometric mean, $\hat{\mu}$, and geometric standard deviation, $\hat{\sigma}$, for Cu concentrations as ppm in runoff and drainage water samples collected from Plainfield loamy sand lysimeter plots during the period May 1 to April 30 during each of the data years 1971-1972, 1972-1973, and 1973-1974. Water samples were collected from fertilized and irrigated control or check plots, 1, and maximum, 4, sludge-treated plots located in either a north, N, or south, S, series of plots adjacent to an instrument house. Summary measurements include data from two control plots and one maximum sludge-treated plot in each of two series of plots.

Year	Location and Treatment	Runoff Water					Drainage Water				
		$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$	$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$
71-72	S1	0.018	0.009	0.016	0.016	1.69	0.010	0.010	0.008	0.007	2.43
	N1	0.033	0.043	0.015	0.016	3.44	0.005	0.005	0.004	0.004	2.00
	S4	0.166	0.113	0.137	0.131	2.13	0.008	0.006	0.005	0.007	2.00
	N4	0.083	0.082	0.071	0.057	2.44	0.009	0.006	0.008	0.007	1.86
72-73	S1	0.049	0.058	0.024	0.025	3.84	0.009	0.018	0.005	0.005	3.20
	N1	0.053	0.078	0.034	0.024	4.54	0.007	0.007	0.005	0.005	2.80
	S4	0.096	0.099	0.072	0.066	2.45	0.011	0.007	0.009	0.009	2.11
	N4	0.220	0.257	0.132	0.125	3.05	0.009	0.006	0.007	0.007	2.29
73-74	S1	0.071	0.159	0.019	0.029	3.07	0.011	0.017	0.008	0.006	4.00
	N1	0.045	0.059	0.022	0.027	2.59	0.013	0.017	0.008	0.008	3.13
	S4	0.060	0.062	0.031	0.041	2.29	0.025	0.040	0.013	0.015	2.40
	N4	0.265	0.336	0.193	0.170	2.65	0.017	0.035	0.010	0.009	3.22

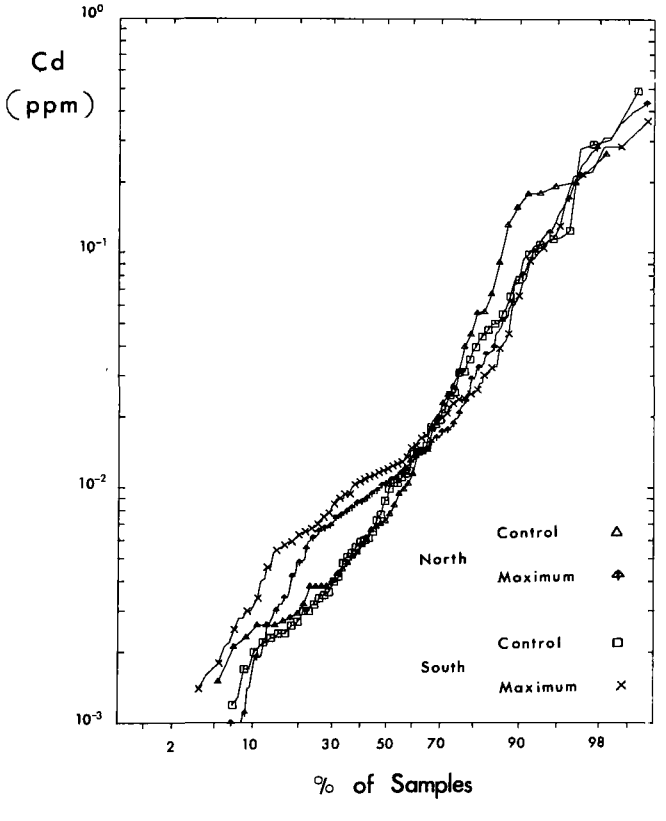

Figure 11: Frequency distribution of Cd concentrations during the period May 1, 1972 to April 30, 1973, in drainage water samples collected from field lysimeter plots containing Blount silt loam soil. Distributions of Cd concentrations are percent of samples containing less than amounts shown on the vertical axis. Median concentrations and standard deviations are presented in Table XV.

Drainage waters from sludge-treated Blount plots in the south series and significantly lower concentrations of Cu in 1971-72 ($Pr < 0.01$) than in all later years. Similarly treated Blount plots in the north series yielded drainage waters having significantly higher concentration of Cu in each succeeding year as compared to the year before, although 1973-74 waters were significantly higher in Cu content than 1972-73 waters at only the 5 percent probability level. Drainage waters from the sludge-treated Elliott plot in the north series had higher Cu levels in 1973-74 than in 1971-72 ($Pr < 0.05$). Copper levels were also higher in drainage waters collected from both north and south series of sludge-treated Plainfield sand in 1973-74 as compared 1972-73 waters ($Pr < 0.05$). Thus, these data indicate that Cu levels in drainage waters tend to increase with increased years of annual sludge applications.

Mean Cd concentrations in drainage waters from Blount silt loam control plots (Table 15) located in the south and north series ranged from 0.003 to 0.009 ppm and 0.003 to 0.011 ppm, respectively. Drainage waters from sludge-treated Blount silt loam plots located in the south series had mean Cd contents ranging from 0.006 to 0.013 ppm and a similar range of 0.004 to 0.010 ppm was observed in the north series. Ranges in mean Cd concentrations in drainage waters from control and sludge-treated Elliott plots were not appreciably different from those observed in waters from Blount silt loam except for samples collected from the sludge-treated plot located in the south series. Drainage waters from the sludge-treated Elliott silt loam plot in the south series had mean Cd concentrations that decreased from 0.043 ppm during 1971-72 to 0.017 ppm during 1973-74. Thus, changes with time in Cd concentrations in drainage waters from this particular plot were in agreement with changes in Zn and Cu concentrations and all these data confirm direct contamination of drains with sludge during early years of operation. Without regard to location, drainage waters from Plainfield loamy sand control plots had mean Cd concentrations ranging from 0.001 to 0.003 ppm as compared to mean concentrations ranging from 0.003 to 0.009 ppm in drainage waters from sludge-treated plots of the same soil type. Sludge applications

significantly increased Cd concentrations (Pr< 0.01) in Blount silt loam drainage waters during 1971-72 and 1973-74 from plots located in the south series. Cadmium concentrations in drainage waters were also increased (Pr< 0.01) during 1971-72 and 1973-74 by sludge applications on the Elliott plot located in the north series. Although drainage waters from the sludge-treated Elliott silt loam plot in the south series always contained significantly higher concentrations of Cd than waters from control plots, it was caused by direct contamination and thus is of little interest with regard to assessing metal transport in soils.

Mean Cd concentrations in drainage waters were increased (Pr<0.01) by sludge applications on Plainfield loamy sand plots during each of the sampling years for the plot in the north series and during 1972-73 from the plot in the south series.

Heavy metal concentrations in drainage waters from field plots or watersheds have seldom been reported. Where metals have been applied to soil surfaces as soluble salts and their concentrations measured at various soil profile depths after leaching with water, it has generally been conculded that they were rapidly fixed in the soil in forms not easily transported by percolating water.

Table XV: Arithmetic mean, $\bar{X}$, standard deviation, s, median M, geometric mean, $\hat{\mu}$, and geometric standard deviation, $\hat{\sigma}$, for Cd concentrations as ppm in runoff and drainage water samples collected from Blount silt loam lysimeter plots during the period May 1 to April 30 during each of the data years 1971-1972, 1972-1973, and 1973-1974. Water samples were collected from fertilized and irrigated control or check plots, 1, and maximum, 4, sludge-treated plots located in either a north, N, or south, S, series of plots adjacent to an instrument house. Summary measurements include data from three replications in each of two series of plots.

Year	Location and Treatment	Runoff Water					Drainage Water				
		$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$	$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$
71-72	S1	0.014	0.031	0.002	0.004	4.25	0.004	0.002	0.003	0.003	2.00
	N1	0.007	0.013	0.002	0.004	3.00	0.003	0.003	0.002	0.003	2.00
	S4	0.021	0.059	0.006	0.007	3.29	0.007	0.005	0.006	0.006	1.83
	N4	0.029	0.039	0.010	0.014	3.43	0.010	0.025	0.005	0.004	3.00
72-73	S1	0.036	0.101	0.006	0.008	5.00	0.035	0.081	0.009	0.009	5.89
	N1	0.023	0.049	0.006	0.007	4.86	0.042	0.077	0.008	0.011	5.64
	S4	0.040	0.082	0.013	0.015	3.80	0.031	0.061	0.012	0.013	3.92
	N4	0.049	0.091	0.015	0.018	4.17	0.038	0.112	0.011	0.010	5.50
73-74	S1	0.016	0.064	0.004	0.004	4.75	0.013	0.051	0.003	0.004	3.50
	N1	0.011	0.012	0.006	0.006	4.17	0.010	0.023	0.003	0.004	3.25
	S4	0.015	0.019	0.009	0.008	3.75	0.012	0.022	0.088	0.008	2.25
	N4	0.028	0.050	0.009	0.011	3.55	0.011	0.042	0.004	0.005	2.80

Table XVI: Arithmetic mean, $\bar{X}$, standard deviation, s, median, M, geometric mean, $\hat{\mu}$, and geometric standard deviation, $\hat{\sigma}$, for Cd concentrations as ppm in runoff and drainage water samples collected from Elliott silt loam lysimeter plots during the period May 1 to April 30 during each of the data years 1971-1972, 1972-1973, and 1973-1974. Water samples were collected from fertilized and irrigated control or check plots, 1, and maximum, 4, sludge-treated plots located in either a north, N, or south, S, series of plots adjacent to an instrument house. Summary measurements include data from two control plots and one maximum sludge-treated plot in each of two series of plots.

Year	Location and Treatment	Runoff Water					Drainage Water				
		$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$	$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$
71-72	S1	0.005	0.007	0.003	0.003	2.67	0.003	0.002	0.002	0.002	2.00
	N1	0.014	0.023	0.004	0.005	4.00	0.002	0.001	0.002	0.002	1.50
	S4	0.011	0.012	0.005	0.007	2.43	0.116	0.172	0.028	0.043	4.33
	N4	0.067	0.156	0.017	0.021	3.48	0.006	0.004	0.007	0.005	2.20
72-73	S1			0.004	0.006	6.33	0.036	0.052	0.009	0.011	6.45
	N1	0.023	0.048	0.007	0.007	4.57	0.031	0.078	0.006	0.006	6.83
	S4	0.037	0.075	0.014	0.016	3.37	0.046	0.050	0.032	0.031	2.77
	N4	0.038	0.036	0.027	0.024	2.83	0.029	0.037	0.014	0.012	5.00
73-74	S1			0.004	0.004	9.00	0.017	0.043	0.003	0.005	3.60
	N1	0.011	0.019	0.005	0.004	5.25	0.008	0.033	0.003	0.003	3.33
	S4	0.036	0.097	0.007	0.008	5.50	0.026	0.050	0.014	0.017	2.06
	N4	0.022	0.022	0.013	0.013	3.31	0.009	0.007	0.006	0.007	1.86

Table XVII: Arithmetic mean, $\bar{X}$, standard deviation, s, median, M, geometric mean, $\hat{\mu}$, and geometric standard deviation, $\hat{\sigma}$, for Cd concentrations as ppm in runoff and drainage water samples collected from Plainfield loamy sand lysimeter plots during the period May 1 to April 30 during each of the data years 1971-1972, 1972-1973, and 1973-1974. Water samples were collected from fertilized and irrigated control or check plots, 1, and maximum, 4, sludge-treated plots located in either a north, N, or south, S, series of plots adjacent to an instrument house. Summary measurements include data from two control plots and one maximum sludge-treated plot in each of two series of plots.

Year	Location and Treatment	Runoff Water					Drainage Water				
		$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$	$\bar{X}$	s	M	$\hat{\mu}$	$\hat{\sigma}$
71-72	S1	0.003	0.002	0.003	0.003	2.00	0.003	0.003	0.002	0.002	2.50
	N1	0.016	0.033	0.004	0.003	6.33	0.002	0.001	0.001	0.001	2.00
	S4	0.079	0.136	0.011	0.027	4.52	0.003	0.001	0.004	0.003	1.33
	N4	0.017	0.011	0.017	0.013	2.31	0.004	0.001	0.004	0.004	1.50
72-73	S1	0.014	0.023	0.007	0.007	3.29	0.020	0.099	0.002	0.003	5.67
	N1	0.012	0.021	0.005	0.005	4.20	0.019	0.051	0.003	0.003	7.67
	S4	0.016	0.020	0.010	0.010	2.60	0.036	0.056	0.010	0.009	9.00
	N4	0.041	0.052	0.016	0.020	3.60	0.033	0.092	0.006	0.008	5.00
73-74	S1	0.013	0.020	0.004	0.005	4.60	0.011	0.033	0.003	0.003	4.33
	N1	0.011	0.012	0.008	0.007	3.43	0.013	0.051	0.003	0.003	4.67
	S4	0.007	0.006	0.005	0.003	5.33	0.005	0.004	0.004	0.004	2.00
	N4	0.035	0.035	0.025	0.019	1.68	0.017	0.059	0.004	0.005	3.20

As a method of predicting limits for sludge applications on land that would assure the protection of groundwaters used for public water supplies against contamination by heavy metals, Jorgensen[7] determined concentration distributions of several metals between liquid and solid phases of sludge-soil-water mixtures. Using several soil types he mixed 100g of soil (wet weight) with 20g of sludge (wet weight) and an unspecified amount of rainwater which were shaken for 24 hours before the samples were filtered. After filtering, contents of Zn, Cu, Cd, Cr, Ni, and Pb in solution were determined and used to calculate the ratio between metal concentrations (ppm) in solution to total metal concentrations in sludge-soil mixtures (ppm) for the several measured metal species. This calculated ratio was called the distribution coefficient. With the use of several soils having clay contents that varied from 2.4 to 34.4 percent and humus contents that varied from 1.7 to 14.3 percent, distribution coefficients as a function of soil pH were shown as graphs for the several elements. Based on the distribution coefficient, water quality standards and amounts in sludge, Jorgensen[7] concluded that Pb or Cr limits the application of sludge. He further concluded that the distribution coefficients as influenced by soil pH was independent of the volume of water and sludge/soil ratio. On this basis he considered adsorption and precipitation as major processes responsible for binding metals in soils. It was estimated that if soils having high contents of humus and clay were maintained at pH 7 or greater, 20 tons per hectare per year of the sludge used in the study could be applied for 10 years without endangering groundwater supplies. However, it was not clear how the loading rate limit was derived from distribution coefficients.

In view of findings reported by others, especially Jorgensen, it is unfortunate that Pb was not one of the elements measured in drainage waters during this study. Considering amounts added to soils as constituents of sludge and the relatively low concentrations recommended as maximum limits in public water sources, Pb, Cr, and Ni should be given priority in further monitoring operations. At this time the findings reported here indicate that while mean Zn contents may sometimes be increased in drainage water where relatively high sludge loading rates are applied, the levels are well within recommended limits for public water sources and Zn levels in drainage waters do not appear to increase with increased years of sludge applications. With regard to mean Cu contents in drainage waters, all were within recommended limits for public water sources, but the trend toward higher levels with increased years of maximum sludge applications cannot be ignored. Like Zn, mean Cd concentrations in drainage waters do not appear to increase with increased years of sludge applications. However, because recommended limits for soluble Cd levels in public water sources are very near background levels to be expected in drainage waters, the limit in terms of total Cd contents was exceeded in waters from both control and sludge-treated fine textured soils in the 1972–73 year. During this particular year mean total concentrations of Cd exceeded recommended soluble Cd limits in drainage water from replicated Blount silt loam control plots located in the north series and sludge-treated plots located in the south series. Also, during this particular year mean Cd levels in drainage waters from Elliott silt loam control plots located in the south series and from the sludge-treated plot in the north series exceeded recommended limits. Thus, ignoring data collected from the sludge-treated Elliot silt loam plot where drainage water was known to have been directly contaminated with sludge, mean Cd levels in drainage waters from four plots exceeded recommended limits during one year. Limits were exceeded by total Cd concentrations in waters from control plots with the same frequency of occurrences as oberved for waters from sludge-treated fine textured soils. Contrary to expectations Cd levels were lower in waters from sludge-treated Plainfield loamy sand plots than in correspondingly treated plots of finer textured soils. Mean Cd concentrations in drainage waters from all Plainfield sandy loam plots were always well within recommended limits for Cd levels in public water sources. However, because of relatively higher amounts of water percolated through the sandy textured soils concentrations were diluted and total amounts of the metal removed from the soil profile were not considerably different.

Summary

In view of the relatively large estimated geometric standard deviations associated with measurements of heavy metals in

runoff waters, attempts to assess water pollution hazards from the results of a relatively few grab samples collected over a relatively short time span presents a considerable risk in underestimating or overestimating the problem. Probably the metal concentrations in runoff and drainage waters found in this study were higher than would be found in streams receiving waters from field-sized areas treated with equivalent sludge and loading rates, assuming that such areas were protected against excessive erosion by water. Lysimeter water samples were never subjected to conditions favoring metal losses by precipitation followed by sedimentation and biological scavenging of heavy metals from waters flowing over soil surfaces protected by close-growing vegetation. Nevertheless, the results from this study will be of value to those concenred with assessing the environmental impacts of utilizing municipal sludges on well drained soils in humid regions. For the metals measured during the study, only Cu appeared to increase in drainage waters with increased years of annual sludge applications, but the highest mean concentration during the last year was relatively low as compared to recommended limits for public water sources. Because Cd contents in both runoff and drainage waters from control plots is so near recommended limits in public water sources, it is likely to be the metal of major concern in the disposal of municipal sludges on land.

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ACKNOWLEDGEMENTS

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Transport Model to Predict the Movement of Pb, Cd, Zn, Cu, and S Through A Forested Watershed*

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INTRODUCTION

The original motivation for the work to be described in this paper was to determine what effects Pb might be having on the forest ecosystem of the New Lead Belt area of southeast Missouri. As the study got underway, its scope was broadened to include effects due to Cd, Zn, Cu, and SO_2. This study had two aspects. The first involved obtaining measurements of quantities for use as input data to a Unified Transport Model (UTM) and measurements of stream flow, heavy metal concentrations and biomasses of various forest components for use in calibrating and validating the UTM. The second aspect was to develop a UTM consisting of modules which modeled the behavior of various subsystems of a forested watershed with emphasis on the transport and effects of heavy metals. This paper presents a summary of results from the second aspect of the Crooked Creek study, the development and application of the UTM.

Some History of the Development of the UTM

Development of the UTM began in late summer of 1972 under the sponsorship of the National Science Foundation—RANN Environmental Aspects of Trace Contaminants Program. The earliest version of the UTM consisted of a merger of the Oak Ridge National Laboratory (ORNL) version of the Wisconsin Hydrologic Transport Model (WHTM) as described by Patterson *et al.*[14] and the Atmospheric Transport Model (ATM) of Mills and Reeves.[11] The WHTM is based on the Stanford Watershed Model - IV of Crawford and Linsley[2] as modified by Huff.[9] The ATM, refined and improved [Culkowski and Patterson[3]] during the course of this study, is built around a Gaussian plume model which was adapted to treat point, line, and area sources.

More physically and chemically based mechanistic submodels were developed to treat atmosphere-soil-plant water flow [Goldstein *et al.*[7]] on a daily basis (PROSPR), plant growth (CERES) which stimulates plant water effects on photosynthesis and growth [Dixon *et al.*[4]], soil chemical exchange of heavy metals (SCEHM) [Begovich and Jackson[1]], and solute uptake by vegetation (DIFMAS-DRYADS) [Luxmoore *et al.*[10]].

All these models mentioned above together form a large subset of a suite of models* which have been developed to allow for flexibility and to provide options for various types of applications. Two versions of the UTM were used in the Crooked Creek study. One, based primarily on the WHTM, was used to simulate heavy metal transport through the entire watershed and to generate the outflow hydrograph and mean daily heavy metal stream concentrations at the watershed outfall. A second version, based on the Terrestrial Ecology and Hydrology Model (TEHM) [Huff *et al.*[9]] which used PROSPR, CERES, etc., was used to simulate heavy metal distribution in the soil profile and plants; to study heavy metal accumulation in the soil profile and plants; and to study the effects of heavy metals and SO_2 on plant growth and litter decomposition.

Some Historical Background for the Crooked Creek Watershed (CCW) Study

Measurements of the distribution and concentrations of the heavy metals in the soils of the New Lead Belt area of southeast Missouri were begun in 1971 under the direction of B. G. Wixson by an Interdisciplinary team from the University of Missouri-Rolla (UMR) [Wixson *et al.*[18]]. Most of the area they studied lies in the Clark National Forest, shown in Figure 1. At the suggestion of the NSF-RANN managers in the Trace Contaminants Program, a group from the Ecology and Analysis of Trace Contaminants (EATC) program at ORNL began a collaboration in 1973 with the UMR team for the purpose of applying the UTM to a watershed in the New Lead Belt area. A watershed in the headwaters drainage area of Crooked Creek was chosen because it had heavy metal sources which could be characterized and which were located along one boundary of the watershed and it was easily accessible for making measurements and for supplying electrical power for various measuring instruments.

Forest ranger stations are located in the towns shown (Figure 1) around the periphery of Clark National Forest. These ranger stations have recording gauges for measuring hourly precipitation. They also collect several different kinds of climatological data. Some of the data from these stations were used in the initial simulations and later as backup data to fill gaps in data obtained from gauges closer to the Crooked Creek Watershed (CCW).

The original goals for application of the UTM to CCW were calibration and validation of the models developed for predicting transport of heavy metals through a forested watershed followed by some long term simulations and studies of various possible scenarios, such as the accidental release of large amounts of SO_2 from the smelter acid plant. The long term simulations would be used to predict accumulation, distribution, and toxic effects of heavy metals in the watershed. The UMR team agreed to supply data needed for calibration and validation of the

*Work supported by the National Science Foundation—RANN Environmental Aspects of Trace Contaminants Program

*These submodels and several different versions of the UTM are available at cost in FORTRAN IV source form. Documentation for these programs also is available. For ore information, write J. K. Munro, Jr., Computer Sciences Division, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, TN 37830.

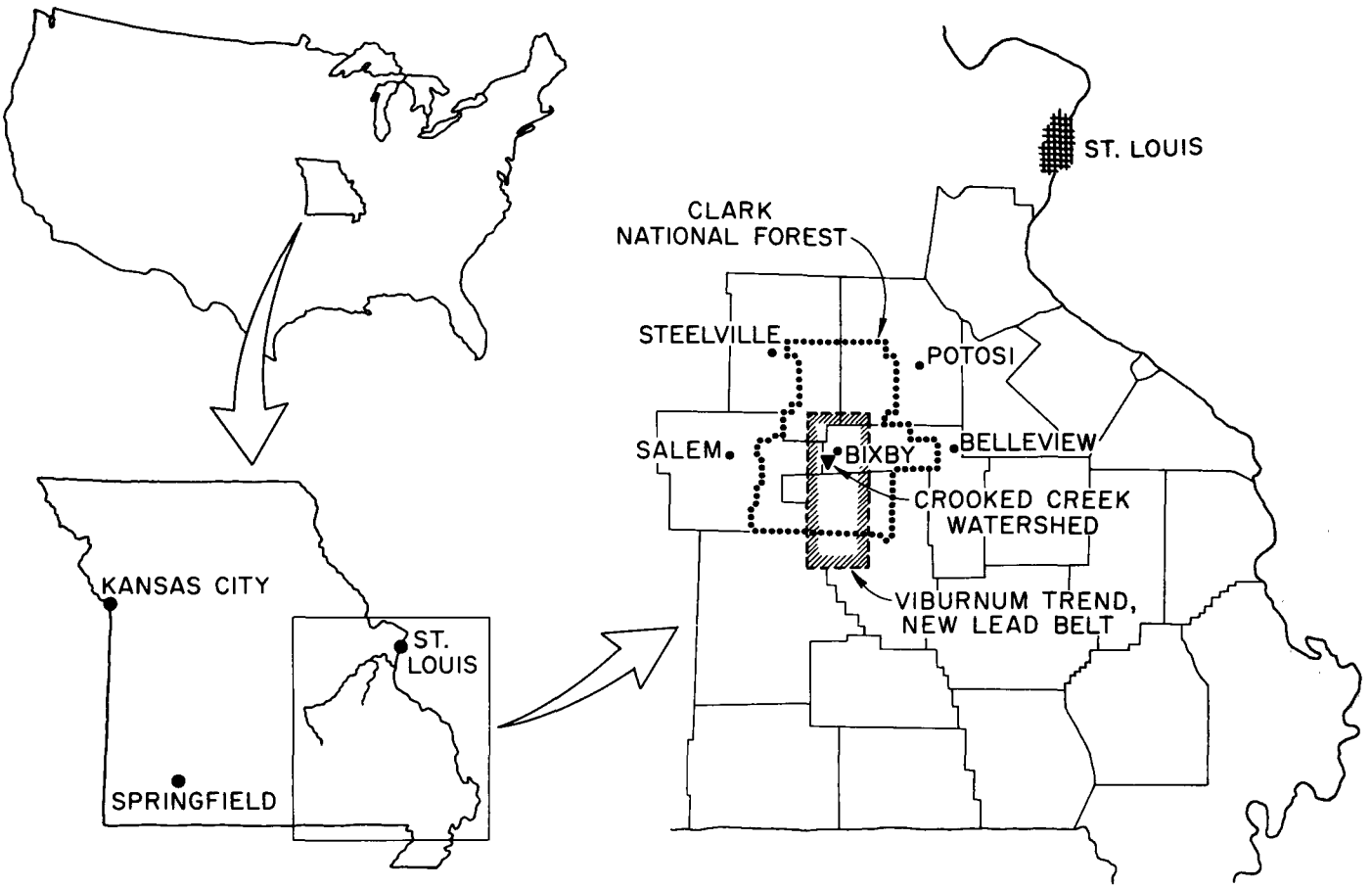

Figure 1: Location of Crooked Creek Watershed (inverted block triangle) with Respect to Nearby Cities.

hydrologic and heavy metal transport components of the UTM. The ORNL group concentrated on development and application of the UTM.

Description of Crooked Creek Watershed

As Figure 2 shows, Crooked Creek Watershed (CCW) is a triangularly-shaped, 466 ha watershed, bounded on two sides by roads maintained by the state of Missouri or the AMAX Lead Company of Missouri (in the vicinity of the smelter) and bounded on the west for the most part by a jeep trail. Roads in this area of Missouri generally run along the ridgelines, so can be used to define surface divides of watersheds. The CCW lies on the Springfield-Salem Plateau, an area characterized by hills alternating with steep valleys [Schwarz and Schwarz[16]]. Second growth canopy species found on the watershed are largely black oak (*Quercus velutina Lam.), white oak (Q. alba* L.), northern red oak (*Q borealis* Michx.), and shortleaf pine (*Pinus echinata* Mill.). Seventy-five percent of the total foliage biomass is provided by oak species; twenty-five percent provided by shortleaf pine [Watson[17]].

Soils of the region are thin, stony, limestone-residual, cherty silt loams. Ridgetops on CCW have a Lebanon soil type with 5-8 cm fragipan; slope soils are dominated by cherty silt loams of the Wilderness (40%) and Clarksville (25%) series. The valley floors are occupied by the alluvial Razort and Ashton soils [G. Gott, C. L. Scrivner, personal communication].

A primary lead smelter located at the apex of the watershed has been in operation since 1968. Most of the watershed is a woodland ecosystem and remains largely intact. Current heavy metal loads on CCW are the result of both stack emissions and fugitive sources. The location and orientation of the major sources with respect to the watershed are shown in Figure 3. Fugitive sources include orehandling processes, yard dusts, and exposed concentrate piles. These sources contribute mostly finely divided sulfide dusts. Stack emissions contain metal sulfates and oxide particulates less than 2 microns in diameter. These soluble oxides and sulfates represent a much greater biological hazard to the watershed than the extremely insoluble sulfides. For purposes of modeling the atmospheric transport of the particulates and gases, three sources were considered: a point source (the smelter stack) and two types of area sources originating from the smelter yard (vehicular suspension and wind resuspension of yard dusts).

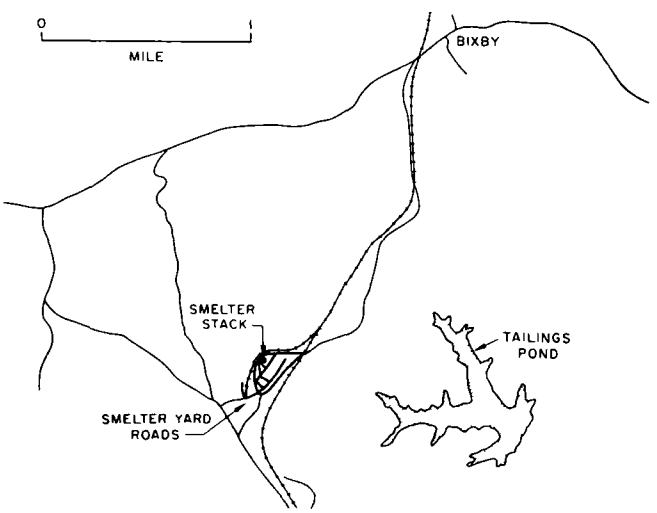

Figure 3: Heavy Metals Source Locations in Relation to Crooked Creek Watershed.

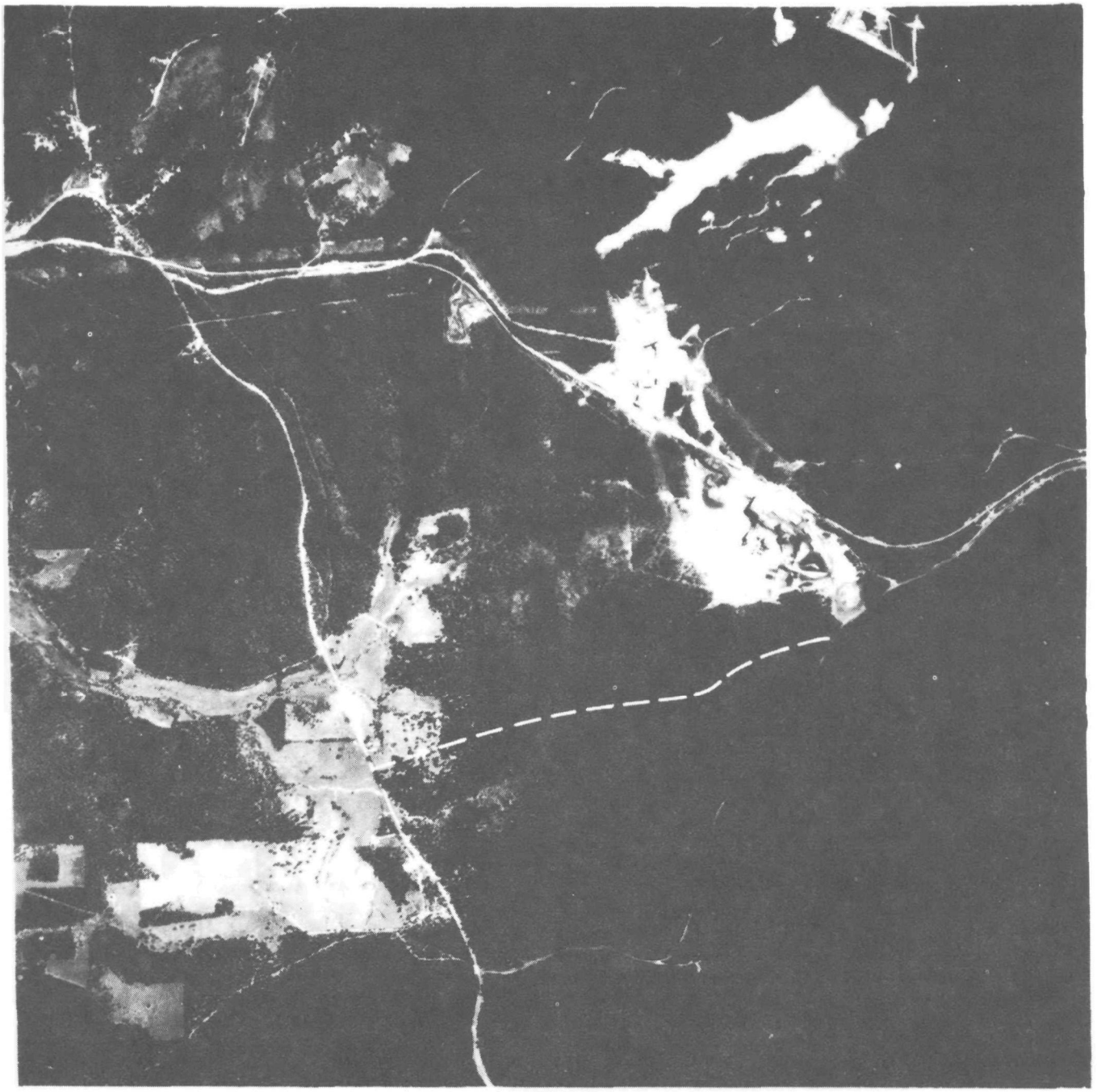

Figure 2: Aerial View of Crooked Creek Watershed. Dashed Line Shows Western Watershed Boundary.

Brief Review of the UTM

Overview of General Features

The UTM was developed for the purpose of simulating the transport of trace toxic substances through an ecosystem consisting of the atmosphere, land surface, vegetation, soil layers, ground water, and streams. It operates with a time resolution of one hour when rain is absent and 15 minutes when it rains. Different versions of the UTM have been applied to watersheds ranging in size from a couple hundred hectares to the order of ten thousand square kilometers. The ATM imposes an upper limit in size of an area having about a 70-80 km radius when it is coupled to the submodels in the UTM.

Input data common to the various versions of the UTM include the historical hourly precipitation, daily values of average wind speed, maximum and minimum temperature, mean dew point, integrated total radiation, values of various quantities characterizing the watershed topography, soil characteristics, and extend of vegetative cover. Hourly wetfall and monthly dryfall contaminant values may be required if the ATM is not used. If the ATM is used, data on contaminant source characteristics, physical character of the contaminant, and hourly wind speed and direction are required.

The current complete set of submodels which can be coupled together within the UTM framework are shown in Figure 4. Application of the UTM to a particular watershed or to a particular problem in a watershed does not usually require consideration of physical and chemical models for all the possible components which can be treated by the suite of models which

are available. So some appropriate subset of models is usually coupled together for a given simulation. Collecting and assembling input data is always a major project. Some versions and some options within versions allow for running with less data or different data. For example, the WHTM version can be run using daily values of evaportation instead of computing evapotranspiration from daily values of average wind speed, mean dew point temperature, integrated incoming solar radiation, etc.

Two versions of the UTM were used in the Crooked Creek study. They are shown in Figure 5 and differ only for the land simulation. The WHTM version is presented on the left; the TEHM version on the right.

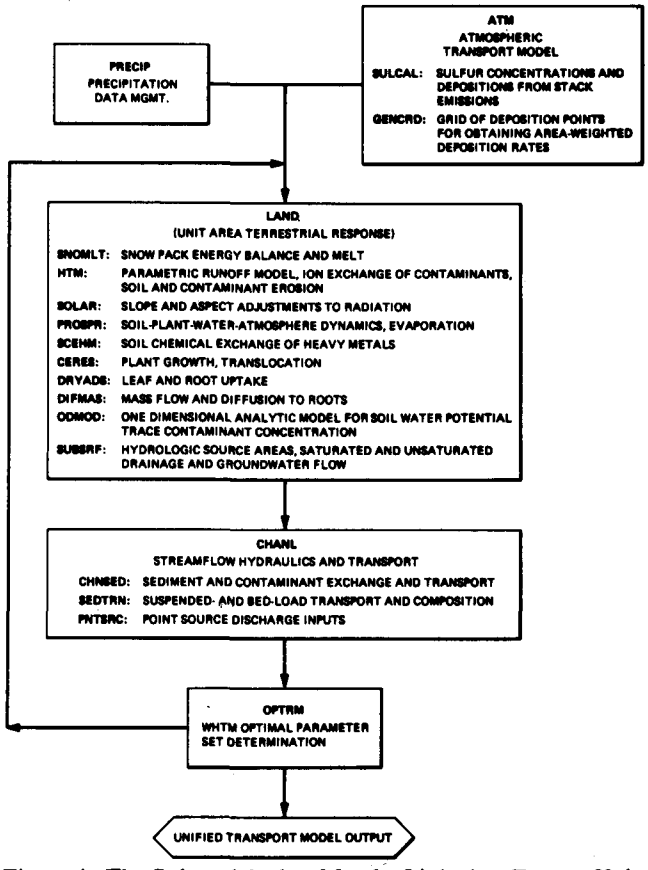

Figure 4: The Submodels that May be Linked to Form a Unified Transport Model.

Description of the WHTM Version

The WHTM version contains only limited treatment of vegetation effects. It allows for interception storage, percent ground cover, and solubility limited leaching of chemicals from a litter layer. It also treats evaporation and transpiration effects together as a single process. The soil profile is divided into surface, upper zone, lower zone, and ground water as indicated in the lower part of Figure 6. The ground water storage volume has active and inactive components. The inactive volume acts like an infinite sink or source and can be used to allow for water leaving or entering a watershed through unobserved aquifers.

Material transport is treated in tandem with the hydrologic flow as indicated in Figure 7. The transition from surface to subsurface soil is represented by a stack of four theoretical ion-exchange plates. In addition, the top inch of the upper zone is also singled out to aid in the transition from soil surface effects to subsurface processes. For each storage volume, contaminant mass is assumed to be mixed uniformly throughout the volume. For a particular contaminant the same ion-exchange distribution coefficient value is used for each storage volume where mixing of soil and contaminant occurs.

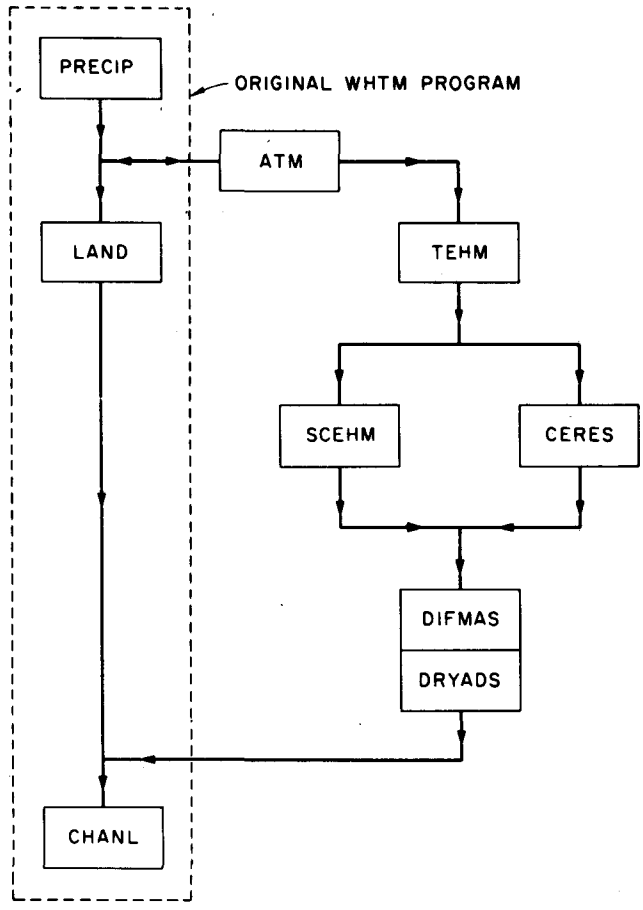

Figure 5: Modular Structure of Submodels Used for the WHTM and TEHM Versions of the Unified Transport Model (UTM).

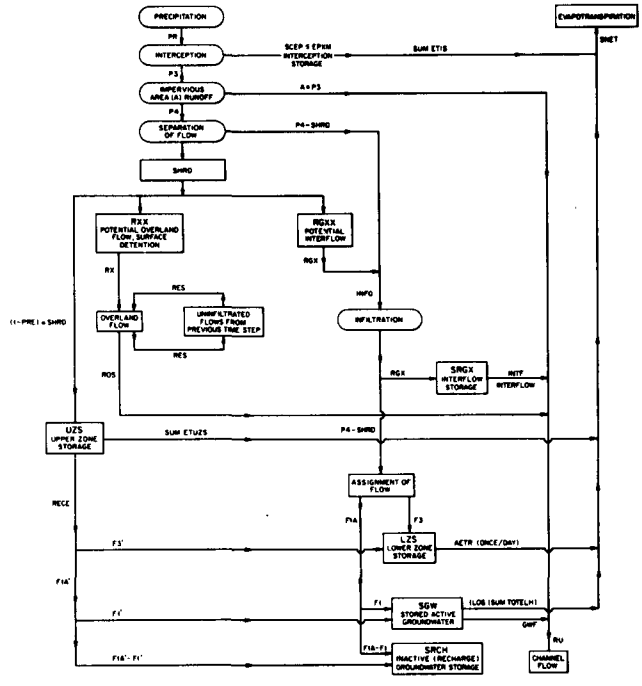

Figure 6: Hydrologic Flow in a Land Area Segment as Represented in WHTM Version of the UTM.

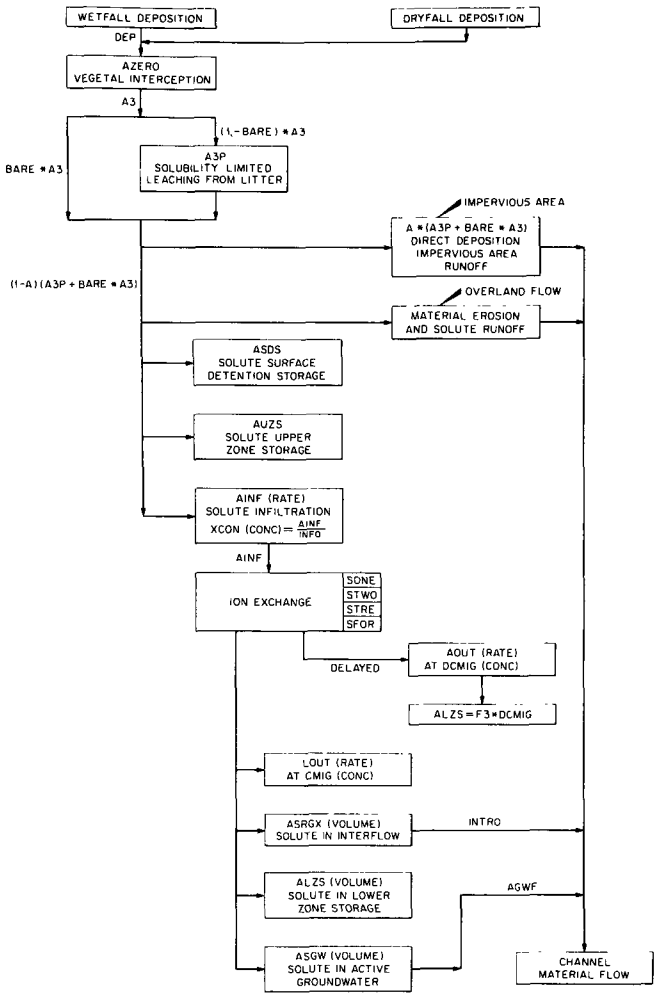

Figure 7: Material Flow in a Land Area Segment as Represented in WHTM Version of the UTM.

Surface erosion and transport are treated in terms of thresholds for resuspension of loose soil particles and for eroding new material. Erosion is driven by the flow power of water moving over the ground surface. Exchange of contaminants can occur between the surface water and sediments so the discharge to the streams includes water, eroded sediments, amounts of contaminants sorbed on these sediments, and contaminants dissolved in the water.

Once the materials discharged from the land surface enter the stream they are carried through the stream network, with the proper delays, to the watershed outfall. The version of WHTM used for the CCW study considered no mixing or chemical exchange of contaminant with the stream bed. So whatever enters the stream network rather quickly passes through the watershed outfall. The total amount of contaminant entering the streams is used for the channel routing calculations, so stream concentrations at the outfall include contaminants both dissolved in the water and sorbed on sediments. Submodels [Fields[5]] were available to treat contaminant-sediment interactions in the streams, but measurements necessary to assemble the input data for these models were not made. So no attempt was made to use these models.

Description of the TEHM Version

The TEHM version was specifically developed to emphasize the relationships between plants and their environment. Mechanistic models for the soil-plant-water-solute relationships are used as much as possible within the basic UTM framework. The TEHM version is more modular in its treatment of the soil-water processes and allows for a variable number of soil layers of varying characteristics. The ion-exchange model (SCEHM) which couples to this version also works within the modular framework of the soil layers and is more general than its counterpart in the WHTM version since it allows for a different value of the ion-exchange distribution coefficient for each soil layer. Contaminant concentration transition from the soil surface to subsoil, modeled by means of a stack of theoretical ion-exchange plates, is not considered in this version. Neither are surface erosion effects.

Figure 8 shows how the various modules in the TEHM version are coupled. Atmosphere-plant-soil moisture relations are simulated by PROSPR [Goldstein, Mankin, and Luxmoore[7]]. Plant water potentials generated by this module are used by CERES [Dixon *et al.*[4]], the submodel which simulates plant growth and respiration, standing crop biomass of leaves, stems, fruits, and roots, and storage pools of sugars, live tissue, and dead or woody tissue. CERES also computes the translocation of carriers (transpired water and phloem sugar movement) of chemical substances. Mass flow of solutes from the soil into the roots is simulated by the submodel DIFMAS and the transport and accumulation of solutes in vegetation and litter is simulated by the submodel DRYADS. These last two submodels can simulate effects of toxic gases and vapors, such as SO_2, in addition to heavy metals.

Since the TEHM version focuses on effects of contaminants on plant growth and litter decomposition, its results were not used with the channel routing simulation. The TEHM simulations were carried out for a typical hillside site about 0.4 km from the smelter stack.

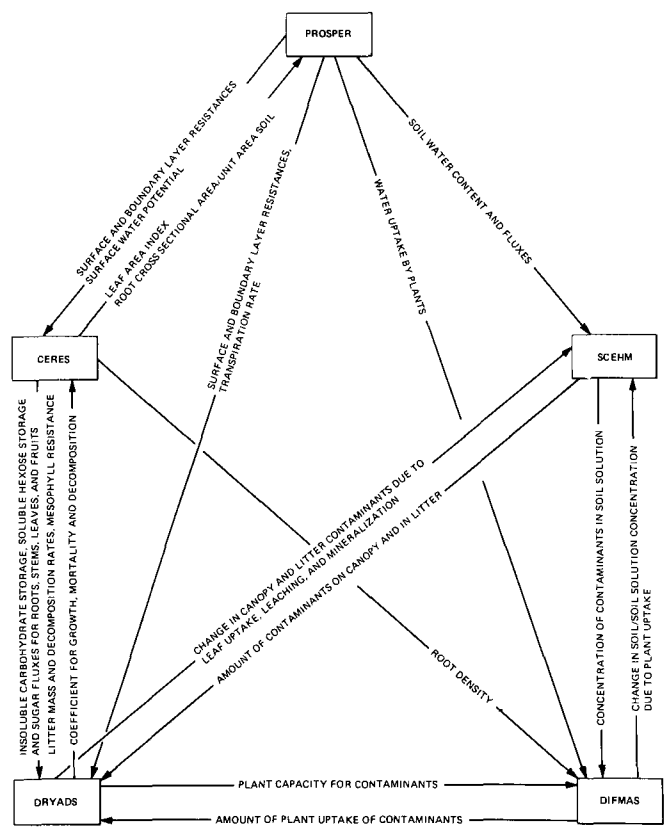

Figure 8: Coupling of the Modules in the TEHM Version of the UTM: PROSPER, CERES, SCEHM, DIFMAS and DRYADS.

Results of Model Applications

Application of the WHTM Version

The WHTM version of the UTM, more than any other, has been applied to many different watersheds, so a large amount of experience has been accumulated about its use. As a result, it was possible to begin application of this version to CCW long before all the input data for CCW had been obtained. Calibration of the model continued as more data became available. Early simulation results showed [Munro and Wixson[12]] that large heavy metal concentrations occurred in runoff from the first storms following an extended dry period. Concentrations in runoff from more storms following soon afterward were considerably reduced. These results suggested that special attention be given to sampling runoff from storms immediately following long dry periods.

Input data for the Atmospheric Transport Model (ATM) were available first so most of the early application efforts centered on calibrating and validating it. The results of this work are described by Patterson et al.[13], so won't be reviewed again. In summary, the ATM simulated wetfall and dryfall values for Pb which were factors of 2-5 higher than those measured, depending on the sampling site location relative to the heavy metal sources. Dusts suspended by the smelter yard vehicular traffic constituted the largest single source of heavy metals. Total monthly deposition rates of heavy metals on the ridge tops are shown in Table I as an example of values typical for the watershed. The Pb values shown were simulated for seasonally averaged wind data; values for the other heavy metals are averages of measured data.

Table I: Monthly Heavy Metal Deposition Rates (mg/ft²/Mo.) for Segment One on Crooked Creek Watershed. Lead Values were Simulated Using the ATM. Values for Other Heavy Metals were Measured by K. Purushothaman (UMR).

Year	Month	Lead	Cadmium	Zinc	Copper
73	Oct	187.	4.0	25.	10.
	Nov	179.	4.0	25.	10.
	Dec	141.	4.0	25.	10.
74	Jan	151.	4.0	25.	10.
	Feb	143.	4.0	25.	10.
	Mar	154.	4.0	25.	10.
	Apr	150.	4.0	25.	10.
	May	155.	4.0	25.	10.
	Jun	174.	4.0	25.	10.
	Jul	176.	4.0	25.	10.
	Aug	175.	4.0	25.	10.
	Sep	183.	4.0	25.	10.

Input data for simulating the unit land area responses were obtained from the UMR team [Wixson and Jennett, eds.[18]], C. L. Scrivner and G. Gott [personal communication] of the University of Missouri - Columbia (UMC), and the AMAX Lead Company of Missouri environmental officer George Carr [personal communication]. The watershed area was divided as shown in Figure 9 into three segments consisting of ridgetops, hillsides and meadow. This division was made on the basis of land use patterns, variation in soil type and pH, and surface topography. The channel system was divided according to the natural nodes of the stream network.

Stream flow data were available for only two storm events, [Foil[6]] both of which occurred in the same season of the year. These two storm events did not provide enough data for a good calibration and validating. Data for a couple of storm events in each season of the year would have been much more useful. Precipitation data for both storms were measured at the watershed outfall. The remainder of the precipitation data were measured at Viburnum, 10 km due north of CCW. Gaps in the Viburnum data were filled using data from one or a combination of ranger stations surrounding the Clark National Forest (Figure 1). Hourly precipitation and measured stream flow for the first storm event are shown in Figure 10. Notice that this event spans parts of two days and contains several gaps in the flow data.

Stream flows were measured with a nitrogen gas bubbler placed about five meters upstream from a culvert which defined the channel cross section geometry. The first set of stream flow data shows a dip at 5:00 a.m. on 28 August 1974 when a rise due to the incoming precipitation would be expected. This suggests that the bubbler arrangement may not have been working properly at this time.

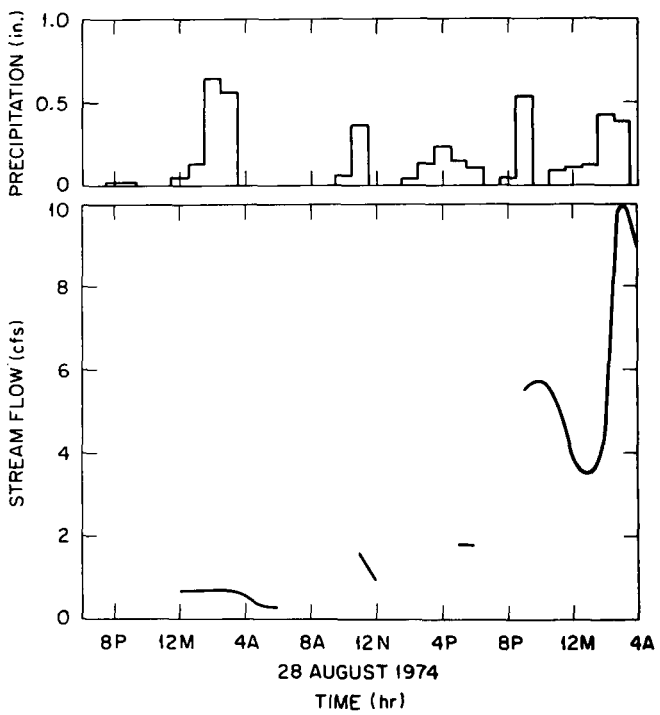

Figure 10: Hourly Precipitation and Stream Flow for Storm No. 1, 28-29 August 1974, Measured by Foil [1975].

The succession of small-to-moderate intensity storms shown here followed a long dry period. Subsurface water storages are being replenished by this event. Data from this series of storms give enough information to be able to adjust parameters governing watershed response for characteristic times less than two weeks.

Data for the second storm event (11 September 1974) are shown in Figure 11. This storm was well isolated in time from storms before and after it. The storm was also intense, so provided a lot of useful information for calibration and validation purposes, especially for parameter adjustments affecting short time response behavior.

These stream flow data limited model calibration basically to those parameters governing overall infiltration rate of water into the soil (CB), intermediate time response of flow recession (IRC, CC), and base flow conditions (K24L). All these parameters were varied except CC. Calibration of the remaining hydrologic parameters which were still free to be adjusted would have been possible if stream flow data for storms in other seasons of

the year had been available. Two parameters in this category, known to govern longer time hydrologic responses, are the nominal storages for the upper (UZSN) and lower (LZSN) zones. UZSN affects hydrologic response on a time scale of several weeks; LZSN affects response on a time scale of several months. These storages had been adjusted in preliminary simulations to approximately correct values by requiring the values of upper (UZS) and lower (LZS) zone storages at the end of a simulated year to be approximately equal to their values at the beginning of the simulated year. Most of the parameters affecting hydrologic response such as fraction of bare soil, overland flow length, average segment slope, etc. are pretty well determined from measurements.

Results of varying the parameters CB, IRC, and K24L in the final stages of hydrologic parameter calibration will be used to give some idea of the success of the calibration efforts. Figure 12 shows what happens when different values of CB are used. There seems to be no way to account for the dip in the first segment of measured flows other than problems with the data themselves. Agreement looks better for the case CB=4.5 at the higher flows than at low flows. With the infiltration rate essentially determined, it was possible to begin adjusting parameters governing hydrograph shape. The parameter IRC seemed to be the best candidate to look at first. Effects of different values for IRC are shown in Figure 13. Analysis of these results suggests a value for IRC determined by the half-life of the intermediate response component of the stream flow recession curve. An appropriate value for IRC lies between 0.05 and 0.1. The value IRC=0.05 was used for subsequent simulations. Parameter CC was not adjusted, but probably could have been used to make some further small adjustment in the time distribution of flow for the intermediate time response component. With a reasonable value for the interflow recession constant having been chosen, attention was finally directed to simulating base flows better. Stream flow data for the region around the CCW indicated considerable drainage of water occurred through unobservable aquifers, perhaps as much as 2/3 of the water entering the watershed. So a value of 0.7 was used for the parameter K24L to

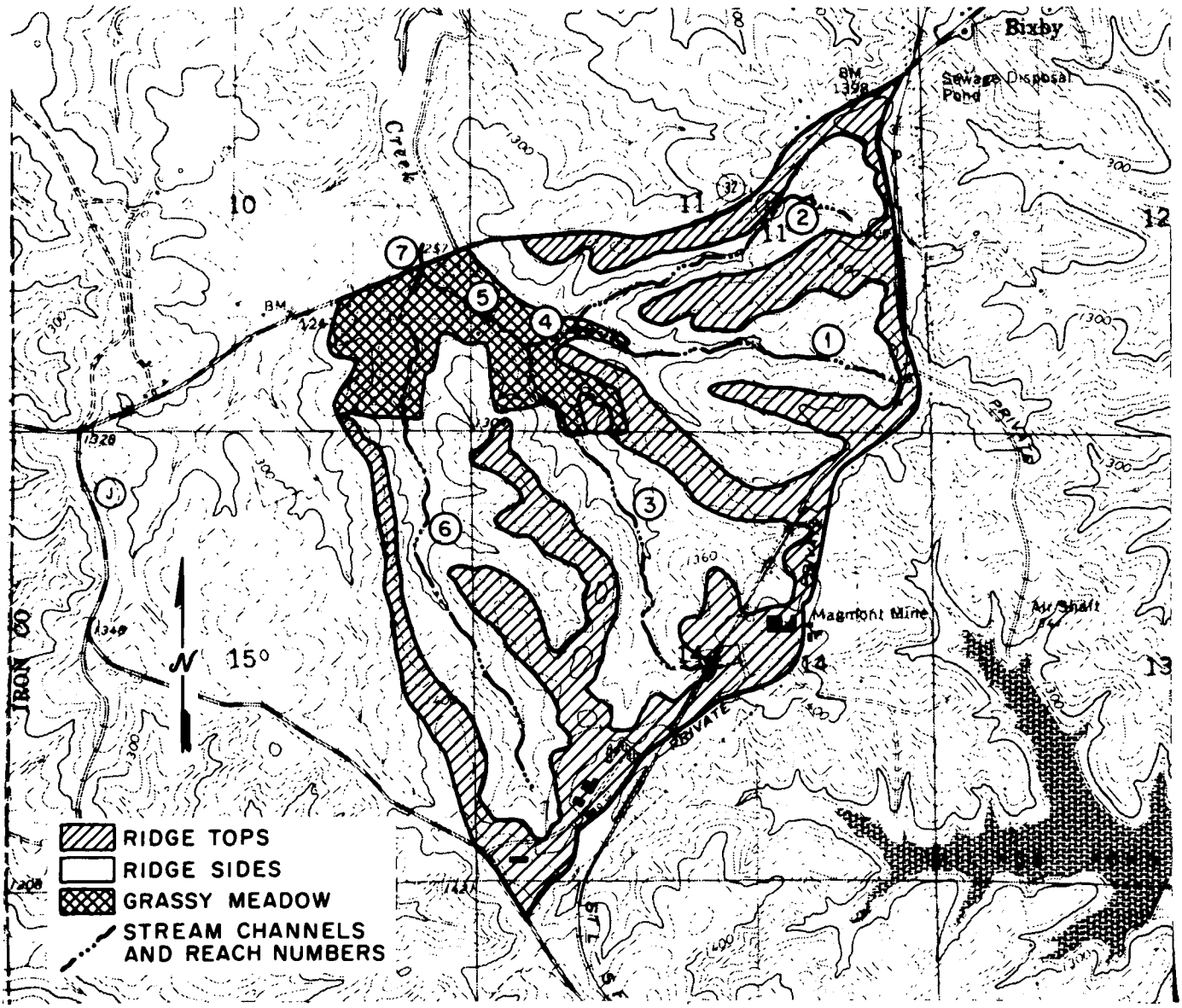

Figure 9: Map of Crooked Creek Watershed Showing Segment Boundaries for Segment Areas Considered in the Simulation Calculations and Showing the Stream Channel Network Used in the Flow Rounting and Timing Calculations.

see what would happen. The result is shown in Figure 14, again using data for the second storm event. Low flows are simulated much better.

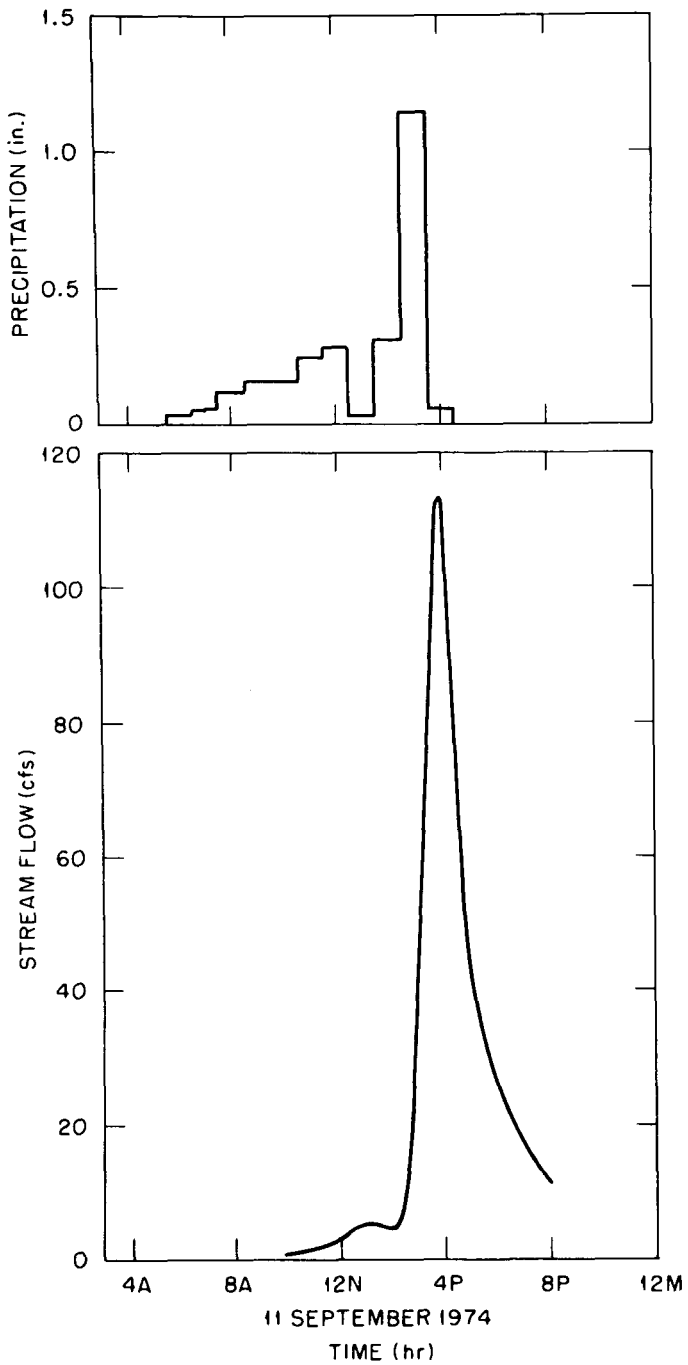

Figure 11: Hourly Precipitation and Stream Flow for Storm No. 2, 11 September 1974, Measured by Foil [1975].

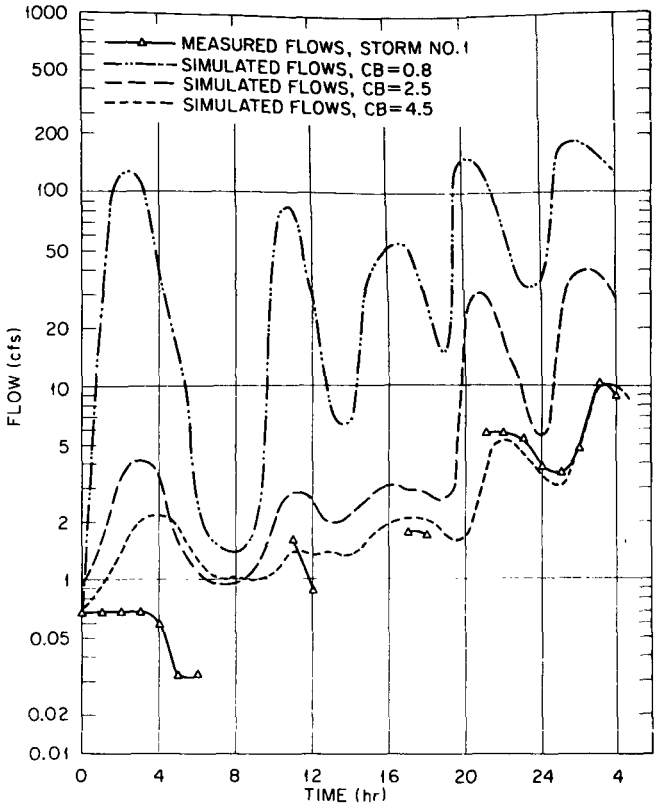

Figure 12: Comparison of Simulated and Measured Stream Flows for Storm No. 1 for the Following Values of CB: a) 0.8, b) 2.5, c) 4.5.

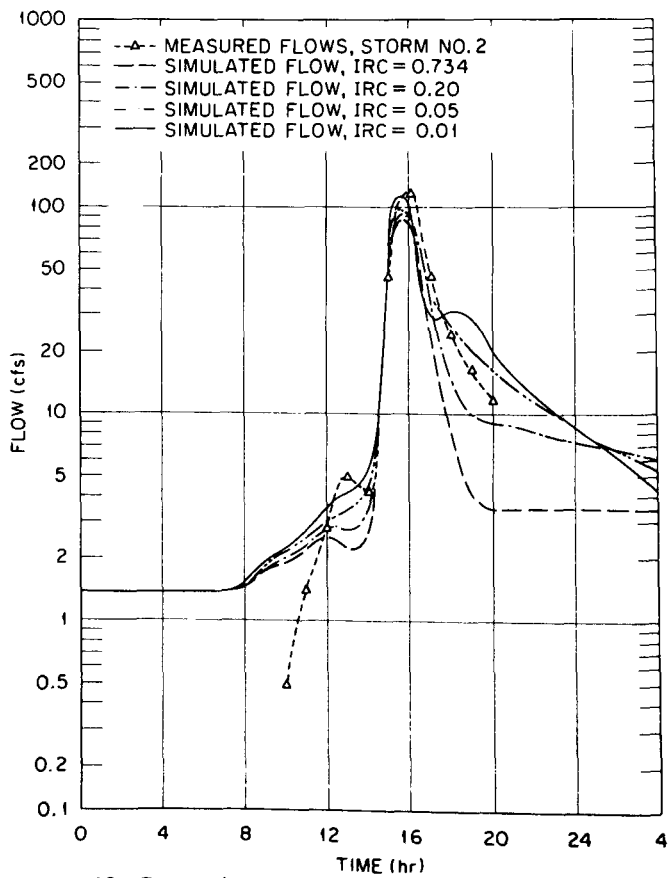

Figure 13: Comparison of Simulated and Measured Stream Flows for Storm No. 2 for the Following Values of IRC: a) 0.734, b) 0.20, c) 0.05, and d) 0.01.

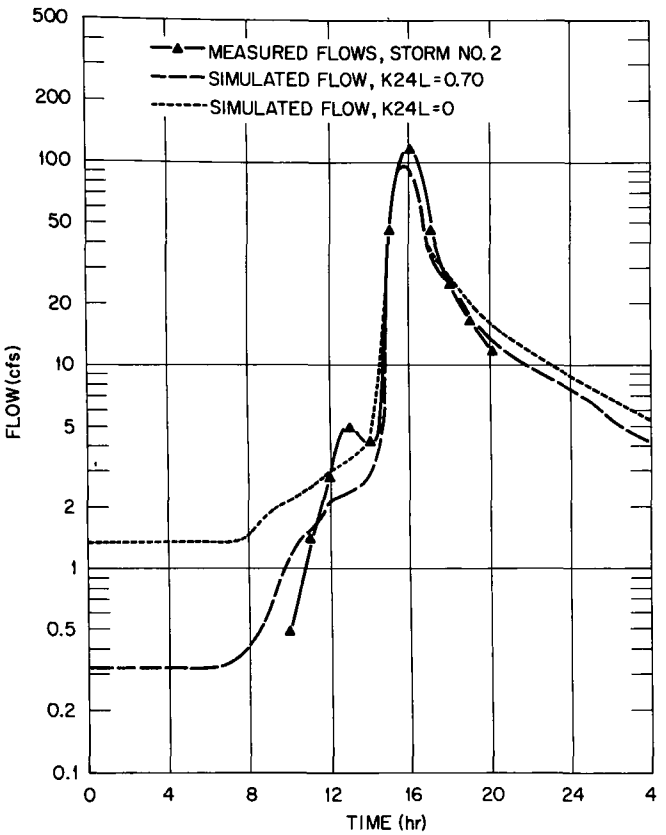

Figure 14: Comparison of Simulated and Measured Stream Flows for Storm No. 2 for K24L Values 0.0 and 0.7.

Once the hydrologic response was calibrated reasonably well, parameters governing the rate of sediment transport were adjusted to give the correct annual erosion rate. The annual erosion rate for a forested watershed is about 0.85 g/ft^2. Though a certain degree of latitude in the parameter values affecting material transport was possible, every attempt was made to keep these parameter values within the ranges suggested by Huff[8] and consistent with whatever was known about the watershed. There was very little room within this framework to play around with the contaminant and erosion parameter values.

A comparison of simulated and measured stream flows and heavy metal concentrations for the two storm events described above is shown in Table II. Overall best agreement is obtained for the second storm event. Results for the two days of the first storm event do not look as good, but this should not be surprising since the measured data available for this comparison is incomplete. It is perhaps encouraging to observe the consistency between measured and simulated heavy metal concentrations except for Pb on 28 August 1974.

Application of the TEHM Version

The TEHM version used considerably more input data than the WHTM version beyond the large subset of input data common to all versions of the UTM. The more mechanistic submodels of the TEHM version require a larger number of parameters to characterize the soil-plant subsystems and their behavior. These parameters also require more effort to obtain because more detailed physical and chemical measurements must be made. For the CCW application many of the parameters relating to the physiological responses of the plants were taken from existing literature since, for different natural systems, the ranges of values were fairly consistent. Required biomass values were taken from measurements made at CCW or the control site 21 km from the smelter stack.

Table II: Comparison of Simulated and Measured Stream Flows and Heavy Metal Concentrations for Several Storms at Crooked Creek Watershed, New Lead Belt, Missouri.

Heavy Metal	Storm Dates	Daily Flows [cfs]		Simulated Total Metal Transported Per Day [kg]	Daily Average Metal Concentration (Unfiltered Samples) [mg/ℓ]	
		Measured	Simulated		Measured	Simulated
Pb	8-28-74	1.69	3.15	58.3	3.7	7.56
	8-29-74	6.75	10.7	22.4	9.0	0.86
	9-11-74	12.7	11.8	110.0	9.9	3.81
Cd	8-28-74	1.69	3.15	2.01	1.8	0.26
	8-29-74	6.75	10.7	3.01	2.8	0.11
	9-11-74	12.7	11.8	6.72	0.57	0.23
Zn	8-28-74	1.69	3.15	14.1	4.57	1.83
	8-29-74	6.75	10.7	10.4	10.01	0.40
	9-11-74	12.7	11.8	62.2	5.43	2.15
Cu	8-28-74	1.69	3.15	0.47	0.18	0.06
	8-29-74	6.75	10.7	1.08	0.50	0.04
	9-11-74	12.7	11.8	6.64	0.55	0.23

Before models of plant growth, litter decomposition, and effects of heavy metals were fully coupled together in the TEHM version, Begovich and Jackson[1] [summary by Patterson et al.[13]] used a version with only the PROSPR and SCEHM submodels coupled to simulate heavy metal build-up in the soil. They found that the simulated amounts of Cd and Zn in the top soil layers reached equilibrium after several years while Pb and Cu continued to accumulate. All heavy metals continued to accumulate in the lower soil layers. Agreement between simulated and measured (1974) concentrations of heavy metals in the top two soil layers at the end of the six-year simulation was quite good. The simulation was started with heavy metals absent from the soil for 1968 and used measured heavy metal deposition rates [Wixson and Jennett, eds.[18]].

The plant stand growth submodel CERES was calibrated to give a mass balance and to simulate a steady state for the plants on an annual basis. The solute uptake, litter decomposition, and toxic effects submodels DIFMAS and DRYADS were also first run with the absence of contaminant input and were calibrated to simulate litter biomass values for the control site. Calibration with contaminant input absent was relatively easy because a lot of data are available for natural plant systems free of toxic chemicals.

Calibration of the TEHM version to simulate heavy metal uptake correctly was difficult because reliable data are scarce, particularly for litter fall rates, litter decomposition rates, and root uptake rates for heavy metals. Diffusion coefficients for heavy metal transport across root membranes and various thresholds for toxic effects on plant growth and litter decomposition had to be adjusted to give reasonable simulated values of biomass and heavy metal uptake rates and concentrations in plant parts.

Heavy metal effects on the CCW forest were simulated with the fully coupled TEHM version for a six year period corresponding to the period of time from the beginning of smelting operations in 1968 to the time when measurements were made on CCW (the "present"). The simulated effect of the atmospheric deposition of Pb on the dynamics of an oak forest litter system is shown in Table III. Year zero values are those simulated for the steady state before heavy metals were introduced into the system. Plant mortality increased only 3% during the six years with almost all loss from roots. The steady annual input of plant litter coupled with a slowing of the litter decomposition rate resulted in a 44% increase in the litter mass. The litter decomposition rate appears to increase from year to year because of the increase in litter mass. On an annual incremental basis, however, the decomposition rate is leveling off, suggesting that the litter mass may be approaching an equilibrium level.

Table III: Simulated Dynamics of an Oak Forest Litter System Subjected to Successive Years of Atmospheric Deposition of Lead

Year	Plant Mortality ($g/m^2/yr$)	Total Litter Mass (g/m^2)	Decomposition Rate ($g/m^2/yr$)
0	720.0	2150.0	438.0
1	720.0	2451.0	438.0
2	741.0	2670.0	522.0
3	742.0	2829.0	581.0
4	743.0	2947.0	624.0
5	744.0	3034.0	655.0
6	744.0	3099.0	677.0

Table IV shows the simulated September plant tissue concentrations of heavy metals for each year of the six year simulation. Heavy metal concentrations at the beginning of the simulation were assumed to be zero. The results show a rapid rise in concentration during the first year for the leaves followed by a constant amount for the succeeding years. Concentrations of Pb in stem and root sapwood increase substantially each year, whereas concentrations of Cd, Zn, and Cu for these plant parts increase rapidly the first year and very slowly or reach the maximum level for succeeding years. Heavy metal concentrations for heartwood components show a gradual increase in all cases due to the large amount of biomass present in the components. Concentrations of Cd, Zn, and Cu in fruit appear to approach a maximum level during the simulation. Although annual fruit production is similar to leaves, transport of solutes to fruits is slower than in other plant parts. Therefore fruit heavy metal concentrations level off only after the maximum concentrations in other plant parts is reached.

Annual uptake of heavy metals by roots and leaves, plant loss of heavy metals from mortality, and litter content of heavy metals are shown in Table V. Annual root uptake of lead increased with the accompanying build-up of Pb in the soil system [Begovich and Jackson[1]]. Root uptake of other metals drops off after the first year because the maximum concentration allowed in the model was reached. Both the reduced rate of contaminant build-up in the plant tissues and the reduced rate of plant uptake with time is due to the decrease in plant demand as the concentration of heavy metals in the various plant parts approached its maximum. Uptake of heavy metals by leaves was constant through the six-year simulation period since atmospheric deposition was assumed constant from year to year. Recycling of heavy metals back to litter from mortality of plant parts increased with time and can be mainly attributed to the fall of leaves and fruits during autumn.

There was build-up of litter Pb of about 10 $g/m^2/yr$ as well as an increase in average litter concentration. The rate of increase in concentration varies from year to year as a result of toxic effects slowing the rate of litter decomposition and causing a build-up of litter mass (Table III). Litter content and mineralization of Pb and Cu increased while that of Cd and Zn decreased slightly (Table V). Although mineralization results from decomposition, it is assumed that the metals that are released are retained by the litter through absorption. There is a decrease in mineralization rate of Cd even though there is an increase in plant mortality input into litter. The decline in mineralization is due to the increased simulated toxic effect of Pb on the rate of litter decomposition.

Results of the simulation of litter and heavy metal accumulation after six years of smelter operation are given in Table VI. Simulated values generally are lower than those experimental values measured on CCW by Watson[17]. The predicted litter mass (not including root litter) is about 47% less than the experimental value. This could result from the low levels of Pb predicted by the model which determines the toxic effect on decomposition or from the estimate of toxic threshold level being too low. The predicted low Pb levels in litter are evident from the comparison of litter concentrations. Since the predicted litter mass is low, the Pb content also must be low. The predicted low heavy metal concentrations in litter apparently are not a result of leaching to the soil and uptake by plants since the plant levels are a small fraction of the litter levels. A reasonable explanation of the predicted low levels is that the estimated rates of heavy metal deposition may be too low and/or that the rate of deposition may have been higher in previous years.

Table IV: Simulated September Tissue Concentration of Heavy Metals (μg/g) in Oak Vegetation Following Successive Years of Heavy Metal Atmospheric Deposition

Years	Leaf	Stem Sapwood	Stem Heartwood	Root Sapwood	Root Heartwood	Fruit
Lead						
1	176.0	1.64	0.010	183.0	1.27	0.180
2	172.0	3.81	0.048	450.0	9.68	0.260
3	172.0	5.73	0.123	524.0	25.6	0.262
4	172.0	9.1	0.231	695.0	44.2	0.459
5	172.0	14.3	0.403	888.0	68.3	0.724
6	173.0	21.7	0.667	1080.0	98.1	1.06
Cadmium						
1	9.84	7.96	0.032	44.3	0.476	9.49
2	10.3	7.98	0.163	47.2	1.98	15.8
3	10.4	7.98	0.288	47.5	3.51	17.7
4	10.5	7.98	0.408	47.7	4.99	18.9
5	10.6	7.99	0.527	47.8	6.12	19.5
6	10.5	7.98	0.646	47.7	6.09	18.4
Zinc						
1	49.6	29.9	0.142	49.0	0.577	48.6
2	49.9	30.0	0.358	49.3	2.14	51.1
3	49.9	30.0	0.838	49.3	3.64	53.1
4	49.9	30.0	1.30	49.3	5.1	54.8
5	49.9	30.0	1.76	49.4	6.51	54.9
6	49.9	30.0	2.22	49.4	7.87	55.1
Copper						
1	9.82	14.8	0.067	9.75	0.110	8.76
2	9.91	14.9	0.312	9.85	0.423	9.90
3	9.97	14.9	0.554	9.87	0.727	10.5
4	10.0	14.9	0.705	9.88	1.02	11.0
5	10.0	14.9	1.02	9.88	1.30	11.2
6	10.0	14.9	1.25	9.88	1.58	11.3

Table V: Simulated Heavy Metal Uptake, Content, and Losses for Successive Years of Heavy Metal Atmospheric Deposition

Years	Vegetation ($mg/m^2/yr$)			Litter		
				End of Year		Mineralization Loss ($g/m^2/yr$)
	Root Uptake	Leaf Uptake	Mortality Loss	Content (g/m^2)	Concentration ($\mu g/g$)	
Lead						
1	98.4	85.7	84.6	18.9	16385.0	2.98
2	171.2	82.8	85.2	32.8	21003.0	7.26
3	107.7	82.8	88.0	43.4	29051.0	10.51
4	175.5	82.8	91.0	51.5	38430.0	12.61
5	216.4	82.8	95.2	57.7	44362.0	14.92
6	245.6	82.8	99.9	62.4	51900.0	16.37
Cadmium						
1	36.3	1.7	5.2	0.0038	2.88	0.0015
2	12.5	2.0	5.8	0.0038	3.69	0.0015
3	11.8	2.0	6.2	0.0038	3.77	0.0015
4	11.8	2.0	6.4	0.0038	4.20	0.0014
5	11.8	2.0	12.6	0.0041	4.94	0.0018
6	11.6	2.0	12.6	0.0041	5.35	0.0013
Zinc						
1	85.2	15.7	26.6	0.057	53.3	0.041
2	16.4	21.6	27.1	0.057	76.0	0.042
3	16.7	21.3	27.4	0.057	81.4	0.039
4	16.8	21.2	27.8	0.057	94.4	0.039
5	16.9	21.2	28.0	0.057	107.6	0.039
6	21.4	21.2	28.2	0.057	120.9	0.039
Copper						
1	28.2	5.3	5.2	0.17	117.9	0.047
2	4.4	4.6	5.4	0.26	207.5	0.075
3	4.5	4.5	5.4	0.31	238.3	0.092
4	4.5	4.4	5.5	0.35	267.6	0.101
5	4.5	4.4	5.6	0.37	334.4	0.114
6	4.5	4.4	5.7	0.40	386.8	0.118

Table VI: A Comparison of Simulated and Experimental Results for Crooked Creek Watershed

	Simulated	Experimental
Total Litter mass (g/m^2)	2448.0	3600.0
Litter Conc. (PPM)		
Lead	51000.0	72000.0
Cadmium	5.3	150.0
Zinc	121.0	2350.0
Copper	375.0	1400.0
Leaf Tissue Conc. (PPM)		
Lead	170.0	467.0
Cadmium	10.0	3.9
Zinc	50.0	47.0
Copper	10.0	10.0
Root Tissue Conc. (PPM)		
Lead	1150.0	2400.0
Cadmium	52.0	46.0
Zinc	52.0	48.0
Copper	10.0	6.0
Stem Tissue Conc. (PPM)		
Lead	27.0	680.0
Cadmium	9.0	3.9
Zinc	35.0	30.0
Copper	18.0	13.0
Soil Conc. Al Layer (PPM)		
Lead	271.0	334.0
Cadmium	4.4	3.55
Zinc	52.0	25.0
Copper	46.0	18.0

CONCLUSIONS/RECOMMENDATIONS

In conclusion the simulation studies indicate or predict the following:

- Fugitive sources of heavy metals from the mining and smelting operations are a significant problem. Roadways around the smelter yard have been paved and are now washed regularly to suppress suspension of dusts.
- Seventy percent of the water entering the watershed leaves it through unobserved aquifers. What is the fate of this water and the amount of heavy metals it may be carrying away?
- Amounts of Cd and Zn in the top soil layer have reached equilibrium; Pb and Cu continue to accumulate.
- Solubility limited leaching of heavy metals from forest floor litter is a significant process in the movement of these metals through a forested watershed.
- Simulated levels of Pb in litter and predicted litter masses are 50% lower than measured values, suggesting that measured Pb deposition rates were too low and/or were higher in years prior to the time monitoring of deposition rates was begun.

Based on experience gained with the application of the WHTM and TEHM versions of the UTM to heavy metal transport on CCW, the following recommendations are made:

- The WHTM version is more appropriate for studying water management, water quality, and land use pattern effects. It should be well suited for assessing strategies to reduce movement of toxic substances through a watershed and for assessing effects associated with the siting of a facility that would be a source of toxic substances.
- The TEHM version is more appropriate for studying effects of water management and toxic substances on vegetation. It can be used to assess effects of SO_2 damage to plants, CO_2 balance in the atmosphere and effects of fossil fuel burning, and effects of toxic substances from waste disposal operations. This version should be well suited for studying the toxic effects of heavy metals on plants and heavy metal uptake and distribution in plants resulting from application of sludges to agricultural land.

The WHTM version is generally easier to apply to a problem than the TEHM and runs faster on a computer. The WHTM is a shorter program and runs in less time, so is to be preferred when plant effects are not an important consideration.

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Leachate From Applications of Fertilizers, Manures and Sewage Sludges to Land

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INTRODUCTION

The application of fertilizers, manures, and sewage sludges to lands may affect the concentrations of various elements in leachates from soils in a variety of ways. The leachate composition will depend upon the solubility of the element in the water draining through the soil, the volume of water that moves through the soil, the composition and amount of material applied, the amount of each element volatilized or removed in harvested crops, and the amounts adsorbed on soil colloids or precipitated within the soil. Also, the chemical, physical, and biological properties of soil have a profound influence on leachate composition. In the sections which follow we will analyze the properties of fertilizers, manures, and sewage sludges and evaluate how applications of these materials will affect leachate composition under a variety of conditions. Although there are a number of similarities between the reactions of elements in the three materials in soil, for the sake of clarity of presentation, they are each discussed separately.

Fertilizers

Composition

The materials known as fertilizers include organic as well as organic materials and mixtures of each type. Because manures and sludges are treated separately in this paper, this section will deal with inorganic salts as fertilizers in which organic materials are added only as fillers or conditioners and do not add significantly to their supplies of nutrient elements.

Fertilizers are added to soils to supply nutrient elements that are present in soil in insufficient amounts to meet the needs of growing crops. Mostly, fertilizers are added to supply nitrogen, phosphorus and potassium, but in some cases they are added to supply other essential elements. The usual fertilizers consist of single salts or various combinations of some of the following: urea, ammonium sulfate, ammonium phosphates, ammonium nitrate, calcium nitrate, calcium phosphates, potassium chloride, potassium sulfate and other soluble salts. Some materials contain calcium sulfate and others contain small amounts of borates and the oxides, chlorides or sulfates of trace metals.

When fertilizers are added to soils, the elements supplied are either 1) removed in harvested crops, 2) precipitated in or sorbed by the soil and become part of the solid material, 3) removed as soluble salts in the leachate that leaves the soil-root zone, or 4) accumulate in the root zone as soluble salts. In addition to these alternative sinks, nitrogen can leave the soil by volatilization of ammonia from the surface or by denitrification and loss of nitrous oxide and dinitrogen gases. The accumulation of soluble salts in soils usually does not take place in humid regions because of their removal by leaching waters. In arid regions under irrigation, deliberate leaching is frequently necessary to remove soluble materials to prevent depressing effects of soluble salts on crop yields, but mostly these salts come from irrigation water and not from fertilizers.

Impact on Leachate Quality

Trace Elements. The reactions of most of these elements with soils insure that they will not be a problem for groundwater water quality with usual agricultural practices. Some of these elements are essential for crop production and others are not essential but are toxic if present in sufficient concentrations in the soil. Those elements that are essential can be deficient in the soil, in which case they are added at low rates to eliminate the deficiency. However, at the rates used to correct deficiencies the adsorption by the soil is sufficiently effective that movement to groundwaters is prevented. Those elements not essential but toxic to plants are added to the soil only as impurities in other chemicals; for example, a number of phosphate fertilizers have some heavy metal impurities, but these impurities are not known to cause problems for groundwaters.

Phosphorus and Potassium. The reactions of P in most soils is such that application rates used in crop production will not cause groundwater problems. The added P is so effectively adsorbed and/or precipitated that movement beyond 15–20 cm below the depth of incorporation over a period of years is highly unlikely. The only exception is on extremely sandy soils in which added P has been shown to move slowly with drainage. Spencer,[30] for example, working with a Lakeland fine sand (99% silica sand plus silt and 1% organic matter) found that surface applied P had moved to the 210-cm depth in a period of 10 years. Obviously, if this is the order of magnitude of the maximum rate of movement, the problem of P moving to groundwaters does not seem serious for most soils which will have rates of movement orders of magnitude slower.

The downward movement of K in most soils, when added at the rates used in crop production, is usually so slow that groundwater quality is not a factor. Potassium reacts into the cation-exchange complex of all soils and in many it is fixed into slowly leachable forms by micaceous clays. The rate of movement is variable depending on the cation-exchange capacity and fixation processes, but no problems are to be expected except in very sandy soils.

Nitrate. A great deal has been written about soil N and its pollution potential. Until recently very little research by agronomists and soil scientists had dealt with tracing the nitrate (NO_3^-) form of N through the unsaturated zone beneath the soil-root system into the groundwater. But recent research has concentrated on this important question.

For purposes of discussing groundwater pollution the N cycle

can be described as presented in Figure 1. The organic N consists of soil humus, residues of plants and the N added in organic wastes. In aerated soils the organic N that is mineralized goes rather quickly through the NH_4^+ and NO_2^- forms to NO_3^-. Commercial fertilizers usually add N in the NH_4^+ or NO_3^- form or as urea which quickly hydrolyzes to NH_4^+. Nitrite oxidizes rapidly to NO_3^- in most aerated soils and does not accumulate. Thus, the N added to aerated soils is either in the NO_3^- form or is converted to this form. In anaerobic soils (water saturated soils with low oxygen content), the NH_4^+ does not oxidize to NO_3^- and the NO_3^- in the soil is reduced to N_2O and/or N_2 by microbial denitrification processes in which organisms use the O from the NO_3^- and release N_2O and N_2 as end products. The N_2O and N_2 thus produced escape to the atmosphere.

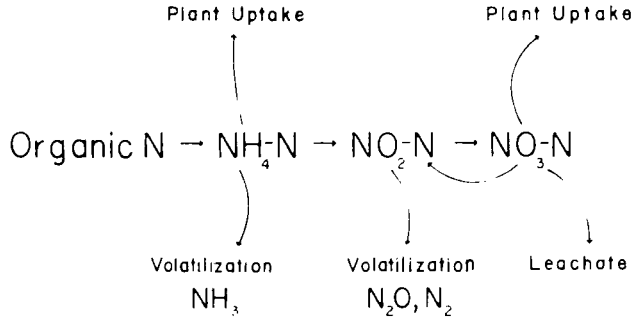

Figure 1: Nitrogen Cycle

Crop plants use either NH_4^+ or NO_3^- and convert the N into proteins. The N thus used goes to market as feed, food and fibers or is returned to the soil in plant residues (roots, stems and leaves). Thus, a simple N cycle can be visualized as a N input that is balanced by outgoes in 1) harvested crops, 2) leaching of the NO_3^- in drainage water, and 3) volatilization from the soil as NH_3 or as N_2O and N_2.

The removal of N in harvested crop plants is usually about 50% of the total inputs, but this removal varies from about 25 to 75% depending on the crop and the level of N inputs relative to crop needs. This low efficiency of use leaves a fairly large portion of the total input for leaching as NO_3^- or loss of NH_3, N_2O or N_2 to the atmosphere. Thus, there is little doubt that NO_3 escapes from the soil-root system and contributes to contamination of groundwaters. The only question is how much is contributed under various situations of soil, climate, cropping system and management.

The direct measurement of losses of NO_3^- from the soil-root system to the groundwater requires data for the volume of water leaving the root zone and the average NO_3^- concentration of this water for the period of time being studied. The concentration of NO_3^- in the water moving to the groundwater is not sufficient, since without an estimate of the volume of drainage, the transit time for the NO_3^- to move through the unsaturated zone and the dilution factor when the drainage water reaches the groundwater the concentration of the groundwater cannot be estimated.

$$NO_3^- - N = \frac{10N}{D} \qquad [1]$$

in which NO_3^-N is the concentration of NO_3^-N in mg per liter in the drainage water, N is the leached N in kg per hectare per year, D is the drainage volume in surface cm per hectare per year and 10 is a proportionality constant to convert from kg N per hectare in a given volume of water, expressed in surface cm, to mg N per liter, has been found to be useful in calculations. This relationship is expressed graphically in Figure 2.

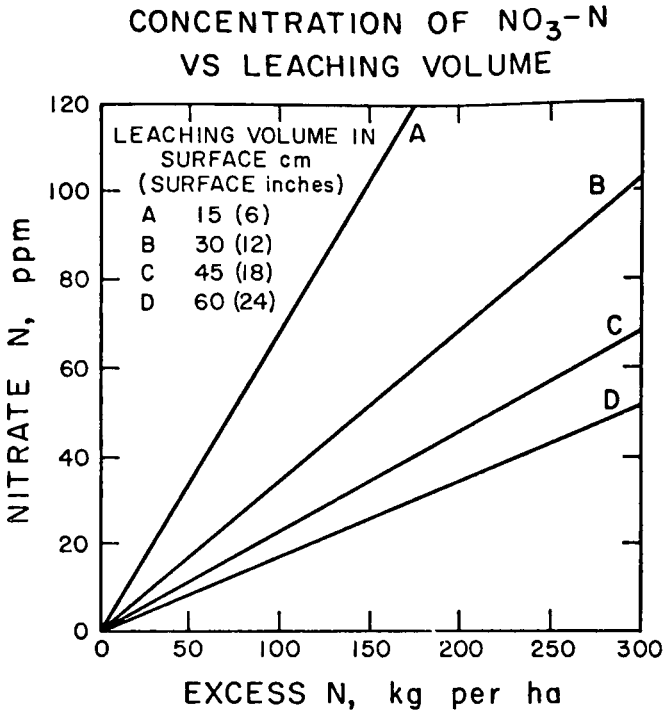

Figure 2: Relationship Between NO_3^-N Concentration and Leached N for Four Drainage Volumes, Calculated Using Equation [1].

The relationships among yield of harvestable crops, total available N input, N use efficiency, denitrification or total volatilization loss and the concentration of NO_3^-N in the drainage water are presented in Figure 3. This is a generalized relationship for a given drainage volume (15 surface inches) and a crop with a high N requirement. Also, the assumption is made that denitrification does not reduce fertilizer use efficiency.

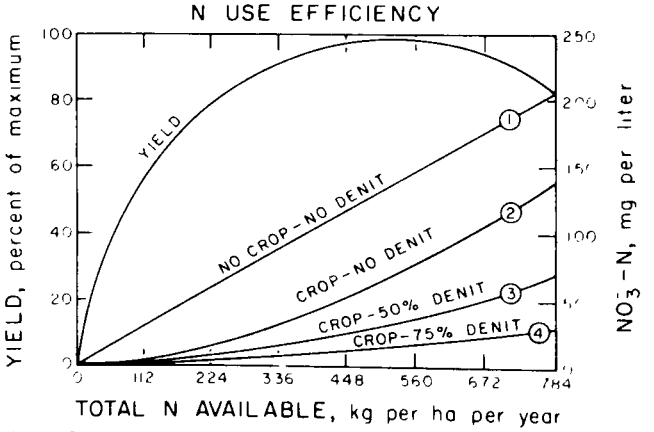

Figure 3: General Relationships of Yield of Harvested Crops, N Use Efficiency, and Concentration of NO_3^-N in Drainage Waters to Total Available Soil N for a Drainage Volume of 15 Surface Inches. Surves 1, 2, 3 and 4 represent concentrations of NO_3^-N in drainage water for 1) no crop-no denitrification, 2) crop-no denitrification, 3) crop-50% denitrification and 4) crop-75% denitrification, respectively. Denitrification is expressed as a percentage of the available N not removed by crops. The efficiency of removal of N by crops is assumed to vary from 90% at 112 kg available N to 4 at 672 kg of available N.

Considering the large numbers of combinations of N inputs, crop removals, leaching volumes and denitrification losses, NO_3-N concentrations from a few to several hundred mg per liter appear to be possible and have been found in the field. And considering all the variables discussed, the accurate prediction of the NO_3-N concentration of drainage water is difficult. However, useful estimates can be predicted from knowledge of fertilizer inputs, water intake and evapotranspiration (ET), removal in harvested crops and soil properties that influence volatilization losses.

The main concept in managing nitrogen fertilizer applications to croplands without increasing unnecessarily the leaching of nitrate is illustrated in Figure 3. In these relationships, the leaching of nitrate increases slowly with increase in available nitrogen until the point of maximum yield is reached. In some cases, where increased available nitrogen and the resultant yield increase cause greatly reduced volumes of leachate, the relationship between nitrate leached and available nitrogen inputs can be negative. In any event, as the point of maximum yield is exceeded the ratio of leached nitrate to nitrogen input increases with further increases in available nitrogen. Thus, only sufficient nitrogen required to reach the maximum yield should be applied.

The leachable nitrate is not a static value but is a highly variable and transient value. The actual amount of leached nitrate depends on how much water leaches, the timing of the leaching relative to the growth and nitrogen use cycle of the plants or the efficiency of the root system in absorbing nitrate during leaching and the amount of denitrification going on during the growth of the plant and during leaching. Thus, crop use of available nitrogen, nitrate leaching and denitrification are mutually competing processes, the final outcome of which is not easily predicted. Both leaching and denitrification or a combination of the two can cause inefficiencies that create the need for higher available nitrogen inputs to produce maximum yields. Increasing the yield of crops by better management of factors other than available nitrogen inputs will also increase the amounts of nitrogen used by the crop and reduce the potential leachable nitrate. Thus, the total yield per unit of available nitrogen needs to be kept at a high level.

The contribution of fertilizer nitrogen to nitrate in the groundwater depends not only on how much nitrogen is used per unit of cropland but also on the yield and removal of nitrogen in harvested crops, losses to the atmosphere and the volume of leachate in which the leached nitrate is dissolved (Figure 2). Thus, the correlations between concentration or amounts of nitrate leached and amount of fertilizer nitrogen are not high. Factors that control leaching, such as the amount and distribution of rainfall or water management in irrigated lands, and soil properties that influence both denitrification and leaching are likely to exert more control over the amount of nitrate leached to groundwater than the amount of fertilizer nitrogen added.

Two possible criteria for the contribution of fertilizers on croplands to the nitrate in groundwaters are concentrations of nitrate in leaching waters or mass emissions of nitrate nitrogen per unit area of land. The more rational of the two is the mass emission criterion. Methods of control should naturally lead to greater efficiency of use of nitrogen by crops. Perhaps the most effective method of increasing this efficiency is to reduce leaching to a minimum by control of the factors that influence water intake into the soil and evapotranspiration, i.e., control of irrigation and control of vegetative cover. But reduced leaching volume can create leachates with higher nitrate concentrations. In irrigated agriculture a quality standard based on nitrate concentration might encourage increased water use to keep the leached nitrate below some designated concentration. Increased water use would promote greater leaching losses and greater inefficiencies of applied nitrogen. A mass emission criterion would promote lower leaching volumes and greater efficiencies of use of both nitrogen and water.

Soluble Salts. The inorganic salts that are the main components of commercial fertilizers become part of the complex of soluble salts in the soil and thus contribute to the salinity of groundwaters. The contribution depends on what fraction of these salts are removed from the land in harvested crops and the fraction that is adsorbed and/or precipitated or in the specific case of nitrogen how much is lost to the atmosphere as ammonia, nitrous oxide and nitrogen. In humid regions, the salt from fertilizers that leaches to the groundwater is probably unimportant as compared to weathering processes that contribute salinity to groundwater. In arid irrigated regions, the salts from commercial fertilizers contribute to the salinity in the soil, however, the main source of soluble salts is the irrigation water itself. And, of course, in newly irrigated land residual salts in the soil and in underlying sediments can contribute substantial amounts of soluble salts to the groundwater.

Manures

Composition

The safest statements that might be made about the composition of manures is that they have low concentrations of the fertilizer constituents nitrogen, phosphorus and potassium as compared to commercial fertilizers, they have traces to small amounts of most elements found in soils and plants and the concentrations of many elements vary over considerable ranges. The composition of manure depends on the source, the ration and the management of manures following their production.

Powers et al.,[21] after reviewing available data that could be expressed on a dry weight basis, found large variations in composition of manures but could not relate these variations to climatic or geographical regions in the U.S.A. Table I, taken from Powers et al.,[21] presents data for the ranges in concentrations of some constituents in manures. Of the manures from beef and dairy cattle, swine and poultry, which represent the bulk of animal manures in the U.S.A., poultry manure usually has the highest and beef and dairy cattle manure the lowest nitrogen contents. But, fresh manure from cattle can have much higher nitrogen contents than aged poultry manures.

Table II presents data for a representative chemical composition of beef cattle feedlot manure from the arid Southwest (Meek et al.[18]). Many other trace elements could have been detected but were not included as part of the analyses. Furr et al.[6] found small concentrations of many trace elements and heavy metals in cattle manure. Most cattle manures that accumulate on corral floors lose 50% or more of their nitrogen contents by volatilization of ammonia before they are collected and spread on cropland.

Table III, which presents data for the concentration of several elements in a number of batches of both dairy corral manure and beef feedlot slurry manure, illustrates the problem of dealing with manures. Even though these batches of manures came from the same areas and were collected at the same times (fall for odd-numbered samples and spring for even-numbered samples), the concentrations were not consistent. The last batch collected was quite different from all other batches.

Impact on Leachate Quality

The effect of any soil amendment fertilizer or waste product added to the soil on the quality of the leachate that moves from the soil-root zone is naturally dependent on (1) the amount added, (2) the constituents contained in the material and their concentrations, (3) amounts of these that go into harvested crops and retained in the soil as insolubles as part of the soil solids. The elements of concern from the application of manures at recommended fertilizer rates for optimum crop production are

nitrogen in the nitrate form and the cations of calcium, magnesium and sodium and the anions chloride, sulfate and bicarbonate that constitute the usual soluble salts.

Trace Elements. The trace elements and heavy metals added in manures are of no concern except in unusual cases where such elements are added as inorganic salts to the rations such as feeding copper salts to swine. The concentrations of these elements are usually of the same order of magnitude as those in plants, residues and foods and feeds.

Phosphorus and Potassium. These elements are held in soils by adsorption and/or precipitation reactions so that they do not leach. Exception can be found in very sandy soils or in peat soils having only small capacities to retain or sorb these elements. However, when rates of application of manure far exceed the recommended rates needed for nutrient supplies, the leaching of phosphorus and potassium can take place depending on the ratio of inputs of these elements to the capacity of the soil to adsorb or precipitate them.

Nitrate. Perhaps the most universal leachate quality factor that results from the application of manures to croplands or to the spreading or incorporation of manures for disposal is the leaching of nitrate. Soluble salts are not necessarily a problem (when manure is used at recommended fertilizer rates) in humid regions where dilution with low salinity water occurs. But, in general, both the nitrate and soluble salt problems become more serious in arid regions. Thus, aside from certain local situations, the problems of nitrates and salts in leachates are inversely related to rainfall.

The problem in the use of manures to supply available nitrogen to meet crop needs is to determine proper application rates. Rates can be adjusted by conducting field experiments in a given local area. A number of such experiments can provide answers for the various combinations of manures, crops and soils. However, a degree of uncertainty always exists because of variations in composition of manures that appear to be the same product that has come from the same source.

Table II: Representative Chemical Composition of Beef Cattle Feedlot Manure from the Arid Southwest (Meek et al., 1974 and 1975).

Constituent	Composition, oven dry basis	
	%	mg/kg
Organic Matter	64	
Soluble ions	10	
Total N	2.0	
Nitrate-N		3.5
Ammonium-N	0.19	
Calcium	2.8	
Potassium	1.1	
Magnesium	1.5	
Sodium	2.8	
Phosphorus	0.27	
Aluminum	0.52	
Iron	0.48	
Copper		30
Lithium		9
Manganese		153
Zinc		99
Boron		137

Table I: Ranges in Concentrations of Four Elements, Expressed in Percent of the Dry Weight, for Manures from Beef, Dairy, Swine and Poultry

Animal	Element			
	N	P	K	Na
Beef	0.6 - 4.9	0.11 - 1.6	0.053 - 3.8	0.05 - 2.8
Dairy	1.5 - 3.9	0.41 - 1.6	1.4 - 3.3	0.35 - 0.90
Swine	2.0 - 7.5	0.56 - 2.5	1.5 - 4.9	-*
Poultry	1.1 - 7.8	0.38 - 6.3	0.73 - 4.8	0.66 - 0.89

*No reliable data available on a dry weight basis.

Table III: Dry Matter and Mineral Element Contents of Batches of Manure Obtained Over a Period of 4 Years in Southern California.

Batch number**	Dry matter	Element***				
		N	P	K	Na	Cl
			-%			
		Dairy manure from corrals				
1	80	2.2	0.55	2.6	1.0	1.3
2	61	1.3	0.38	2.7	1.0	1.3
3	49	2.2	1.25	4.8	1.1	2.0
4	62	1.4	0.81	3.5	0.76	1.2
5	75	2.1	0.48	3.1	0.75	1.4
6	68	1.5	0.54	3.4	0.82	1.4
7	80	1.5	0.37	2.4	0.40	1.7
8	77	0.75	0.34	2.6	0.47	2.2
		Beef feedlot slurry for slatted floor				
1	9.7	5.6	0.93	3.9	2.7	3.7
2	12.2	4.4	0.78	2.3	2.1	3.1
3	10.0	5.0	1.9	3.4	1.6	2.4
4	10.9	4.3	1.7	3.4	1.6	2.2
5	10.2	5.2	1.0	4.1	1.8	3.2
6	10.7	4.1	0.81	2.9	1.4	2.6
7	9.0	5.2	0.95	3.6	1.2	2.6
8	15.8	2.4	0.51	2.5	0.54	0.92

* From a field experiment by P.F. Pratt and Sterling Davis, Department of Soil Science and Agricultural Engineering, University of California, Riverside, California 92502.

** Odd-numbered batches were obtained in the fall and even-numbers in the spring.

***Element concentrations expressed on a dry weight basis.

A more rational approach would be to determine the availability of nitrogen in the manure based on its properties. For example, one could analyze each batch of manure for its nitrogen content before it is applied and then calculate amounts to add based on previously determined nitrogen availability coefficients. Pratt et al.[22] developed a simple method of calculating the mineralization of nitrogen added in manures. The mineralization rates, referred to as decay series, were related to the nitrogen contents of manures as well as the nature of the manure. Poultry manure and cattle manure do not necessarily have the same nitrogen mineralization rates at the same nitrogen contents. Dry chicken manure at 3% nitrogen on a dry weight basis will provide much more available nitrogen than fresh feedlot slurry manure that has 3% nitrogen on a dry weight basis. Powers et al.[21] developed an approach for estimating manure rates based on the decay series and the soluble salt content of the manure.

The decay series is a set of coefficients for the yearly mineralization of a given application of a manure. For example, the series 0.35, 0.15, 0.10, 0.05—implies that 35% of the nitrogen will mineralize the first year, 15% of the residual nitrogen will mineralize the second year, 10% the third year, and 5% of the residual will mineralize the fourth and each subsequent year. By keeping records of how much manure is added and the decay series of each application, one can calculate the amount of nitrogen that will be mineralized each year for an indefinite period of time. This concept is presented in Figures 4 and 5. Figure 4 shows the increase in yearly mineralization over a 20-year period if manure is added at a constant rate, whereas Figure 5 shows the downward adjustment of yearly rates of application of manure to adjust for mineralization of residual organic nitrogen that accumulates so that various constant rates of yearly mineralizations are obtained.

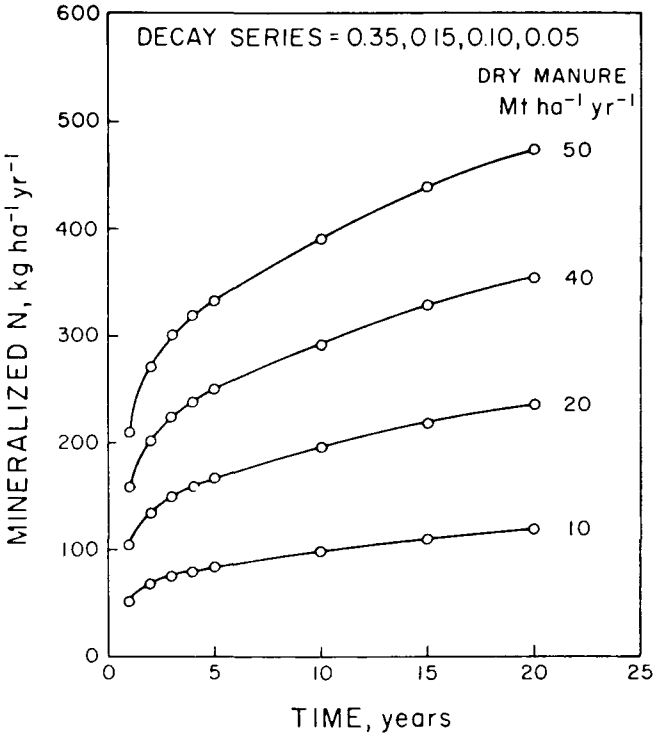

Figure 4: Yearly Mineralization Rate in Relation to Time for Various Constant Rates of Corral Manure Having 1.5% N and the Decay Series Indicated

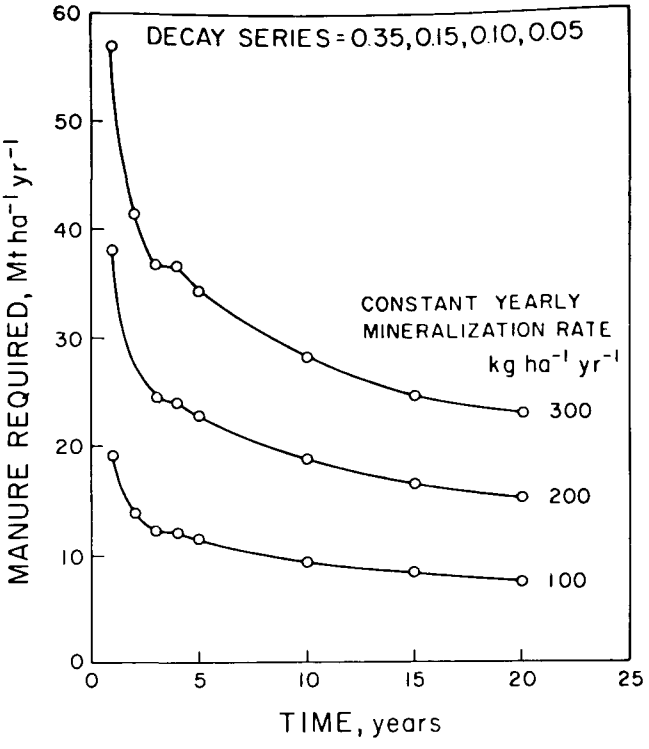

Figure 5: Yearly Rates of Application of Manure Having 1.5% Nitrogen and the Indicated Decay Series Required to Give Various Constant Yearly Rates of Nitrogen Mineralization.

Powers et al.[21] developed a formula for calculating the rate of manure based on the nitrogen requirement of the crop, the nitrogen content of the manure, the available nitrogen in the soil and expected inefficiencies of available nitrogen because of volatilization losses and denitrification. The equation, expressed in English units, is

$$R_J = \frac{N_C - N_S + N_L}{20\,C\,[D_1 + \sum_{J=1}^{J-1} D_{J+1}\,(1-\sum_{i=1}^{i=J} D_i)]}$$

where R_J = application rate for the Jth year in tons manure per acre.

N_C = nitrogen used by the crop in pounds per acre.

N_S = nitrogen available in the soil in pounds per acre.

N_L = nitrogen loss expected from denitrification and volatilization.

C = concentration of N in the manure in percent.

D_1 = first term in the decay series (dimensionless).

D_{J+1} = the (J+1)th term in the decay series (dimensionless).

D_i = ith term in the decay series (dimensionless).

The limit to R_J was based on a value, R_m, which is a factor for build-up of inorganic salts and is a function of soil, salinity of the irrigation water, amount of leaching and the salt content of the manure.

This decay series approach requires that (1) the manure be analyzed for nitrogen and soluble salts, (2) the farm manager keep accurate records of manure applications and their decay series, (3) estimates of losses to the atmosphere by denitrification and by ammonia volatilization are predictable, (4) available nitro-

gen in the soil at the start of each season be determined, and (5) crop needs are known. The practical application of this approach as a management procedure is doubtful even if it were possible. An alternative and much simpler approach would be to analyze the soil each year to determine the available nitrogen and the expected mineralization during the season, analyze the manure to be added and estimate how much to add to supply the needed extra nitrogen based on a first-year mineralization rate for that material. Unfortunately, we do not have reliable methods for determining the available nitrogen and expected mineralization of nitrogen that can be used for all soil-climate-management conditions but estimates of both can be obtained for many such combinations.

The decay series approach may not be useful directly in making management decisions because of the lack of specific information and lack of record keeping, but the concept can and has been used to illustrate improper management principles. Pratt et al.[23] used decay series to calculate the large potential leaching of nitrate from large applications of manure followed by a period of years of no applications as compared to smaller yearly applications. Decay series and calculations based thereon can be used as models to predict effects of various management alternatives. Meek et al.[18] found in field plots that more nitrate leached from a fine-textured soil when a large application was followed by two years with no manure as compared to manure applications each year. The annual application of manure apparently provided a yearly input of available carbon that promoted increased denitrification.

Soluble Salts. The amounts of soluble salts provide an upper limit to the use of manures on cropland because of reduced crop yields as a result of increased soil salinity. This upper limit depends on the salinity of the soil, of the water if the land is irrigated and of the manure, the salt tolerance of the crop and management factors that promotes leaching to remove the salt. These upper limits in most cases are usually not far above the point of optimum supplies of plant nutrients. Thus, management to use the manure for crop production is not compatible with using the soil to dispose of the manure.

The amounts of soluble salts contributed by manures to groundwaters depends on (1) the composition of the manure and amount added, (2) the amounts of elements removed by crops, and (3) the quantities of various constituents precipitated and/or adsorbed in the soil. These are all highly variable factors making general predictions rather unreliable.

In acid soils of humid climates, the precipitation of calcium carbonate and calcium phosphates are effectively prevented leaving the calcium to leach. On the other hand, in alkaline soils of irrigated arid regions, both calcium carbonate and calcium phosphate precipitate as a result of adding manure such that much less of the added calcium leaches. In fact, the addition of manures to some irrigated lands may not increase the leaching of salt in direct proportion to the salt content of the added manure because of precipitation reactions.

Sewage Sludges

Composition

Sewage sludge is a by-product of the treatment of domestic wastewater. In the sewage treatment process inorganic and organic substances in the wastewater are separated, and these in addition to biomass produced in the treatment process and excess water make up the bulk of sludges.

The solids content of sludges varies and tends to increase with the degree of treatment. Primary and secondary sludges have bonded water and settle out slowly; their solids content ranges from 1 to 5%. Digested sludges characteristically retain less water and their solids content commonly ranges from 6 to 12%. Greater amounts of water can be removed from sludges by heat treatment, chemical additives and/or mechanical aids. The degree to which sludges are dewatered has a marked influence on the concentration of inorganic nitrogen. The inorganic forms of nitrogen in anaerobically and aerobically digested sludges are ammonium (NH_4) and nitrate (NO_3) ions, respectively. Since these forms of nitrogen are highly soluble, they tend to remain in the liquid phase, and as the degree of dewatering increases, their concentrations in sludges tend to decrease.

The chemical composition of sludge is highly variable. Being an aggregate of impurities originating in wastewaters, the chemical composition of sludges depends upon the source water, the kind and extent of sewage treatment, the nature of the sewage treatment process, the nature of the collection and conveyence system, local conditions relative to consumer products entering sewers through domestic use, and the kinds and percentages of industrial input. Because of these factors the composition of sludges are highly variable within the same treatment plant in relation to time and among treatment plants in different communities.

Data considered representative of the chemical composition of sludges generated in the U.S.A. are presented in Table IV. Although sludges are seldom treated to reach a completely dry stage, all data are expressed on a dry weight basis to provide more convenient comparisons. The data have been derived from recent published reports (Baker and Chesin,[2] Furr et al.,[6] Konrad and Kleinert,[15] Page,[20] Singh, Keefer, and Horvath,[29] Shipp and Baker,[27] Harter,[7] Blakeslee,[3] and Sommers[29]). The concentrations given may differ from those of other published reports because we have exercised some judgment in eliminating extremes at both ends of the scale where abnormally high or low concentrations for various elements occurred in sludges from only a very limited number of those surveyed.

As with all materials which in one way or another find their way into the surface of soils, the extent to which sludges may contribute to the quality of the leachate depends upon (a) the chemical composition, (b) the amount applied, (c) amounts removed by volatilization or in harvested crops, and (d) amounts precipitated in soil or dissolved from soil. The cation exchange complex in soils will influence the ionic composition of electrolyte in the leachate, but will not alter the total composition when expressed in chemical equivalents.

Impact on Leachate Quality

When sludges are applied to soil, a series of complex chemical and microbial reactions take place. These reactions are time and temperature dependent, and are governed largely by the chemical properties of the soil and sludge. The systems have not been studied in sufficient detail to predict the time required to achieve a steady state leachate composition in the sludge-soil mixtures. The information which is available, however, suggests that at temperatures which are not extreme, after a few months changes which occur in leachate composition are gradual. Following sludge application leachate composition will depend upon the quality and quantity of water which enters and moves through the mixture.

Trace elements. For major changes in leachate composition in sludge amended soils most probably occur in a transition zone immediately below the depth of incorporation of the sludge. The extent to which the concentrations of trace elements are changed in this zone are determined largely by the chemical properties of the soil. The chemical properties of soil are governed largely by the amount and kind of colloidal clay and organic matter. Solutions passing through soils low in organic matter and with high percentages of sand-sized particles generally have a lower capacity to attenuate the composition of the solution passing through them than do soils with high percentages of clay and organic matter. Generally, those trace elements which occur in solution in a molecular or anionic form tend to migrate to greater depths

in the soil profile than do trace elements which occur as cations in solutions.

Following application of sludge to soil, the composition of the leachate in relation to depth will depend largely on the factors which control the solubility of the various trace elements. Soils and sludges are dynamic complex systems and although progress has been made in our knowledge of their chemistry, we still lack the necessary basic information to predict concentration of trace elements in even the most simple sludge-soil mixtures. Generally, when sludges are incorporated into soil the solubility of most trace elements is reduced considerably.

Where sludges are used in agriculture as a plant nutrient supplement, application rates are commonly based upon the nitrogen requirement of the crop grown, and usually would not exceed 40 metric tons per hectare per year. At annual sludge application rates of this order of magnitude for periods of at least 10 years, the available information indicates that movement of elements such as Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, and Zn beyond one meter depth in the soil profile is unlikely. Kirkham,[14] for example, did not observe movement of Cd, Cu, Ni, Pb, and Zn below 61 cm depth following applications of approximately 28 metric tons of dry sludge per hectare per year for a 35-year period. Page[20] evaluated data presented by Andersson and Nilsson[1] and demonstrated that following annual applications of seven metric tons of sludge per year for twelve years, essentially all of the applied Mn, Zn, Cu, Ni, Co, Cr, Cd, Hg, As, and Se were recovered in the surface 20 cm of soil. Only B moved in substantial amounts to depths lower than 20 cm in the soil profile. In a study at the Werribee Sewage Farm at Melbourne, Australia, Johnson et al.[9] observed practically no movement of Zn, Cu, Ni, and Cd below 45 cm in a field which had been irrigated with raw sewage for 70 years.

In systems involving long-term, high rate volume operation for the disposal of sludge, movement of trace elements to depths of at least three meters has been observed. Lund, Page, and Nelson[17] presented data which show movement of Cd, Cu, Ni, and Zn to a depth of at least three meters in a soil beneath a sewage lagoon which had been used to pond sewage sludge for a period of at least 20 years.

In summary, soils except for sands have a high capacity to retain As, Cd, Cr, Cu, Hg, Ni, Pb, Se, and Zn. In situations where sludges are applied to agricultural soils to supplement plant nutrients or as a source of irrigation water, the probability that leachate below one meter depths will show enrichment in the above elements is light. Boron, however, is an exception. Except in highly alkaline soils (pH >8.5), B occurs in soil solutions as undissociated boric acid [$B(OH)_3$]. It is sorbed by active oxides of iron and aluminum in soil, but its affinity for these solid surfaces is low compared to affinities of other trace elements for these surfaces. For this reason, boron is quite mobile in soils. In sandy soils low in organic matter and active iron and aluminum oxides, B in water passes through soils essentially unchanged. Organic matter and active iron and aluminum tend to limit the mobility of B in soils, but generally the equilibrium is such that substantial percentages of the B remain in solution and move with the percolating water.

Phosphorus and Potassium

Phosphorus concentrations of sewage sludges range from about 0.5 to 3.0% with typical concentrations of about 1.5% (Table IV). In liquid sludges dissolved P occurs as orthophosphates, polyphosphates, and organic phosphates. In acid soils phosphorus is adsorbed or precipitated by crystalline and/or amorphous iron and aluminum oxides. In neutral or calcareous soils, orthophosphate reacts with calcium to form, depending upon ionic composition, a number of slightly soluble or insoluble calcium phosphates.

Table IV: Typical Concentrations of Various Elements in Sewage Sludges from the U.S.A.

Elements	Range	Median	Mean
		%	
N	1.0 -10.0	3.0	4.0
P	0.5 3.0	1.5	2.0
S	0.5 1.5	1.0	1.0
K	0.05- 1.0	0.3	0.4
Ca	1.0 -10.0	4.0	5.0
Mg	0.2 1 0	0.4	0.5
Fe	1.0 6.0	1.0	1.5
Al	0.5 -10.0	0.5	1.5
Cl	0.1 1.0	0.4	0.4
	ug/g		
B	5- 150	40	70
Cu	100-4,000	750	1,000
Mo	1-40	5	15
Mn	100-800	300	500
Zn	1,000-6,000	1,800	2,800
As	5-50	10	25
Cd	5-500	15	80
Co	1-20	10	10
Cr	200-20,000	400	2,000
F	2-400	50	170
Hg	0.5-50	7	10
Ni	10-4,000	60	350
Pb	20-20,000	450	1,800
Se	2-20	4	10

A number of long-term fertility trials and studies involving land applications of sewage sludges have demonstrated that phosphorus movement to lower depths in soil profiles is quite restricted. Pratt et al. (1956) reported that following application of a total of 1756 kg P per hectare (as treble superphosphate) over a 28-year period more than 80% of the applied P remained in the surface 30 cm of soil and no movement of P was observed at depths greater than 90 cm. Similarly, William and David[31] observed essentially no movement of P below 10 cm depth in a soil which had received 2500 kg P per hectare over a forty-year period.

In systems where liquid sludges are applied at high rates, phosphorus movements to considerable depths in soil profiles has been observed. Hook et al.[8] observed movement of phosphorus to a depth of 120 cm after irrigation with a sewage effluent at a rate of 5 cm per week for a six-year period. The concentrations of phosphorus at the depths sampled were greater for a sandy loam soil than a clay loam soil. Bray extractable phosphorus (0.025 *N* HCl - 0.03 *N* NH_4F) increased to a depth of 90 cm in a sandy loam profile, but only to 30 cm in a clay loam profile. In the sewage farm serving Melbourne, Australia, Johnson et al.[9] reported total concentrations of phosphorus at depths between 25 and 45 cm in soils irrigated with primary sewage effluent for a period of 45 to 73 years which were twice those of the non-effluent treated soils. Most of the phosphorus, however, accumulated in the surface 25 cm of soil. Lund, Page, and Nelson[17] followed the movement of phosphorus in soil beneath lagoons used as percolation ponds for liquid sludges. In their study movement of phosphorus to a depth of at least 3 meters was observed.

It seems reasonable to conclude that in situations where

sludges are used in agriculture as a nutritional supplement for long periods of time (>25 years) the probability that this practice would cause P contamination of leachates from soils at depths greater than a few meters is remote.

Potassium concentrations of sludges on a dry weight basis are usually less than those of animal manures. The rate of movement of K in soil is minimal, and except in very sandy soils, the probability of a significant K contribution from sludge applications to leachate below one meter depth in soil is nil.

Nitrogen

Concentrations of nitrogen in sewage sludges range from 1 to 10% (Table IV). In liquid anaerobically digested sludges from 30 to 60% of the total N is present in the ammonical form and the remainder in the organic form (Metcalf and Eddy[19]). If liquid sludges are applied directly to land, a certain percentage of the ammonical N is lost by volatilization as NH_3 as the sludge dries in the field. The actual amounts lost by volatilization reported in the literature vary widely and range from a few percent to almost complete loss (Coker[5]; Ryan and Keeney[25]; King[12]). Incorporation of liquid sludges below the soil surface serve to minimize N losses by this process.

Nitrogen in organic forms applied to soils must undergo mineralization to inorganic forms (NH_4^+ and NO_3^-) before it can be utilized by plants or to NO_3^- form before it is readily leachable. The rate of mineralization, a microbial process, depends upon a number of soil factors such as water content, aeration, pH, and temperature. Although precise rates for various soil types and climatic regions have not been completely worked out, the available data indicate that from 15 to 35 percent of the organic N is mineralized the first year of the application (Pratt, Broadbent, and Martin[22]; Keeney, Lee, and Walsh[11]; Ryan et al.[26]; King[12]). Lesser percentages of the remaining organic N are mineralized in subsequent years. For example, Keeney, Lee and Walsh[11] suggest 15% mineralization in a sandy loam soil the first year, 6% the second year, 4% the third year, and 2% thereafter.

The first product of mineralization of organic N is NH_4^+ ions. If the pH of the system is less than 4.5, further conversion to NO_3^- is completely inhibited and the N remains as NH_4^+. The NH_4^+ is adsorbed on the negatively-charged surfaces of the soil colloids and, as such, leaching of N is highly restricted. In most soils (sands are possible exceptions) leaching of N in the NH_4^+ form is so small that for all practical purposes it can be ignored. If the pH of the soil exceeds 9.0, sufficient NH_3 forms to inhibit nitrification to NO_3^- and N can be lost by NH_3 volatilization.

At soil pH's in the range 4.5 to 8.5, and under conditions when the dissolved O_2 exceeds 0.2 mg/l, the NH_4^+ formed by mineralization of organic N is rapidly oxidized to NO_3^-. Nitrate is quite mobile in soils and that which escapes the zone in soil under the influence of evapotranspiration will leach with water to lower depths in the soil profile. In soils where regions of low dissolved O_2 (<0.2 mg/l) occur at depths within or below the rooting zone, if there is sufficient organic carbon, NO_3^- can be reduced and lost as N_2 gas. Bouwer and Chaney[4] state that about one milligram of organic carbon is required to reduce one milligram of nitrate nitrogen to N_2 gas.

Once NO_3-N escapes the zone in soil where it is removed by plants or denitrified, its leaching in soil parallels quite closely the movement of water. The amounts of N available for leaching are therefore the difference between the amount applied and the sum of amounts removed by harvested crops plus volatilization losses as either NH_3 or N_2.

A number of studies have demonstrated substantial concentrations of NO_3^- at depths in soil well below the root zone. Lund, Page, and Nelson[16], for example, reported concentrations of NO_3^-N greater than 400 mg/l at a depth of 12 meters below a sludge lagoon. The lagoon had been used to dewater sludge at the treatment plant for about 20 years. On an offsite control at a comparable depth (12 meters) the concentration of NO_3^-N was 30 mg/l. King and Morris[13] and Kardos and Sopper[10] have observed substantial increases in NO_3N in soil solutions at a depth of 1.2 meters beneath fields receiving either sludge or effluent applications.

Although the above observations show high concentrations of NO_3N in leachate at lower depths in the soil profile, it is not possible to evaluate the impact on groundwater quality. As mentioned previously, mass emissions of NO_3^-, which depend on volume of flow, must be determined before an evaluation of the extent of groundwater contamination can be made.

SUMMARY

The amounts of elements in fertilizers, manures, and sewage sludges which when applied to soils will enter leachates are determined by the difference between the amounts added plus amounts solubilized in soils less the amounts removed in harvested crops, lost by volatilization, and precipitated or sorbed by the soil. Organic forms of nitrogen added to soils, regardless of source, must undergo mineralization to NO_3^-N forms before extensive leaching of the added nitrogen will occur. The rates of mineralization are not precisely known for the various materials and environmental conditions, but most likely they are from 15 to 35 percent of the applied organic nitrogen during the initial year following application, with progressively lesser percentages of the remaining organic nitrogen mineralized each subsequent year. Once NO_3^-N leaches to depths in soil not influenced by evapotranspiration, the NO_3^-N will migrate with water essentially unchanged. To minimize NO_3^-N leaching, quantities of plant available nitrogen in excess of that required for optimum crop production should not be applied.

Nitrogen applied to soils can be volatilized as NH_3, N_2, or N_2O gas. Ammonia is lost when ammonical sources of N dry on the surface of soils or in soils where the pH is greater than 8.5. In soils under anaerobic conditions NO_3^-N is reduced to N_2 and N_2O gas and lost from the soil system.

Commercial fertilizers are applied to soils in amounts sufficient to meet nutritional requirements of the crop. Potassium and phosphorus are relatively immobile in most soils (sands are exceptions) and the probability that soil applications of commercial fertilizer sources of these elements will cause substantial enrichment of leachates in soils below depths of one meter in the soil profile is remote. Trace elements (Cu, Zn, Mn, Fe) are frequently added to commercial sources of N, P, and K in small amounts to serve as sources of the plant essential micronutrients. Since amounts added to fertilizers, or those that occur naturally as contaminates are very small and soils have a high capacity to attenuate these elements, commercial fertilizers are not expected to serve as a source of enrichment of trace elements in leachates from soils.

Leachate enrichment resulting from the practice of spreading manures is usually restricted to soluble nitrate, chloride and bicarbonate salts of sodium, calcium, and magnesium. Phosphorus and potassium present in manures are retained by the soil and will not contribute to leachate contamination below one meter depth in most soils. The concentrations of trace elements in animal manures are low and, as such, the probability that manures will cause trace element contamination of leachates is also low.

Sewage sludges can be considered low analysis fertilizers. Their composition varies widely and depends largely upon the composition of the wastewaters entering the treatment plant. In situations where sludges are applied to soils at rates sufficient to supply fertilizer nitrogen, as with manures, enrichment of leachate below one meter depth in the soil profile is usually restricted to soluble nitrate, chloride, and bicarbonate salts of

sodium, calcium and magnesium. Prolonged use of sludges or where application rates greatly exceed those required to supply fertilizer nitrogen, however, may cause trace element and phosphorus contamination of leachates at considerable depths in the soil profile. The extent of contamination will depend upon the composition of the sewage sludge, the total amounts applied and the physical, chemical, and biological properties of the soil.

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The Effects of Industrial Sludges on Landfill Leachates and Gas

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INTRODUCTION

Environmental effects from landfilling result from not only soluble and slightly soluble material disposed of in the landfill, but also from the products of chemical and microbial transformations. These transformations should be a consideration in management of a landfill to the extent that they can be predicted or influenced by disposal operations. The motivational aspects of this project were the lack of quantitative data on the decomposition process under field conditions, and, in particular, the effects of the introduction of solid and semi-solid industrial waste materials with municipal solid waste.

Previous reports on this study have dealt mainly with placement of the waste materials and concentration/time relationships. This presentation will deal with total mass flows emanating from these cells.

Approach

In an effort to evaluate the many variables which may effect gas and leachate production within a sanitary landfill environment, nineteen (19) large scale environmental test cells are being monitored to achieve the following objectives:

1. Assess the effects of varying rainfall regimens, 203.2 to 812.8 mm/yr (8.0 to 32.0 in/yr).
2. Determine the impact of municipal sewage sludge additions on the rates of decomposition and gas and leachate production.
3. Determine the impact of decomposition rates by the addition of a pH buffer (limestone) into waste during landfill construction.
4. Determine the survival of polio virus in a landfill environment.
5. Determine if differences in ambient soil temperatures significantly effect the rates of decomposition and gas and leachate production.
6. Determine the impact on decomposition in gas and leachate production from the co-disposal of six (6) selected industrial residuals with municipal solid waste.
7. Determine the ability of duplicate test cells to generate similar physical and analytical data.
8. Determine the impact on decomposition rates by rapidly bringing the municipal solid wastes to field capacity.

The test cells (experimental landfills), employed for this study were epoxy coated steel, 1.8m (6 ft) in diameter and 3.6m (12 ft) in height; capable of holding approximately 3000kg (6600 lbs) of municipal solid waste in a manner comparable to large area landfills. The size of the test cells was selected to minimize the problems of scaling factors generally associated with smaller laboratory lysimeters and to avoid the use of shredded refuse. A total of fifteen (15) cells were placed in the ground outdoors with the remaining four (4) cells in the enclosed bay area where higher ambient temperatures were maintained. Prior to placement of any solid and/or industrial wastes, a layer of silica gravel, 300mm (1 ft) deep, was placed in all cells as a base for the solid waste and to allow leachate to permeate to the drain system. All test cells were coated with coal tar based epoxy paint which was proven to be resistant to leachate degradation.

All test cells were loaded simultaneously in a period of five (5) days employing municipal solid waste from the City of Cincinnati. The solid waste was placed into experimental landfills in 370kg (800 lb) increments and compacted to a height of 300mm (1 ft), and a density of 470kg/cu m (800 lb/cu yd) until each test cell had received 2.4m (8 ft) of solid waste or approximately 3000kg (6600 lbs) of compacted material. Industrial residuals were added to the solid waste as it was placed into the experimental test cells.

The solid waste was then covered with a layer of compacted clay and all cells were shielded from both moisture and sunlight. Temperature and gas monitors are installed throughout all cells and in the soil. Water addition to the cells is at a rate of 406mm (16 in) per year and is accomplished on a monthly basis in accordance with anticipated net infiltration for the midwestern portion of the country, Figure 1.

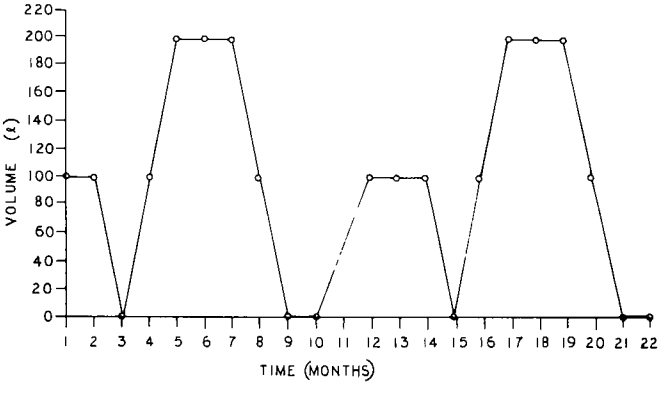

Figure 1: Water Addition Regimen

Industrial Residuals Under Study

The industrial process residuals evaluated include a refinery sludge (RS), a battery production waste (BPW), an electroplating waste sludge (EW), an inorganic pigment sludge (IPW), a

chlorine production brine sludge (CPBS), and a solvent based paint sludge (SBPS). Physical characteristics and amounts of each industrial waste added is provided in Table 1.

Refinery sludge is a byproduct of the refining of crude oil. The waste material obtained is an API bottoms sludge. This is material resulting from gravity oil/water separator which is very high in biological activity.

The battery production waste is a composite from all phases of a lead/acid storage battery manufacturing operation, with the exclusion of the battery plate assembly section. This operation is a closed system from which the waste material is shipped to a smelter for the recovery of lead. The waste obtained goes to a neutralization process before entering a settling pond from which the sludge was obtained.

The electroplating waste was obtained from a large plating firm which employs a variety of plating processes including: chromium, nickel, cadmium, copper, iron and zinc. No tin plating occurs at this location. These wastes were treated in various categories.

Chromium wastes were converted to trivalent chromium by the addition of sulfur dioxide in an acid system (pH of 3). The pH was then raised to approximately 8.0 with caustic to precipitate the trivalent chromium. The cyanide containing wastes were treated by raising the pH of the water with caustic and then breaking down the cyanogen system by the addition of sodium hypochlorite. All other acid wastewaters were treated with base to elevate the pH to approximately 8 to 9. Wastewaters were then pumped to a lagoon for settling.

The inorganic pigment waste is a byproduct of the processing of raw ore and the production of titanium dioxide. Wastewaters from various manufacturing operations are pumped to a single facility and treated simultaneously. This waste material was then pumped to a primary settler during which the pH was raised with base and an alkaline precipitate formed. The sludge was then dewatered and the residue removed for disposal.

The chlorine production brine sludge is from a mercury cell chlorine production plant. In this facility the production of chlorine was accomplished by the electrolysis of sodium chloride in a mercury cell. The majority of the sludge (60 to 80%) was from the brine saturator. While the remainder was from the clarifier after settling.

The solvent based paint sludge used was representative of a paint sludge produced in industries involved in painting large numbers of metal products. The paint overspray was caught in a water curtain and was pumped directly to a holding tank for disposal with little or no pre-treatment.

The chemical analyses of these waste materials, Table 2, indicated that the sludges contained significant levels of potentially toxic materials. The leachability of these materials, however, still was not known.

Leachate Composition

Immediately after compaction, small volumes (less than 1 liter) of leachate were obtained from the majority of the cells. Based on the chemical characteristics and time of appearance it was concluded that these initial volumes of liquid were interstitial waters squeezed from the refuse or refuse/sludge mixtures as a result of the compactive effort and were not truly leachate derived from infiltrating water and decomposition processes. After collecting and the initial squeezings from the test cells, no further liquid was produced for a period of approximately six (6) months. The early occurrence of leachate was attributable to several factors, first, the number of available moisture retention sites was reduced by the addition of the moist industrial wastes and for this reason field capacity was approached at a much earlier date than originally expected. Secondly, it appeared that

Table I: Waste Stream Characteristics

CELL	WASTE STREAM	MOISTURE CONTENT[a]	AMOUNT ADDED[b]	CHARACTERISTICS
9	RS[c]	79.00	1518	HIGH BACTERIAL ACTIVITY; BLACK MOIST
10	BPW[d]	89.25	1291	GREY, HIGH LIQUID CONTENT
12	EW[e]	79.53	1191	BROWN, SOUPY
13	IPW[f]	51.75	1420	BLACK, SOLID, NO ODOR
14	CPBS[g]	24.11	2039	VERY DENSE, NO ODOR, LIGHT BROWN, MOIST
17	SBPS[h]	24.75[i]	1604	RED TO WHITE COLOR, PUTTY CONSISTENCY, STRONG ODOR

[a]PERCENT BY WET WEIGHT
[b]Kg
[c]REFINERY SLUDGE
[d]BATTERY PRODUCTION WASTE
[e]ELECTROPLATING WASTE
[f]INORGANIC PIGMENT WASTE
[g]CHLORINE PRODUCTION BRINE SLUDGE
[h]SOLVENT BASED PAINT SLUDGE
[i]MAINLY ORGANIC SOLVENTS

there was channelling within the solid waste/industrial waste test cells. Channelling prolongs the time required to reach field capacity, but allows the early appearance of leachate.

The behavior of the organic fraction of the solid waste/industrial waste leachate is represented by graphical displays of chemical oxygen demand (COD), Figures 2-4. The concentration histories for COD in leachates from the refuse alone and from the refuse/industrial waste cells are very similar and after approximately two years of monitoring appear identical. During the initial phases of this study, the COD from several of the industrial waste cells (electroplating waste, battery production waste) indicated a significantly higher chemical oxygen demand than did the solid waste leachates. This is attributable to a chemical demand being asserted on the leachates and not from the presence of organic carbon analyses. After approximately eight (8) months from placement of the solid waste or solid waste/industrial waste mixtures, the graphical displays for COD are almost identical.

Table II: Industrial Waste Chemical Analysis[a]

WASTE CELL NUMBER	RS[b] 9	BPW[c] 10	EW[d] 12	IPW[e] 13	CPBS[f] 14	SBPS[g] 17
TOTAL SOLIDS[h]	21.00	10.75	20.47	48.25	75.89	75.25
TOTAL VOLATILE SOLIDS[h]	31.00	7.94	8.98	22.25	1.17	55.25
MOISTURE[h]	79.00	89.25	79.53	51.75	24.11	24.75
Cr	125	155	1.56[h]	0.50	5.00	75.0
Ni	23	32	35	10	65	0.5
Cu	3500[i]	1125	100	110	125	2.0
Fe	5560	2950	1.37[h]	1000	2000	150
As	1.0	72	460	3.4	14.5	12.8
Be	4.8	1.8	0.25	20.2	<1.0	<1.0
Se	26.0	180	4.50	16.0	16.5	7.60
Cd	0.50	29.0	38.5	10.5	0.70	0.50
Cn	1.0	4.2	460	3.4	14.5	12.8
Pb	182	3.48[h]	267	120	697	12.6
Cl[h]	2.35	1.12	1.35	10.0	20.0	0.75
ASBESTOS[j]	3.00	208	23.0	45.0	110	9.00
Hg	10.6	4.80	14.7	7.60	227	16.7
Sn	NA[k]	6800	NA	NA	NA	NA
Sb	NA	1.32[h]	NA	NA	NA	NA
CLAY VOLATILE FIBERS[j]	40.0	720	86.0	185	480	65.0
Zn						
V	NA	120	NA	40	NA	NA
B	7.20	8.10	19.0	28.5	1.70	11.4
Ti	NA	NA	NA	NA	<0.1	NA

[a] ALL VALUES IN PPM UNLESS OTHERWISE SPECIFIED
[b] REFINERY SLUDGE
[c] BATTERY PRODUCTION WASTE
[d] ELECTROPLATING WASTE
[e] INORGANIC PIGMENT WASTE
[f] CHLORINE PRODUCTION BRINE SLUDGE
[g] SOLVENT BASED PAINT SLUDGE
[h] PERCENT BY WET WEIGHT
[i] UNDERLINED VALUES INDICATE MAXIMUM SLUDGE CONCENTRATIONS
[j] FIBERS/100 G.
[k] NOT ANALYZED

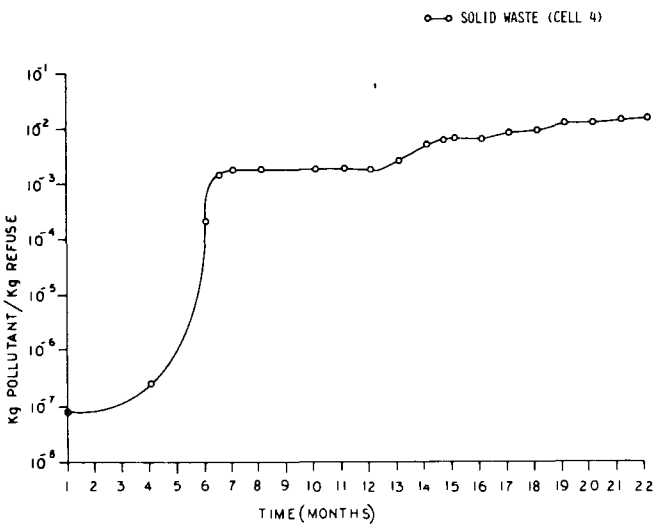

Figure 2: Chemical Oxygen Demand

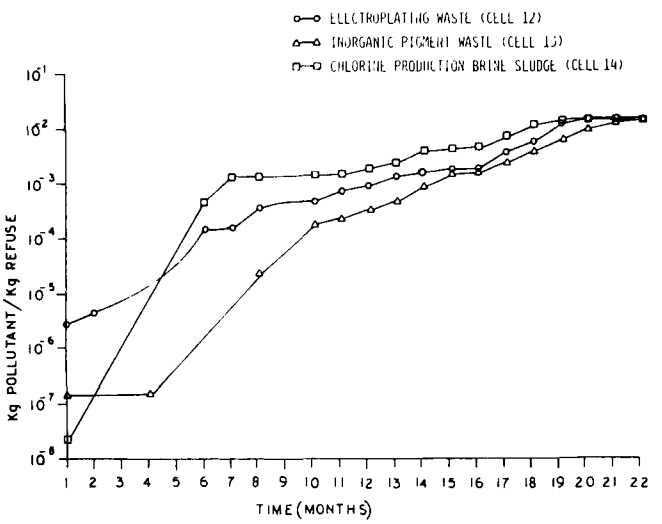

Figure 3: Chemical Oxygen Demand

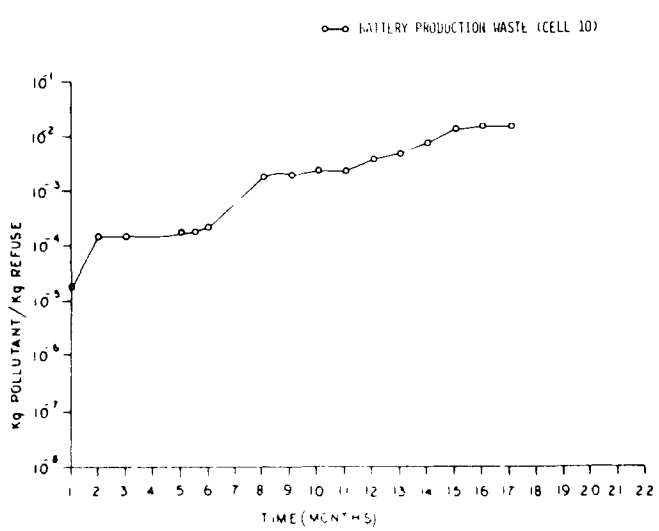

Figure 4: Chemical Oxygen Demand

In an effort to show the effects of a co-disposal of industrial residuals upon the release of the nutrient parameters, the concentration histories for total Kjeldahl nitrogen (TKN), Figures 5-8, are given. Initially the solid waste only was generating more TKN than the solid waste/industrial waste admixtures. This is probably due to the fact that the nitrogenous compounds within the industrial waste cells were not as amenable to degradation. After a period of approximately eight (8) months, however, the mass flows of TKN are approximately equal.

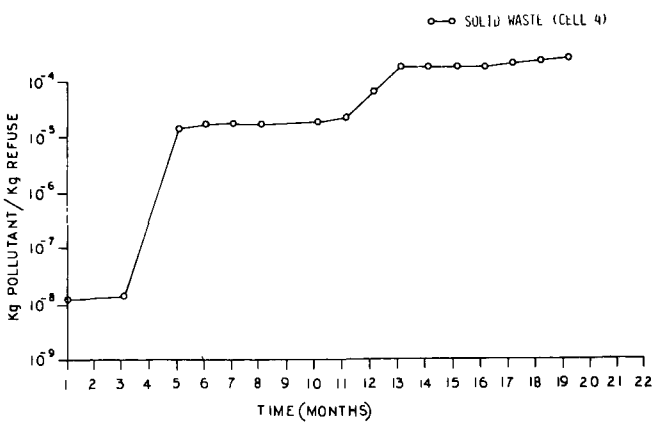

Figure 5: Kjeldahl Nitrogen

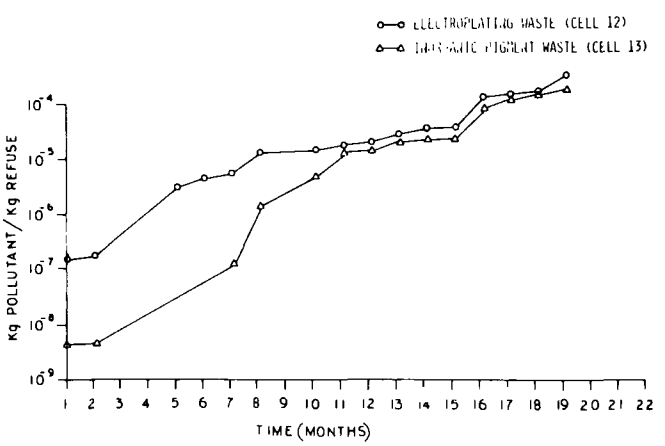

Figure 6: Kjeldahl Nitrogen

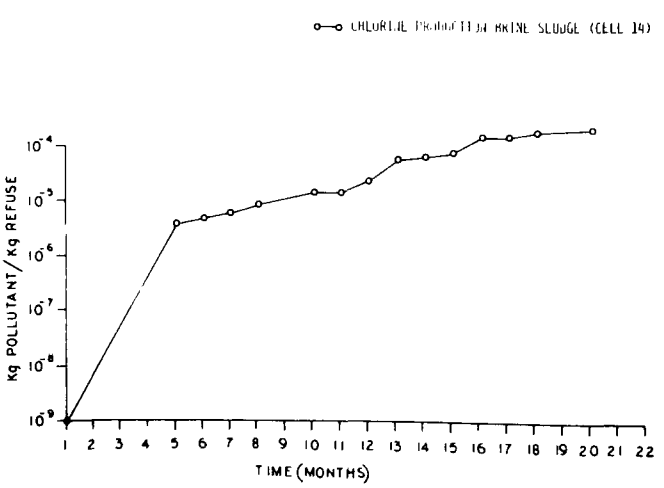

Figure 7: Kjeldahl Nitrogen

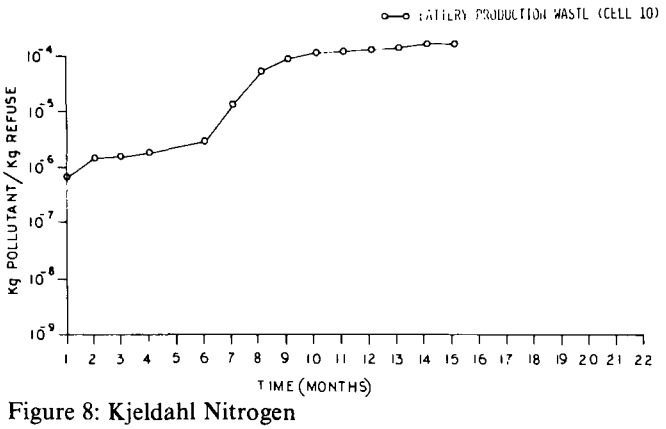

Figure 8: Kjeldahl Nitrogen

Total solids, Figures 9-11, is one of the few parameters where variances between the solid waste only cell and those containing industrial wastes are evident. The mass flow diagrams for the solid waste; the battery production waste, and the electroplating waste are almost identical. The total solids leached from the inorganic pigment waste is considerably lower than that leached from the other cells while the chlorine production brine sludge is substantially higher. The solids content within the leachate is relatable to the concentration of several other pollutants, in particular metallic ions, but at this time we have not been able to statistically evaluate the exact nature of this relationship. It does appear, however, that the higher the solids content the higher the pollutant potential of the leachate stream.

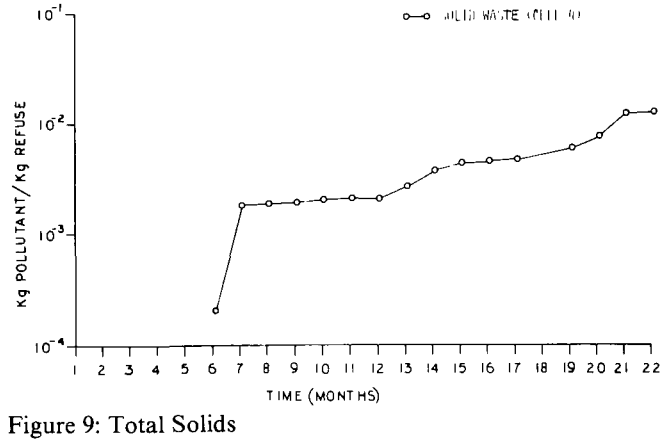

Figure 9: Total Solids

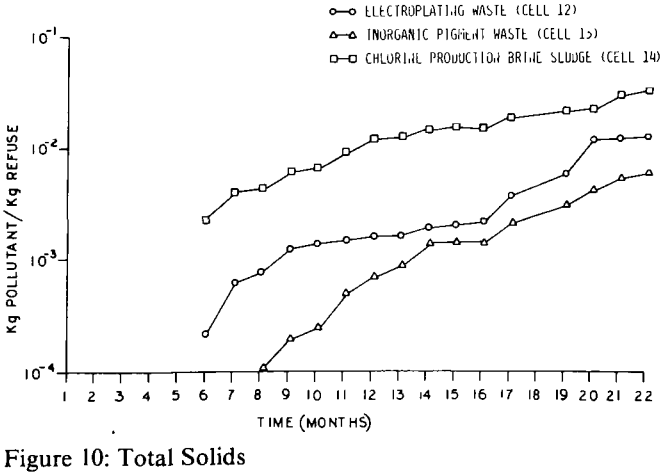

Figure 10: Total Solids

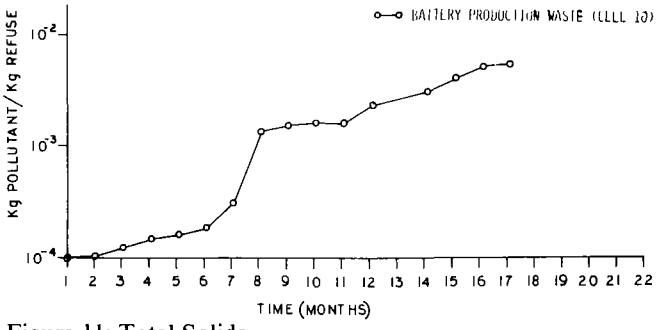

Figure 11: Total Solids

It has been felt for some time that the co-disposal of industrial residuals with municipal solid waste would generate a leachate stream which would be higher in metallic ion content than that from the municipal solid waste alone. In examining the total mass flow of pollutants from these experimental landfills that conclusion does not appear to be always valid.

The solid waste test cell is leaching zinc at a higher rate than any of the industrial waste/solid waste mixtures, Figures 12-14. During the initial phases of decomposition, the organic acid content increased within all test cells and as it did the amount of metallic ions being leached increased at a substantial rate. After approximately twelve (12) months, the organic acids content began to level out as well as the amount of metallic ion leaching. At this point in time all test cells are leaching zinc at approximately the same amounts. It is interesting to note the already solubilized zinc within the electroplating waste. The initial amounts of zinc leached from the electroplating waste cell were relatively high and no substantial increase above these values has occurred.

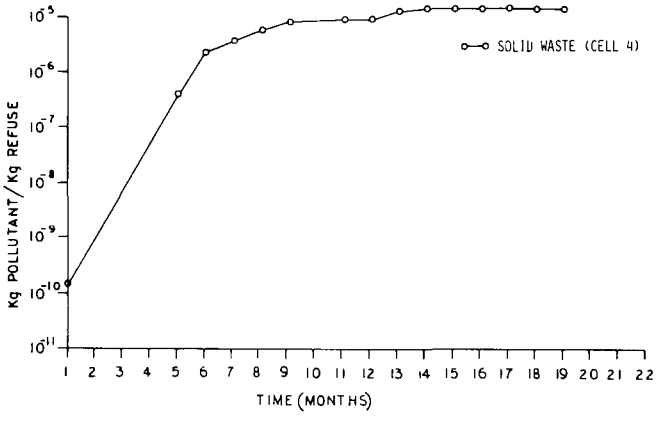

Figure 12: Zinc

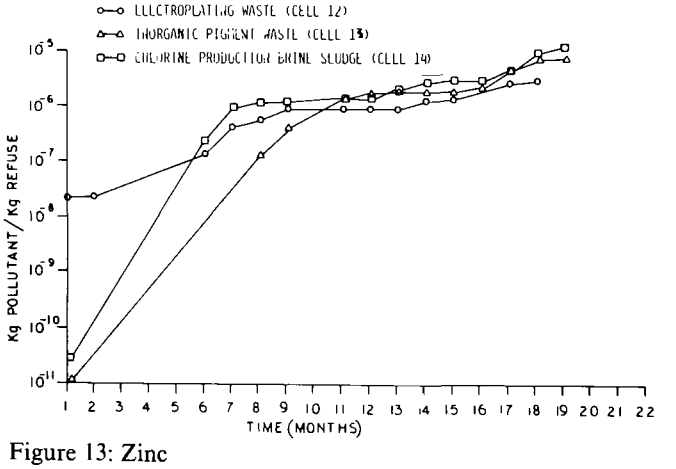

Figure 13: Zinc

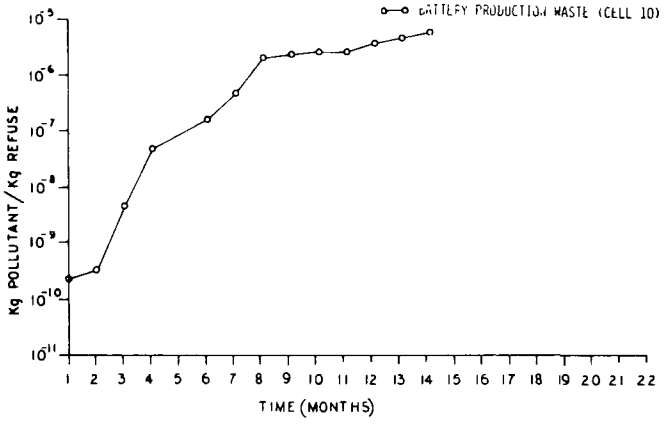

Figure 14: Zinc

The increase in lead leached, Figures 15-17, with the increased organic acids content indicates the solubilization of the lead within the solid waste. This is also evident within the cells containing the inorganic pigment waste and the chlorine brine sludge. Initially, the already solubilized forms of lead within the electroplating and the battery production wastes are present even though both wastes had been treated with caustic to form an "insoluble" hydroxide material. However, the amount leached from the solid waste, the inorganic pigment waste, the electroplating waste, and the battery production waste all are presently at the same levels. The one cell which is leaching lead at a higher rate, is the chlorine production brine sludge which appears to be leaching many materials in greater amounts. It is interesting that the industrial residuals containing ten to fifty times the amount of lead initially present within the solid waste itself are not leaching lead at any greater rate or duration than the solid waste alone.

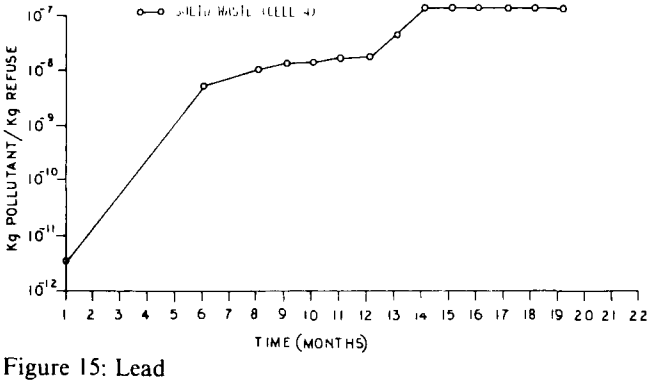

Figure 15: Lead

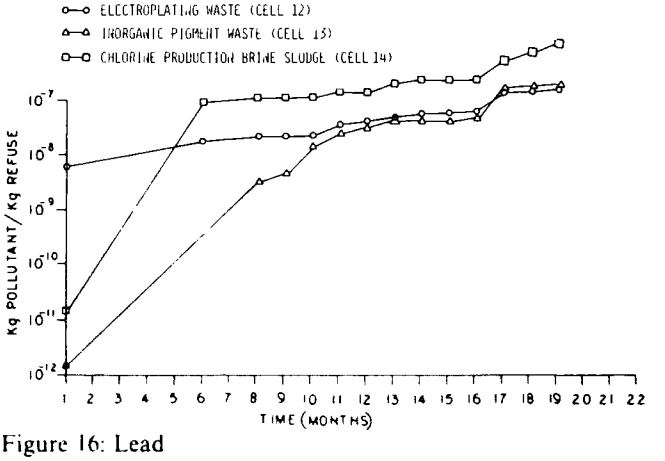

Figure 16: Lead

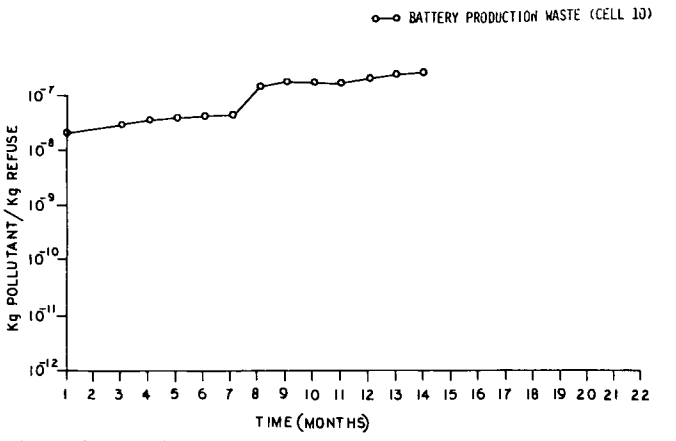

Figure 17: Lead

The graphical displays for nickel, Figures 18-20, indicate the same increased solubilization with time, due to the presence of organic acids, with the exception of the electroplating waste and the battery production waste which contained solubilized forms of nickel. As time progresses, a majority of the concentration histories appear to equilibrate with the exception of the chlorine production brine sludge and the electroplating waste. Both industrial waste cells are leaching higher amounts of nickel than the solid waste control cell.

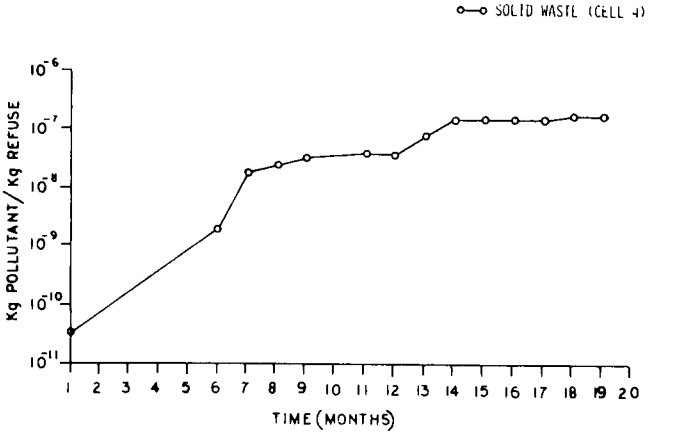

Figure 18: Nickel

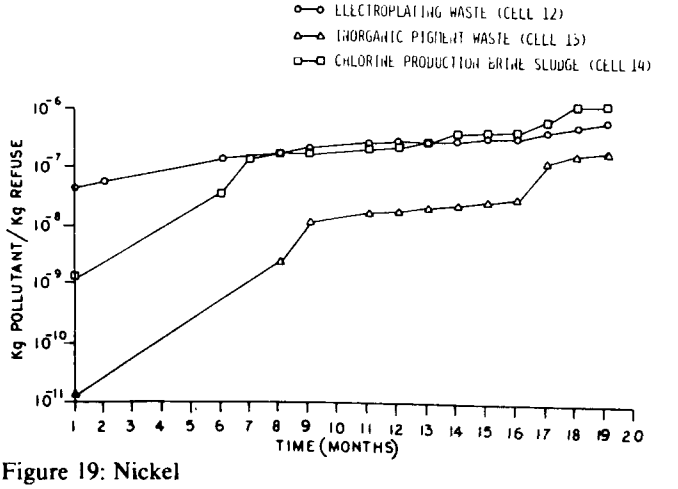

Figure 19: Nickel

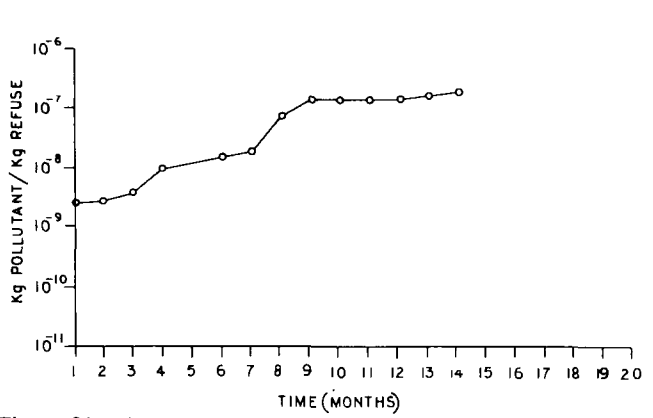

Figure 20: Nickel

There was an initially high concentration of solubilized chromium leached from the electroplating waste cell, this has continued to leach at a high level. The chlorine production brine sludge and battery productionste cells are leaching high levels of chromium. All these cells are leaching at greater rates than from the solid waste alone. It is yet too early in this project to determine if the present rate will continue or whether it will level off, Figures 21-23.

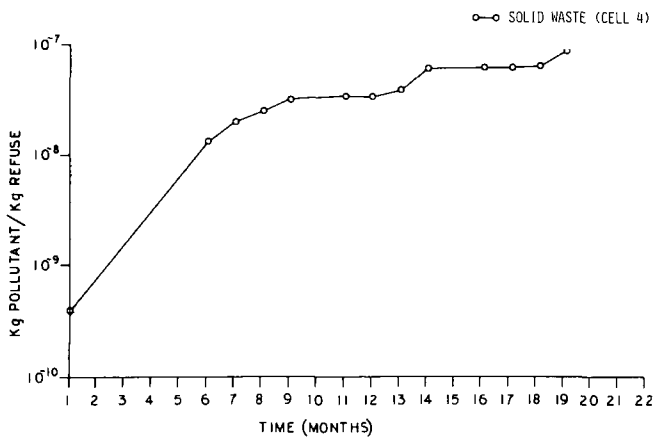

Figure 21: Chromium

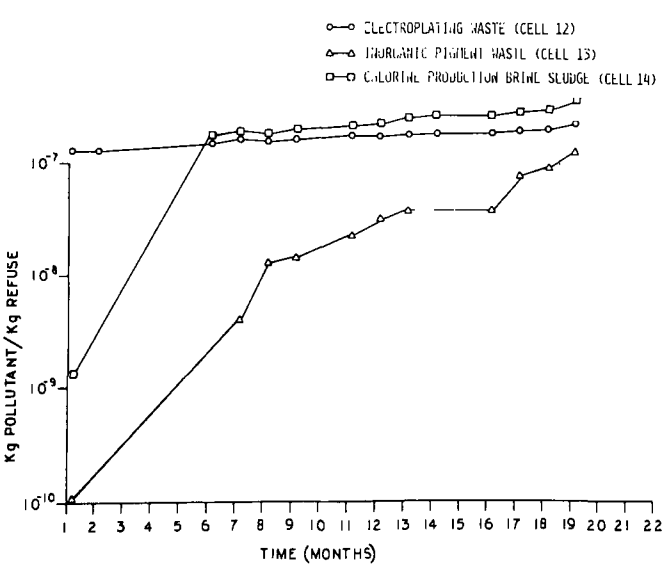

Figure 22: Chromium

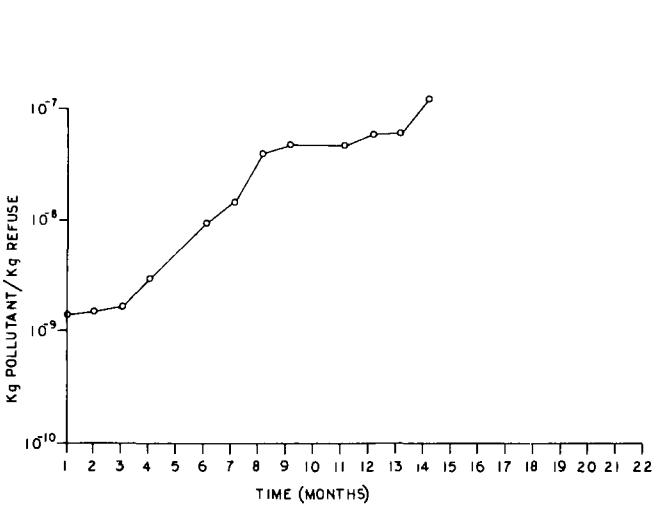

Figure 23: Chromium

Other leachate parameters were also monitored but on a less frequent basis. Sustained maximum concentrations of several parameters were determined but only those concentrations which occur on a somewhat continual basis are shown in Table 3. It would appear that certain of the waste materials (chlorine production brine sludge) are leaching materials at a higher rate and duration than the solid waste only test cell. The chlorine production brine sludge has shown thirteen (13) contaminants exceeding those concentrations which appear from the refuse only cell. Of those thirteen (13) which exceed the solid waste leachate, ten (10) of those are maximums for all the lechates evaluated. We, at this time, do not have sufficient data on these parameters to draw statistically significant interpretations and therefore it is impossible to presently assess the effects of many of these pollutants.

Microbial Analyses

Monitoring of the bacterial activity within all test cells indicates no survival of the coliform group and increased survival for the fecal streptococci. Attempts to increase bacterial recovery employing EDTA (ethylenediaminetetracetic acid) at various concentrations (0.05 , 0.1 and 0.15 molar EDTA) has shown inconsistent results. The data generated so far on the bacterial EDTA suspensions do not indicate increased bacterial recovery employing this technique. It does not appear that metallic ion concentrations within the industrial waste test cells is having any effect upon microbial activity within those cells.

Gas Production

Gas production within the solid waste test cells has been approximately 55 liters per day. Only one industrial test cell is, at this time, being monitored for gas production and it is producing gas at a substantially lower rate. Major problems have been encountered in sealing the test cells against gas leakage and we have only recently been able to collect the gas for quantitative measurement. For these reasons, it is too early to draw any definitive conclusions as to the effects of industrial waste upon gas production in a municipal landfill environment.

Summary

The addition of industrial residuals to the conventional solid waste landfill appears to have the following effects: (1) A reduction in field capacity by the addition of solid and semi-solid industrial waste materials. (2) No difference in the total amounts of leached organic or nutrient parameters from the solid waste

only or the solid waste/industrial waste mixtures has been seen. (3) Initially high amounts of leached pollutants from the industrial waste test cells indicates already solubilized forms of these pollutants present within the waste stream. (4) No substantial difference has been noted in the amounts of metallic ions leached from solid waste only or the solid waste/industrial waste mixtures.

ACKNOWLEDGEMENT

This work was accomplished under EPA contract 68-03-2120 under the direction of the Municipal Environmental Research Laboratory (MERL), Cincinnati, Ohio.

Table III: Sustained Maximum Concentrations of Leachate Contaminants[a]

WASTE CELL	SW[b] 4	SS[c] 7	RS[d] 9	BPW[e] 10	EW[f] 12	IPW[g] 13	CPBS[h] 14
VANADIUM[i]	<0.03	<0.03	<0.03	[(0.29)][jk]	<0.03	[(0.23)]	<0.03
ARSENIC[l]	12.2	10.7[m]	<3.0	(14.9)	6.3	(21.2)	[(214)]
SELENIUM[l]	<5	<5	(13)	<5	[(230)]	(10.0)	<5
ANTIMONY[i]	0.59	(0.7)	0.19	0.54	(0.98)	(0.84)	[(1.82)]
TIN[l]	150	NA[n]	(800)	(1200)	(3000)	(2400)	[(8000)]
SULFUR[l]	674	289	NA	491	68	(846)	[(3362)]
ASBESTOS[p]	<100	(200)	<100	<100	<100	[(6000)]	(3000)
CYANIDE[l]	<1	<1	<1	(1.2)	<1	[(5.0)]	<1
ALUMINUM[i]	<0.05	<0.05	(1.2)	(8.1)	<0.05	(5.4)	[(11.2)]
PHENOL[i]	4.3	[(18.0)]	[(22.9)]	NA	NA	NA	NA
BERYLLIUM[l]	<0.3	<0.3	(0.9)	[(45)]	(30)	(4.5)	[(48.0)]
LEAD[l]	1510	1064	1450	(3380)	(1820)	(2140)	[(6460)]
TITANIUM[i]	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	[(0.6)]
MERCURY[l]	19.7	[(284)]	(31.2)	7.2	(26.9)	(67.1)	[(328)]
BORON[i]	18.1	(19.0)	2.8	13.3	(22.0)	(24.0)	[(83.0)]
NICKEL[l]	1360	(3400)	1010	1319	(3505)	(1490)	[(6020)]
ZINC[i]	4.3	2.9	2.1	(5.2)	0.5	[(11.2)]	(8.0)
HEXAVALENT CHROMIUM[l]	<2.5	<2.5	[(19)]	<2.5	<2.5	[(12.0)]	<2.5
SUMMATION		4 (6) [2]	6 (7) [2]	4 (8) [2]	3 (8) [1]	0 (16) [5]	0 (13) [11]

[a] HIGHER CONCENTRATIONS MAY HAVE BEEN DETECTED
[b] SOLID WASTE
[c] SEWAGE SLUDGE
[d] REFINERY SLUDGE
[e] BATTERY PRODUCTION WASTE
[f] ELECTROPLATING WASTE
[g] INORGANIC PIGMENT WASTE
[h] CHLORINE PRODUCTION BRINE WASTE
[i] mg/1.
[j] ( ) INDICATES EXCEEDED SOLID WASTE
[k] [ ] INDICATES MAXIMUM SUSTAINED CONCENTRATION OBSERVED
[l] μg/1
[m] UNDERSCORE INDICATES LESS THAN SOLID WASTE
[n] NOT ANALYZED
[p] FIBERS/1

A Preliminary Examination of Vinyl Chloride Emissions From Polymerization Sludges During Handling and Land Disposal

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INTRODUCTION

In January, 1974, the deaths of four workers in the vinyl chloride/polyvinylchloride (VCM/PVC) industry were attributed to VCM exposure. Since then angiosarcoma of the liver, a rare and fatal tumor, has resulted in the death of at least 15 workers in U.S. PVC facilities. In addition, other forms of cancer, certain nonmalignant liver diseases, and acroosteolysis, a unique occupational disease, also have been found in workers within the industry[1].

Thus it was decided by the EPA that a need existed to investigate VCM emissions from PVC waste sludges and typical disposal sites representing a cross section of climate conditions, disposal methods, and contiguous population densities. Consequently the present study was initiated as a preliminary, low-level effort, to determine approximate VCM concentrations in landfill air and to perform initial measurements, in the laboratory and under controlled conditions, on the rates at which VCM is released from PVC sludges.

Polyvinyl Chloride Production

PVC, commonly known as vinyl plastic, is produced from VCM, a colorless, faintly sweet smelling gas. VCM is converted to solid PVC by one of four different batch polymerization processes. U.S. PVC production for 1974 was about 4.75 billion pounds[2]. The processes used and the percentages of total production they represent are listed in Table I.

Table I: PVC Processes

Process Type	Polymerization Medium	Percent of Total PVC Production
Suspension	Water	78
Emulsion	Water	12
Bulk	Monomer	6
Solution	Organic Solvent	4

Regardless of the process used, we are interested here only in those steps of the PVC production process which result in byproduct wastes containing suspended solid matter and VCM. Since most PVC is produced in aqueous media these by-product streams consist basically of water suspensions of fine, particulate PVC containing small amounts of various polymerization processing aids, and dissolved and/or absorbed VCM. It is this entrapped VCM which is of concern.

The aqueous waste streams are treated in various ways at different PVC plants. Basically the processing consists of steps to concentrate the solids content of the waste as much as possible while discharging waste water of acceptable quality to the local water treatment system, or natural outlets such as rivers. The processing includes chemical treatments to coagulate and sediment the solids and physical separation procedures such as large, specially designed settling and concentrating tanks and specialized centrifuging and filtration procedures. The final waste material is a water-based sludge ranging from about 15 to 40 percent solids. Physically these sludges range from waterlike, thin slurries to thick pastes approximating the consistency of a concrete premix.

At the present time most, if not all, of these sludges, are discarded at municipal or privately owned landfills. Typically the sludges are transported to the landfill in pressure-controlled tank trucks or open-bed trucks and dumped into bulldozer-prepared pits or trenches that are 0.6 to 3 or more meters deep. They are then covered with compacted layers of trash and soil to a depth of 0.3 to 1 meter or more.

Sample Collection

Arrangements

At the beginning of this study three PVC plant site/landfill combinations were selected for sampling purposes. These combinations were chosen to provide good cross-sections of geographical location and climate, PVC plant technology, sludge type, and landfill practice. The protocol established for sample collection included the following steps:

(1) Visit to PVC plant by EPA and Battelle personnel
(2) Tour of PVC sludge processing, isolation, and storage facilities
(3) Observations of PVC sludge collection by waste hauling company
(4) Collection of PVC sludge samples for VCM analysis
(5) Follow sludge hauling truck to landfill with PVC company and/or hauling company personnel
(6) Meet landfill operating personnel and gain access to landfill
(7) Collect background air grab sample before PVC sludge disposal
(8) Observe PVC sludge disposal practice
(9) Collect air and sludge samples during disposal
(10) Collect air samples after PVC sludge disposal and coverage
(11) Collect air samples at same landfill site approximately 1 day later.

Air Samples

Grab air samples were collected at landfills before, during, and after sludge disposal and coverage, downwind of the known VCM emissions sites. Several samples were also collected outside the boundaries of one landfill. The samples were collected in preevacuated (10^{-8} torr at 150 °C) 3.5-liter stainless steel cylinders by opening the entrance port at normal breathing levels. The date, time, weather, and wind conditions were recorded for each sample taken.

Sludge Samples

During this study samples of the PVC sludges were collected both at the plants and at the landfills. Sludge collections at the landfill were done during the actual disposal operation except at Landfill 1 where sludge was collected both after disposal and after bulldozing and partial coverage. Sludge samples were collected in tightly sealed glass containers to prevent VCM evaporation, returned to the laboratory and stored at 5 °C until analysis could be performed.

Analytical Methods

The standard equipment used for VCM analysis in this study was a gas chromatograph-flame ionization detector (GC-FID) apparatus. Seven crosschecks were performed using a mass spectrometer (MS), with excellent agreement found. Grab air samples were analyzed directly, by injection of air aliquots into the GC-FID or, in one case, the MS. Headspace and liquid phase portions of PVC sludge samples were also analyzed by direct injection into the GC-FID or MS. PVC sludges were routinely analyzed for VCM content by extraction with tetrahydrofuran (THF) and injection of an aliquot of the THF extract into the GC-FID[1]. One direct analysis of a PVC sludge sample was also performed using the MS.

VCM Concentrations

VCM concentrations are expressed in parts per million (ppm). VCM concentrations in air are based on a volume ratio, or microliters of VCM per liter of air. Thus 1 ppm equals 1 μ l VCM/liter of air. However, VCM concentrations in PVC sludges are based on a weight ratio, and micrograms of VCM per gram of sludge. Thus 1 ppm VCM in sludge equals 1 μ g VCM/gram of sludge.

VCM Analysis by GC-FID

The analyses were done on a Packard Series 800 gas chromatography instrument using the following conditions:

Column
Porapak Q in an 8' x 316" stainless steel tubing

Temperatures
Column 120 C, Detector 120 C, and Injector 120 C

Flows
Nitrogen Carrier 30 ml/minute; Air 300 ml/minute; Hydrogen 30 ml/minute

Electrometer
500 volts; 1 x 10^{-10} amps

Detector
Hypodermic syringe septa and six way gas sampling valve

Detector
Flame Ionization.

The GC was calibrated using commercial (Matheson Gas Co.) standards of VCM in nitrogen, supplied with a certified analysis. These were reanalyzed in our laboratory by MS. One standard contained 20.5 ppm VCM in nitrogen and the other 0.45 ppm. The 20.5 ppm standard was used routinely for this work.

In addition, a mixture of saturated and unsaturated hydrocarbons including methane, ethene, acetylene, ethane, propane, propene, isobutane, 1-butene and n-butane was chromatographed. Also individual samples of dichlorodifluoromethane (Freon 12), isobutylene and 1,3-butadiene were chromatographed separately. The total set of compounds chromatographed and their retention times in comparison to VCM are listed in Table II.

Table II: Resolution of VCM from Potential Contaminants

Compound	Formula	Retention Time, minutes
Methane	CH_4	0.6
Ethene	C_2H_4	1.0
Acetylene	C_2H_2	1.0
Ethane	C_2H_6	1.1
Propene	C_3H_6	2.8
Propane	C_3H_8	3.1
Freon 12	CCl_2F_2	3.7
VCM	$CH_2{=}CHCl$	5.7
Isobutane	$CH(CH_3)_3$	7.9
1-butene	$CH_2{=}CHCH_2CH_2$	8.7
Isobutene	$CH_2{=}C(CH_3)_2$	8.8
n-butane	$CH_3CH_2CH_2CH_3$	9.9
1,3-butadiene	$CH_2{=}CHCH{=}CH_2$	18.3

Freon 12 and isobutane have the nearest retention times to VCM of the thirteen compounds listed. However even these two compounds show differences in retention time of 2 minutes or longer, which is a substantial difference resulting in total separation of the elution peaks.

VCM Analysis by MS

The MS used for the crosscheck of the VCM analysis was a Consolidated Electrodynamics Corporation Model 21-620, equipped with a calibrated inlet system specially designed for gas analysis. Inlet sample pressure is measured using a micromanometer. Ionization conditions used were 50 volts at 40 milliamps. Pure VCM was used for calibration so that standardization of the GC and MS were completely independent.

Seven MS verification analyses were performed during this study to confirm GC analysis of VCM. These are summarized in Table III.

Table III: Crosscheck VCM Analyses by MS

Sample	VCM, ppm MS	VCM, ppm GC-FID
1, Sludge, Vapor Phase	2,200.	2,700.
2, Sludge, Vapor Phase	2,300.	1,900.
3, Landfill Air	0.05	0.07
4, Sludge, Dry Solids	210.	200.
8, Plant Stream Liquid	23,000.	28,000.
9, Plant Stream Vapor	8,600.	8,600.
10, Plant Stream Vapor	30,900.	37,400.

Discussion

In the following sections data obtained on VCM concentrations in air samples and PVC sludge vapor, liquid and solid phases are discussed. Also the results of a very preliminary study of VCM release rates from PVC sludges are discussed. Finally a brief analysis of the VCM emissions potential of the sludges is presented.

Grab Air Samples

The results of laboratory analysis of grab air samples collected at three landfills are listed on the following page in Table IV.

VCM concentrations ranging from 0.07 to 1.10 ppm were found at normal breathing levels at three landfills. At Landfill 1, the levels found were relatively low and the spread in concentrations was quite small (0.07 to 0.11 ppm). At Landfill 2 concentrations ranging from 0.13 to 0.49 ppm were found while concentrations found at Landfill 3 ranged from 0.16 to 1.15 ppm. Three important features of these data are noted. First, there appears to be a VCM background level of about 0.1–0.3 ppm in the air at all three landfills. Secondly, instantaneous VCM concentrations as high as about 1 ppm are on occasion observed, even as long as 24 hours after the PVC sludge is buried under compacted soil. The third observation concerns an air sample which was collected about 5 cm from a stream of liquid sludge discharging from a truck during landfill disposal. This air sample was, in effect, "spiked" with extra VCM. The fact that this particular air sample showed an appreciably higher VCM analysis (1.90 ppm) than the other air samples collected at the same landfill provides good indirect proof that the VCM peaks in the chromatographs of landfill air are correctly identified.

Three grab air samples were also collected outside the boundary of Landfill 2 in August 1975. The VCM data are presented in Table V together with a control sample collected at the landfill. Collection of these air samples was not correlated with PVC sludge disposal. The instantaneous levels found outside the landfill ranged from 0.12 to 0.37 ppm. The 0.37 ppm sample was collected in a residential area approximately 1.3 kilometers from the landfill disposal area. This random sample concentration is of the same order of magnitude as those found by the EPA beyond the fence line at VCM and PVC plants[1].

Sludge Samples

The PVC sludges were analyzed to determine VCM contents. The vapor phase (head space) and liquid filtrate portions of the sludge samples were analyzed first. It was determined that the VCM content of these phases was <1 percent of the total sludge VCM content with even moderately high total VCM contents ($\geq$200 ppm, dry solids). Thus the amount of VCM in these two phases is negligible in terms of potential landfill VCM emissions.

VCM Contents of Sludge Solids

The PVC sludges were filtered and the sludge solids subjected to VCM analysis as described earlier. The results obtained are shown in Table VI.

VCM concentrations found in the sludge samples ranged from 7 to 520 ppm in the wet filtered sludge, and from 20 to 1260 ppm on a dry solids basis. These concentrations can be compared with the values found in EPA studies (1) in the spring of 1974 at six PVC plants. In that work, VCM concentrations found ranged from <1 ppm to 3520 ppm in wet sludge and from <1 ppm to 4200 ppm in dry sludge but with most of the samples containing >10 ppm on either a wet of dry basis. Thus the VCM concentration range found in the present work is similar to that observed in the earlier studies, although the highest concentration level found in the present work is about 7 times lower than the highest values found by the EPA workers in the spring of 1974.

Table V: VCM Concentrations in Grab Air Samples Taken Outside Landfill Boundaries

Air Sample Number	Collection Information: Temp, C	Weather	Wind Velocity, kph[a]	Sampling Location[b]	VCM[c] ppm
10	29	Very cloudy	8-16	180 meters inside landfill adjacent to sludge disposal area (8/18/75)	0.49
18	27	Cloudy — Hazy	0-8	Residential housing area closest (~1.3 kilometers) to the landfill. Also the site is the lowest elevation point in that area (8/15/75)	0.37
19	29	Very cloudy	8-16	Beach Club ~ 0.8 kilometers east of the landfill and lower in elevation (8/18/75)	0.19
20	22	Cloudy	0-8	Public boat landing ~ 900 meters from the landfill and lower in elevation (8/20/75)	0.12

(a) Wind velocity in kilometers per hour measured with a portable windmeter.
(b) All samples taken at times when the wind was blowing from the landfill toward the site (downwind).
(c) GC-FID

Table IV: VCM Concentrations in Grab Air Samples Taken at Landfills

Air Sample Number	Collection Information: Temp, C	Weather	Wind Velocity, kph[a]	Sampling Location	VCM[b] ppm
Controls		Analysis of laboratory air grab samples			<0.01
			Landfill 1		
1	14	Very cloudy	0-8	30 meters from disposal site just before sludge dump (date 4/24/75)	0.11
2	14	Very cloudy	0-8	At leading edge of freshly dumped sludge (4/24/75)	0.10
3	14	Very cloudy	0-8	30 meters from disposal site after dumping and dozing (4/24/75)	0.07[c]
			Landfill 2		
4	17	Very cloudy, raining	5-11	At disposal site before sludge discharge started (6/12/75)	0.13
5	17	Very cloudy, raining	5-11	Edge of sludge pit as soon as discharge is completed (6/12/75)	0.13
6	16	Cloudy	3-11	At previous days disposal site before fresh discharge (6/13/75)	0.27
7	16	Cloudy	3-11	About 5 centimeters from sludge discharge stream (6/13/75)	1.90
8	23	Partly cloudy	0-8	Edge of sludge pit during second dump (6/13/75)	0.30
9	23	Partly cloudy	0-8	Edge of sludge pit during third dump (6/13/75)	0.12
10	29	Very cloudy	8-16	180 meters inside landfill, near sludge disposal area (8/18/75)	0.49
			Landfill 3		
11	22	Partly cloudy	5-11	30 meters from disposal site before sludge discharge (6/24/75)	0.16
12	23	Partly cloudy	5-11	Edge of sludge pit between two trucks, while both are discharging (6/24/75)	0.40
13	23	Partly cloudy	5-11	Same as (12) near the end of the discharge period (6/24/75)	1.03
14	23	Partly cloudy	5-11	30 meters from disposal site after sludge pit is covered (6/24/75)	0.16
15	21	Partly cloudy	0-8	Standing over previous days covered disposal site (6/25/75)	0.17
16	26	Partly cloudy	0-8	Same as (15) (6/25/75)	1.00
17	27	Partly cloudy	0-8	Same as (15) (6/25/75)	1.10

(a) Wind velocity in kilometers per hour measured with an anemometer.
(b) Gas chromatography with flame ionization detector (GC-FID).
(c) This sample was also analyzed by MS as a crosscheck and 0.05 ppm were found.

Table VI: VCM Concentrations Found in PVC Sludges

PVC Sludge No.	Sludge Solids, Weight Percent C(b)	F(c)	VCM ppm(a) W(d)	D(e)
		Plant 1		
1(f)	34	42	150	360
2(g)	--	55	210	380
3(h)	35	41	520	1260
4(i)	34	42	90	200
5(j)	36	41	90	200
		Plant 2		
6(k)	17	40	7	20
		Plant 3		
7(k)	30	60	90	130

(a) VCM analysis of wet, filtered sludge solids by GC-FID analysis of THF extract.
(b) As collected.
(c) After filtration.
(d) Wet sludge.
(e) Dry solids.
(f) Freshly centrifuged sludge.
(g) Sludge from partly filled truck loader.
(h) Full truck loader.
(i) Sludge just unloaded at landfill.
(j) Sludge (i) after bulldoze burial.
(k) Fluid sludge collected during discharge from tank truck.

VCM Release Rate Studies

Release rate studies were performed using a cylindrical glass chamber with ¼ in. ID stainless steel inlet and outlet tubes for an air sweep over the sludge. The tubes extended 1 cm below the apparatus cover. A Teflon®baffle was provided between the air entrance and exit ports to insure that the air sweep was directed onto the bottom sludge layer. The baffle extended within about 1 cm of the thickest sludge and overlayer samples studied (2.6 cm). The air exiting from the chamber could be vented to the atmosphere or injected into the GC-FID at will.

Release rate experiments were performed at 25 °C using 13 to 15 grams of sludge No. 2. This provided a layer about 1.3 cm deep in the release rate apparatus. In release experiment 2 an equal thickness layer of loam soil was placed over the sludge. A 30 cc/minute air flow was passed over the sludge. This gas flow rate is equivalent to a calm day at a landfill. It is under these conditions that maximum VCM concentrations might be expected to accumulate at landfills. The VCM concentrations are instantaneous values obtained by injecting a 5.28 cc portion of the constantly outflowing air into the GC apparatus. The release rate data collected are given in Table VII expressed as percentages of the total VCM content of the given sludge sample.

The results obtained indicate that a minor portion of the VCM in PVC sludge may be quickly released at the landfill but that a major portion of the VCM is released very slowly over a long time period. This means that as PVC sludge is disposed, absolute amounts of VCM will probably continue to rise for a long, indeterminate period until a "quasi-steady-state condition" is reached. At this point continuous, slow evolution of VCM will probably occur for a long time after sludge is no longer disposed of at the landfill. This is consistent with the finding that a VCM air concentration in the range of 0.1 to 0.3 ppm was found at each landfill.

Table VII: Fraction of VCM Available in Sludge Samples Released at Specified Time Intervals

Run	Sludge Grams	VCM, mg	Percent VCM Released Time Interval, hr 2	8	24	110
1	13.6	2.86	5	16	25	32
2	13.3(a)	2.79	2	5	8	11

(a) 1.3 cm loam soil cover.

VCM Emissions Potential

The VCM emissions potential of the PVC sludges was calculated based on the VCM concentrations in Table VI and data supplied by the PVC companies on the amounts of PVC sludge being disposed of at the landfills. The results of these calculations are shown in Table VIII.

Table VIII: Potential VCM Emissions from Landfills Based on Company Supplied PVC Sludge Disposal Rates and Analytical VCM Contents

PVC Sludge Number	PVC Dry Sludge Solids Disposal Rate, kg/day	Dry Sludge VCM Content, mg/kg	VCM, Daily Disposal Rate kg	liter(a)
		Plant 1		
3	4,626	0.00126	5.83	2,285
4	4,490	0.00020	0.90	353
		Plant 2		
6	2,948(b)	0.00002	0.059	23
		Plant 3		
7	172(c)	0.00013	0.022	9

(a) (kg VCM)(10^3)(24.5 l/mole)/(62.5 g/mole).
(b) Company supplied figure - 35,000 gal/wk. Dry solids based on 159,110 l/wk and 1.1 kg/l.
(c) Company supplied figure - 4,000 gal/mo. Dry solids based on 18,184 l/wk and 1.1 kg/l.

The amount of VCM being disposed of at the landfills thus varied between 0.022 and 5.83 kg or 9 and 2,285 liters on a per day basis. However, it is pertinent to note that PVC production levels were well below normal during the time this work was being done. This resulted in less PVC sludge being produced and disposed. When the PVC industry returns to former high production levels the amount of VCM being disposed of in sludge at

landfills will probably increase. This may be true even though more efficient removal of VCM from PVC products has now been accomplished to meet the new OSHA and EPA standards pertaining to allowable levels of VCM in working place air and escaping to the atmosphere. The effects of these changing economic conditions and PVC technology factors can only be ascertained through additional sampling and analysis of VCM concentrations in PVC sludges and in air at or near landfills where PVC sludge is disposed.

CONCLUSIONS

The following conclusions are indicated by the findings of this study:

(1) A background air concentration of about 0.1 to 0.3-ppm VCM appears to be present in air at landfills where PVC sludge has been disposed of for several years.

(2) Instantaneous VCM air concentrations on the order of 1.0 ppm can occur at normal breathing heights (~1.5 meter) above ground level at these landfills as long as 24 hours after PVC sludge deposits are covered.

(3) Instantaneous VCM air concentrations on the order of 0.1 to 0.4 ppm can occur outside landfills where PVC sludge is disposed.

(4) Time-weighted average sampling (15-minute, 8-hour, 24-hour) is required to determine whether concentrations of VCM in air that pose a health hazard occur either at the landfills or in adjacent residential or public access areas.

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Land Disposal of Organic Hazardous Wastes Containing HCB

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INTRODUCTION

The problem of land disposal of hazardous industrial organic wastes containing hexachlorobenzene (HCB) affords the unique opportunity to examine in detail the phenomenon of vapor phase transport in the absence of any other significant transport process. Hexachlorobenzene (HCB) is essentially insoluble in water so that leaching with moving water will be insignificant. The persistence of HCB is long enough that degradation as a means of dissipation can be considered insignificant and vapor phase movement will be the primary means of dissipation of hexachlorobenzene.

Hexachlorobenzene is present in industrial waste as a by-product in the commercial production of several chlorinated solvents, like perchloroethylene and carbontetrachloride[7]. HCB is a registered fungicide used as a seed protection chemical for seed grains. In addition significant quantities of HCB are produced as impurities or by-products in the production of certain pesticides, like PCNP, dacthal, mirex, simazine, atrazine, and propazine. Industry has used several methods to dispose of the large quantities of HCB-containing waste (hex waste). These methods include municipal landfill, land burial, lagooning, deep well injection, incineration, and product recovery. Land disposal in municipal landfills and land burial will be the topic of this paper. Land burial differs from municipal landfill in that land burial is a procedure used by the waste manufacturer on his own property. Lagooning is a method whereby hex waste is temporarily stored under water in an unlined reservoir before being placed into a landfill. Hence, this project includes the effectiveness of a water cover in decreasing volatilization.

A typical industrial operation where land disposal of hex waste is used is shown in Figure 1. The solid phase, remaining after the water admixture, may be either hauled directly to the final land disposal site or left temporarily in a lagoon. When lagoon storage is used, the cooling and crystalization step (water admixture) and lagooning are the same; i.e., the waste stream from the production process is fed directly below the water surface of a lagoon, where it is stored temporarily. Periodically, the lagoon is emptied and the hex waste carried by truck to the land disposal site.

This study was initiated because of a specific report of HCB contamination of beef cattle in December, 1972 in southern Louisiana. Beef cattle to be slaughtered for human consumption were quarantined from sale in a 200-square mile area because high levels of HCB were found in their fat tissue. After extensive investigations by local, state, and federal agencies and the cooperation of the area's HCB-producing industries, the HCB source was traced to a municipal landfill where waste containing HCB was disposed. Uncovered trucks were used to haul hex waste from the industrial source to the landfill. This had caused spillage and contamination along the pathways followed by the trucks. Waste material deposited at the landfill sites was left uncovered. Reportedly hex waste was used as a fly-repellent covering over municipal waste. However, no hex waste is presently being disposed of in municipal landfills in affected areas in southern Louisiana. The uncovered waste at these landfills has been collected into a small area of the landfill and covered with 4 to 6 feet of soil, with a 10-mil thick sheet of polyethylene film buried about midway in the soil cover.

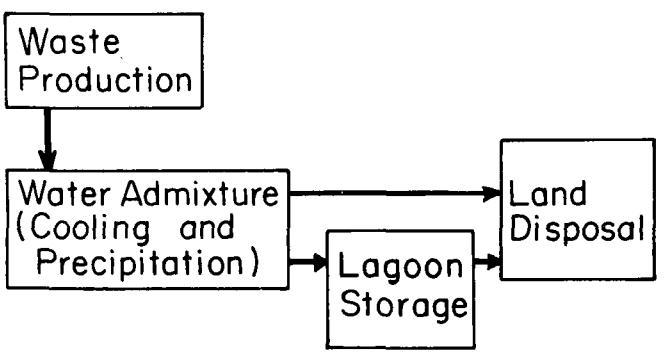

Figure 1. Typical hex waste handling procedures used in land disposal

The disposal of hex waste in landfill sites in southern Louisiana has caused a pattern of HCB contamination of residents in the area, operators of the municipal landfills, beef cattle, and soil, plant and air samples[1,6,11,12]. The HCB content in soil and plant samples taken from near landfill areas used for disposal of hex waste decreased as distance from the landfill increased[6].

Burns and Miller[1] reported high HCB levels in the plasma of individuals exposed to HCB from the transporting and disposing of hex waste in southern Louisiana. A sampling of 29 households located along the route of trucks containing hex waste showed that the average plasma residents' HCB level was 3.6 ppb, with a high of 23 ppb. The range for landfill workers was 2 to 345 ppb plasma HCB. The average plasma HCB-level from control group was 0.5 ppb, with a high of 1.8 ppb.

Hexachlorobenzene is a stable persistent compound of low water solubility and moderate vapor pressure. It is a white powder at room temperature. Its empirical formula is C_6Cl_6. HCB has a melting point of 230 C, sublimes at 322 C,[4] and HCB is essentially insoluble in water. We have measured its solubility

in water as 6.2 μg/l. Sears and Hopke[7] reported a vapor pressure of 2.10 x 10-5 mm Hg at 25 C for HCB. We measured its vapor pressure as 1.91 x 10-5 mm Hg at 25 C. HCB is soluble in several organic solvents, like benzene and hexane, and in fats and oil. Hence it tends to accumulate in fatty tissues.

Based on the pattern of HCB contamination of soils and plants in Louisiana, its moderate vapor pressure, its low water solubility, and its long-term persistence, we concluded that its volatilization and subsequent transport by moving air currents would be the principal mechanism by which HCB would move about the environment. Presently, no information is available to indicate that degradation of HCB is significant in the environment.

Therefore, we initiated research on the volatilization of HCB from hex waste land disposal. The objective of this study was to determine the effectiveness of various coverings—soil, water, polyethylene film—in decreasing HCB volatilization from land. When investigating the effectiveness of a soil cover, the influence of soil water content, soil compaction and temperature were included. Recent rereview articles by Spencer, Farmer, and Cliath[10] and Letey and Farmer[5] have detailed discussions of factors affecting the volatilization of organic compounds from soils and on vapor phase movement in soils.

Simulated Landfill

To determine the effectiveness of various coverings on HCB volatilization from industrial waste, the simulated landfill apparatus, as depicted in Figure 2, was constructed and operated in the laboratory so that critical factors like temperature and air flow rate could be controlled and monitored.

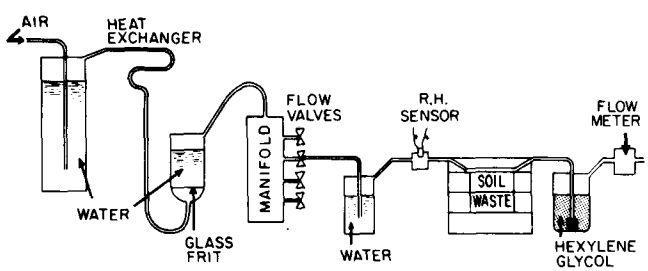

Figure 2. Closed air flow system for collecting volatilized HCB from simulated landfill

The soil used for the volatilization experiments had been collected from a municipal landfill in Louisiana where industrial, hazardous waste containing HCB had been previously deposited. The soil was a silty clay loam with an organic matter content of 1.4% and a field bulk density of 1.2 g/cm³. Samples of hex waste were collected directly from two separate manufacturers of chlorinated solvents. Hex waste samples A and B as collected from the manufacturer contained 54.9 and 56.9% HCB, respectively. These samples were air-dried at room temperature before being used in the simulated landfill experiment. After air drying, the HCB contents of samples A and B increased to 65.7 and 90.5% HCB, respectively. A third material used in the volatilization experiment was recrystallized, practical grade, HCB which was 98+% pure. We found no differences in the volatilization of HCB from these materials in the simulated landfill. That is, HCB volatilized from all the materials as if they were pure HCB, except for waste not air-dried. This wet hex waste contained an amount of reddish-brown organic liquid. One waste sample collected before the water admixture step contained as much as 76.8% of the reddish-brown liquid by volume. The samples used in the simulated landfill study were collected after adding water to the waste stream, and they contained only a small amount of the reddish-brown liquid. Except when stated otherwise, for the studies reported here the hex waste samples were air-dried to remove the organic liquid before starting the experiments.

The volatilization cell consisted of plexiglass sections bolted together with O-ring seals between the sections. Hex waste was placed in the bottom section and the soil to be tested placed on top. The cover (top section) of the volatilization cell contained a cavity (2 mm deep) which allowed air flow over the surface of the covered hex waste. An air flow rate of 0.769 l/minute was used in this study which provided an air speed (21.5 cm/sec or 0.48 mile/hr) across the soil surface. The apparatus utilized a closed, air-flow system with the volatilized HCB collected in hexylene glycol traps, like that used by Farmer et al.[3] to measure the volatilization of insecticides from soils. The entire landfill operation was simulated inside a temperature-controlled cabinet maintained at 25 C, since volatilization processes are extremely dependent on temperature, due to the temperature dependence of vapor pressure. The hexylene glycol traps were replaced with fresh traps at suitable intervals and the trapped HCB extracted into hexane to be analyzed by gas liquid chromatography (GLC) using an electron capture detector. In order to make possible the analysis by GLC, most of the HCB samples obtained by volatilization from the industrial wastes required a column cleanup on activated neutral alumina to remove several interfering compounds present in the industrial waste samples.

Research Findings

Since soil is a naturally porous body, storage of volatile materials under a soil cover will always result in some volatile loss to the atmosphere. The extent of this loss can be controlled by controlling the size or number of pores in the soil. The factors investigated for their effect on soil porosity included soil compaction, soil water content, soil depth, temperature, source of waste, as well as using as coverings polyethylene film and water. HCB volatilization through these coverings were compared with HCB flux from uncovered wastes. The flux from uncovered hex waste in the simulated landfill apparatus at 25 C and 0.769 ml/min air flow rate was 8700 ng/cm²/day.

Soil Compaction and HCB Volatilization

A limited number of choices are available in a field situation with a landfill site on which volatilization of an organic compound from a buried waste must be decreased. One choice is to compact the soil cover over the landfill, since soil cover can be used to decrease HCB volatilization. HCB diffusion in the vapor phase is the major mode of movement through soil. Soil compaction or soil bulk density determines the porosity of a soil and thus affects HCB vapor flux. Data in Figure 3 show that HCB fluxes from cover soil with a bulk density of 0.96 g/cm³ (low compaction) are greater than those from cover soil with a greater bulk density of 1.15 g/cm³ (high compaction). The final soil water contents were very similar for these experiments, and the major effect can be attributed to the effect of bulk density on air-filled porosity. Calculation of the effect of air-filled porosity on steady state diffusion showed that increasing the relative air-filled porosity by 24% increases HCB flux by more than twice. Similar exponential effects of air-filled porosity on vapor phase diffusion flux has been shown for lindane[2].

Soil Water Content and HCB Volatilization

To obtain maximum compaction of the cover soil, water must often be added to the soil during compaction. Natural rainfall also adds water to the soil. The amount of water in a soil affects the air-filled porosity, or the pore space available for HCB vapor diffusion. Figure 4 shows the effect of soil water content on HCB flux. Clearly HCB flux from 1.8-cm cover soil with a water content of 16.7% is greater than that from cover soil with 23.5%

water content. Calculation of air-filled porosity showed that decreasing soil water content by 6.8% (dry weight basis) increases relative air-filled porosity by 21%, but because of the exponential effect of air-filled porosity on vapor diffusion, the HCB flux increases almost twice. From previous considerations of the effect of soil compaction, it is obvious that lower soil water content will have effects similar to that of lower soil compaction. The lower the soil water content of the cover soil, the more rapidly will the HCB flux reach steady state.

Shearer et al.[8] studied lindane diffusion in soil and observed a similar exponential effect of soil water content on vapor phase diffusion. Increasing soil water content will decrease HCB volatilization flux. When soil is saturated with water, the effect will be the same as a covering of water.

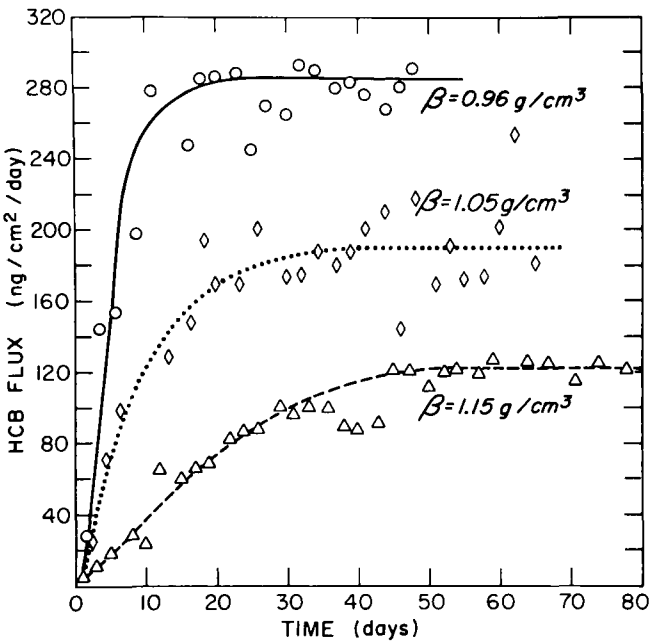

Figure 3. Effect of soil bulk density on the volatilization of HCB from industrial hazardous waste covered with 1.8 cm soil

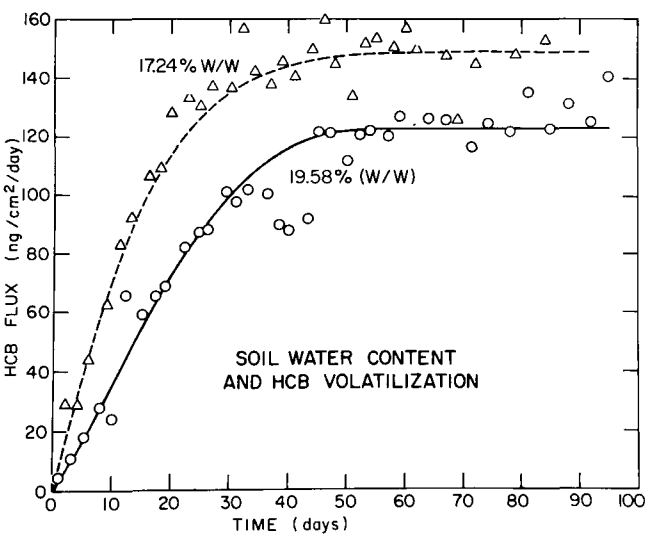

Figure 4. Effect of soil water content on HCB volatilization from industrial waste covered with 1.8 cm soil at a bulk density of 1.19 g/cm³

Water as a Cover Over Hex Waste

A water cover was found to be very effective in preventing HCB volatilization. Covering the hex waste with 1.43 cm (9/16 in) of water in the simulated landfill apparatus reduces the flux 1000 times compared to uncovered hex waste.

Polyethylene Film and HCB Volatilization

Polyethylene film has been used with soil in a municipal landfill as a cover for hex waste to decrease or prevent HCB volatilization. Its effectiveness was tested using the simulated landfill. Four-mil polyethylene film was placed between two 0.95 cm soil layers. The film decreased HCB flux by approximately 40% compared to a soil cover alone and increases the time to reach maximum HCB flux. However, the amount of decrease is not very large considering the cost of the film indicating the film is not very effective as a barrier to HCB volatilization.

In a second experiment polyethylene film (6-mil) was used alone without soil and was placed next to the waste. Polyethylene film decreased HCB flux 37% as compared with uncovered hex waste. The film did not seem to be very effective as a barrier to HCB volatilization. This supports the conclusion obtained with a composite soil and film cover that the addition of polyethylene film to a soil cover was not very effective in reducing HCB volatilization compared to a soil cover alone.

Hex Waste Origin and HCB Volatilization

HCB volatilization from hex waste from two different industrial sources covered with 1.8 cm soil was studied to determine if different sources of hex waste would have significantly different HCB volatilization rates. There was little difference in HCB volatilization from these two wastes. Both had a steady state flux of approximately 130 ng/cm²/day. Experiments with practical grade HCB also gave the same steady state HCB flux. Thus the HCB vapor pressure in these two hex wastes must be similar to that in practical grade HCB.

Temperature and HCB Volatilization

Table I shows HCB saturation vapor densities from practical grade HCB and hex waste at 15, 25, 35, and 45 C.

Table I: HCB saturation vapor densities from practical grade HCB and hex waste at four temperatures

Temperature C	HCB ug/l	Hex waste ug/l
15	0.0630	0.0686
25	0.294	0.286
35	0.95	0.92
45	3.007	3.095

The vapor density of HCB at 25C is equivalent to a vapor pressure of 1.91 x 10^{-5} mm Hg. Vapor densities from practical grade HCB and from hex waste are essentially the same. Increasing the temperature 10 C increases the vapor density about 3.5 times.

Vapor diffusion rate depends upon the vapor density gradient and the diffusion coefficient. Both increase as temperature increases. However, as temperature changes, vapor density

changes are considerably greater than changes in diffusion coefficient. Since HCB moves through soil by vapor diffusion, temperature effects on HCB volatilization flux will be about the same, but somewhat greater than effects on HCB vapor density. Thus, the effect of temperature on HCB volatilization flux is exponential. Ehlers et al.[2] who studied lindane diffusion in soils found there was a similar exponential relationship between temperature and the amount of lindane diffused.

Problems Associated with Liquid Components of Waste

Additional experiments were performed with the simulated landfill using the hex waste which had not been air-dried and which contained a small amount of reddish-brown liquid waste. HCB fluxes from this wet hex waste covered with 6-mil film were greater by about 20% than those from air-dried hex waste covered with the same film. This liquid portion of the waste was observed to deposit on the polyethylene film and to cause the film to partially dissolve and expand. Thus the liquid waste may affect the HCB transmission property of the film. Conceivably this liquid waste may also have deleterious effects on other synthetic membranes and thus decrease their effectiveness as barriers to liquid and gas movement, when used in a landfill.

The liquid portions of the waste contained 1.4% HCB with a density of about 1.67 g/ml. Because it is heavier than water, it may move downward in a landfill with the potential of leaching HCB into groundwater.

SUMMARY

Table II illustrates the effectiveness of various coverings in decreasing HCB losses from industrial wastes.

Table II: Summary of the effectiveness of various coverings in decreasing HCB volatilization losses from industrial hazardous wastes containing HCB

Cover	Thickness (cm)	Volatilization flux (kg/ha/yr)
None		317
Soil (experimental)*	1.8	4.56
Water	1.43	0.38
Polyethylene	0.015	201
Soil (predicted)**	120	0.066

* For a bulk density of 1.19 g/cm^3 and 17% water content.

** Calculated assuming diffusion in the vapor phase as the mechanism of movement.

The effectiveness of the materials are in the order of water > soil > polyethylene film. (Polyethylene film and water are about equally effective in decreasing HCB flux when compared on an equal layer thickness. The cost of polyethylene film, however, precludes its use in thick layers.) Increasing soil bulk density and/or water content decreases HCB flux through soil. HCB flux decreased proportionally as the thickness of all materials increased. Thus, soil cover appears to provide an efficient means of decreasing the loss of volatile materials placed in a landfill. This assumes that the integrity of the soil cover is maintained. Factors such as erosion, settling, and cracking of the soil cover would also have to be evaluated when considering landfill disposal of volatiles.

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Sludge Farming of Refinery Wastes as Practiced at Exxon's Bayway Refinery and Chemical Plant

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INTRODUCTION

Sludge farming or land farming as we refer to it has been practiced on a full scale at Exxon's Bayway Refinery and Chemical Plant Complex since mid-1973. The existing farm is 8 acres and is utilized for the disposal of up to 3500 tons/year of oily waste materials. The process has proven to be reliable as well as less expensive and more environmentally sound than other available disposal methods.

Background

The Bayway Complex, which occupies an area of 1500 acres, is located in Central New Jersey in the town of Linden. The facility is an integrated petroleum refinery and petrochemical plant which processes about 300 MB/D of crude. Motor gasoline, home heating oil, fuel oils, jet fuel, diesel fuel, asphalt, and white oils are among the products produced by the Refinery. The Chemical Plant produces alcohols, solvents, industrial chemicals, and lube oil additives.

In a complex operation such as this, there are many processes that produce solid residues, often containing oil and other contaminates, that must be disposed of properly. Solvent extraction, land filling and land farming are the primary final disposal techniques used by Bayway. Land farming is the disposal of oily wastes (oil, water, and solids) by incorporation into the soil and the subsequent biological degradation of the waste hydrocarbons. It should be emphasized that this is an ongoing process and is an important part of our waste disposal program. We do not grow or plan to grow any crops on the site.

The initial experimental work to develop this technique for use at Bayway was conducted on three small plots (1/1000 acre each) outside our Main Laboratory in 1972. Application rates, degradation rates, soil analysis, and runoff contamination were studied for two materials: waste activated sludge (from our biological water treatment plant) and tank cleanings. The results indicated that loadings of 150 tons/acre/year of oils and solids were possible without overloading the soil or producing any oil runoff contamination. These results were in general agreement with other published results and those obtained at another Exxon Refinery where sludge farming of separator bottoms had been practiced since 1954.

From this pilot work, the process was scaled to $\sim$ 2 acres for testing of application methods, soil cultivation methods, and overall operability. From there we expanded to the existing 8 acre farm in mid-1973.

Existing Land Farm Site

The existing 8 acre farm of which approximately 7 acres are farmable is located on a completed sanitary landfill site within the refinery. Figure 1 shows the layout of the Sludge Farm. Note the following features of the farm:

- Topography reaches a maximum grade elevation of 21 ft. in the center and decreases steadily to grade elevation 11 ft. on each side.
- A network of dirt roads surrounds the site and divides it into quadrants. These roads provide easy access for vehicles.
- Earth dikes are located at the low ends of the site to pond water and control runoff.
- Soil borings, which were required for registration of the site with the State of New Jersey, show that a 2' layer of impermeable clay exists below the site.
- Unconfined, *non-potable,* saline ground water exists above the clay which interacts with the creek.
- Three (3) monitoring wells have been installed around the site.

Figure 2 is a photograph of the northwest quadrant of the farm and shows the farming equipment—a bulldozer and a disc harrow.

Operating Details of Sludge Farming

Figure 3 shows the types of oily sludges that are farmed. Cleanings from crude, slop emulsion, distillate, and additives tanks; API separator bottoms, and other cleaning residues such as sewer, desalter, and spill cleanings are the bulk of the sludges disposed of on the farm. Some waste biological sludge and filter clays have been farmed on an infrequent basis. The average composition of the farmed sludges are $\sim$25% oil, $\sim$40% solids, and the rest water.

The key operating parameters and guidelines for the land farm are shown on the next slide (Figure 4). Soil loading and waste characteristics are very important parameters since overloading the soil with oil can cause loss of biological activity as well as runoff problems. Likewise, low pH materials could cause leaching of metals. For these reasons the initial loads going to the farm from each individual cleaning operation are analyzed for oil, pH, and metals before they are applied.

Since 1974 an average of 3200 tons/yr of sludge has been deposited on the farm. This corresponds to a total loading of 450 tons/acre of oil, solids, and water. Expressed in terms of oil only this is equivalent to $\sim$100 tons/acre. We believe this application rate is moderate and could easily be increased to 150 tons/acre/year. In fact, since the farm is only operated for 9 months out of the year we are effectively at a loading rate of 133 tons/acre/yr. During the winter months the farm is not operated because the ground is either frozen or too wet. In addition biological activity is low due to lower temperatures.

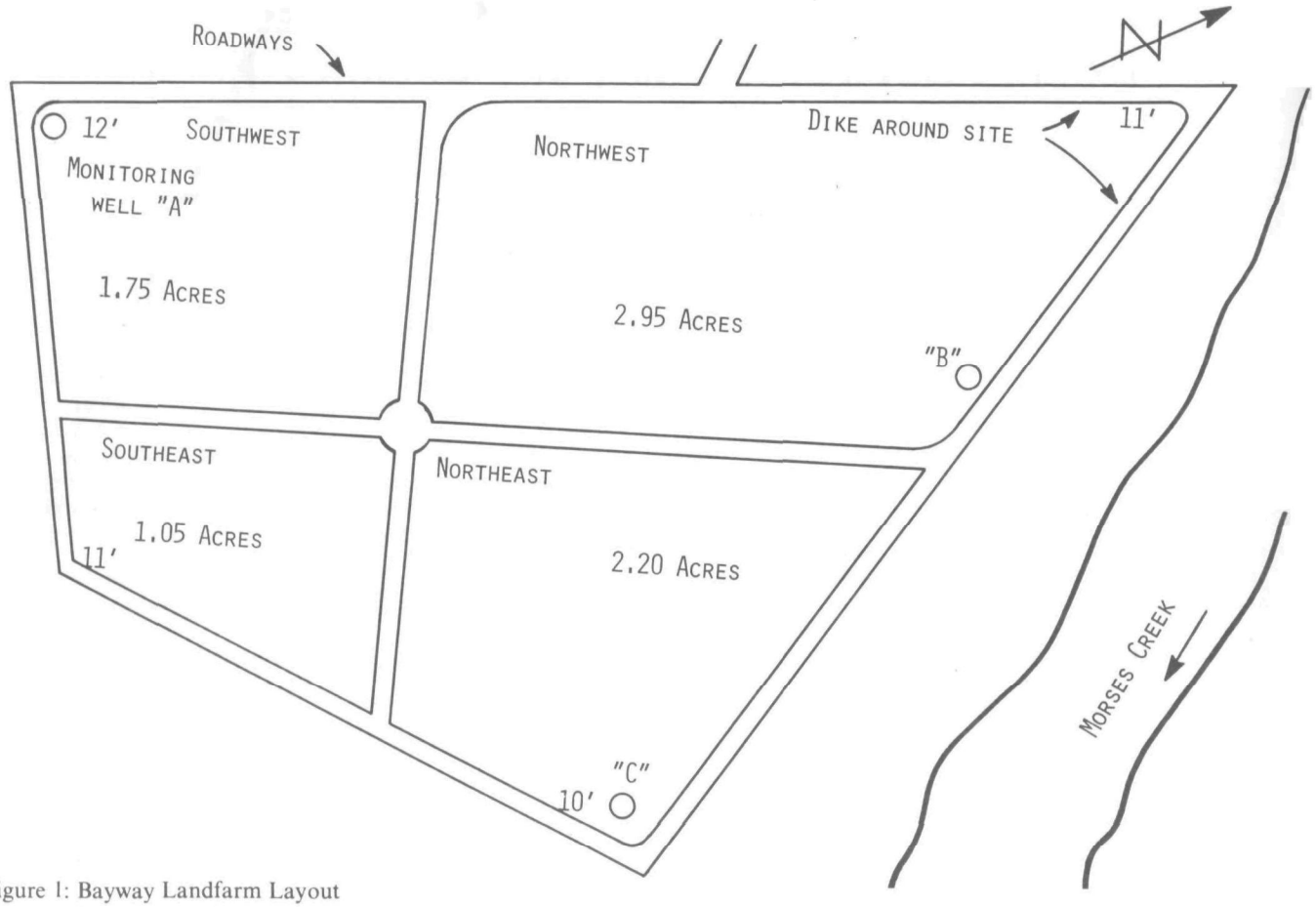

Figure 1: Bayway Landfarm Layout

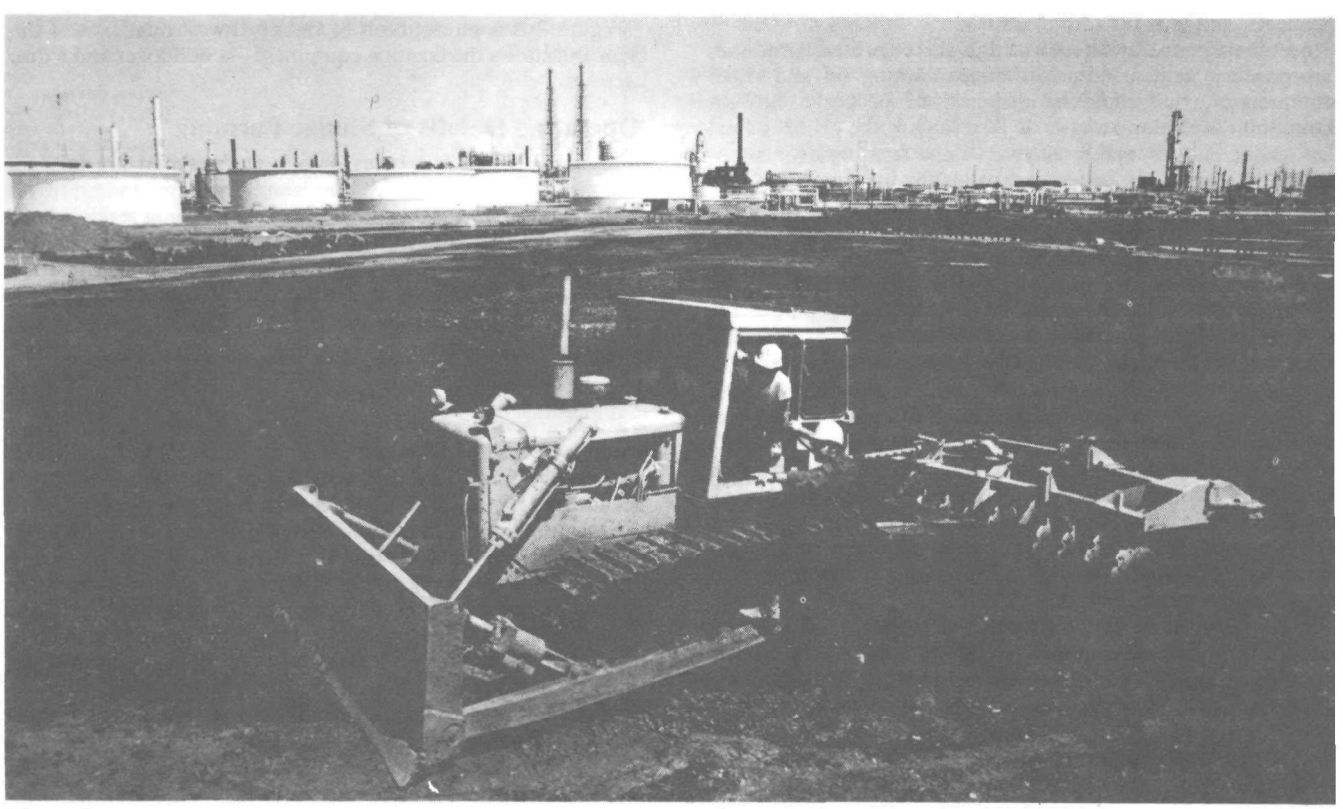

Figure 2

1) Tank Cleanings - 20-30% oil
   - Crude tanks
   - Slop emulsion bottoms
   - Distillate tanks
   - Paramins tanks

2) Separator Bottoms - 15-20% oil
   - Refinery separators
   - Chemical Plant separators

3) Other Cleanings - 10% oil
   - Sewers
   - Desalters
   - Spills

4) Treatment Plant Sludge (Infrequent) - 5% oil
   - Waste biological sludge

5) Filter Clays (Emergency Basis) - 8% oil
   - Jet filters
   - White Oil filters

Figure 3: Materials Presently Being Land Farmed

1) Soil Loadings and Waste Characteristics
   - Oil, metals, pH
   - Permit system
2) Application and Spreading
   - 6" maximum
   - Quadrant rotation
   - Material storage
3) Harrowing
   - Industrial disc harrow
   - Frequency depends on loadings
4) Visual Inspection
   - Color
   - Consistancy
   - Temperature
5) Soil Analysis
   - Oil
   - pH
   - Nutrients
   - Metals
6) Runoff and Leachate Control
   - Runoff - disking
     - Evaporation, dikes, ponding
   - Leachate - pH
     - Monitoring wells

Figure 4: Operating Techniques, Parameters, and Guidelines

On a daily operating basis, loadings are not calculated but the operator's experience is relied on to spread the loading. In addition, a permit system is enforced to provide records as well as control over the dumping of wastes. Waste materials are applied to the farm by means of vacuum truck or dump truck depending on the nature of the material. Dump trucks generally drive onto the farm and dump while moving to spread the material. Vacuum trucks either use hoses or spray nozzles from the roadways to spread the material. Again close operator attention is required in order not to overload any one area.

The sludges are spread to a final depth of ~3" (6" maximum) by a bulldozer and then disced into the ground. The quadrants being worked are rotated so that while one is being used actively the others are in various stages of recovery. During the winter and peak generation periods, the oily sludges are stored in an abandoned, concrete separator for application at a later date. In general, the farm's capacity has been adequate to avoid double handling of the sludges since most of the cleanings occur during the non-winter months. Figure 5 shows the dumping and spreading of separator bottoms on the farm.

Figure 5

Mixing of the sludges with the soil and aeration of the soil is accomplished through frequent discing to a depth of 6–8 inches. A construction type disc harrow is used as shown in Figure 6. Figure 7 shows the discing operation. The required frequency of discing is dependent on the loading being applied to the farm. We began discing at a frequency of once per month but have progressed to once/wk. Increased frequency results in faster oil

decomposition. With moderate loadings and weekly discings a quadrant is ready for another application in about 2 months.

Figure 6

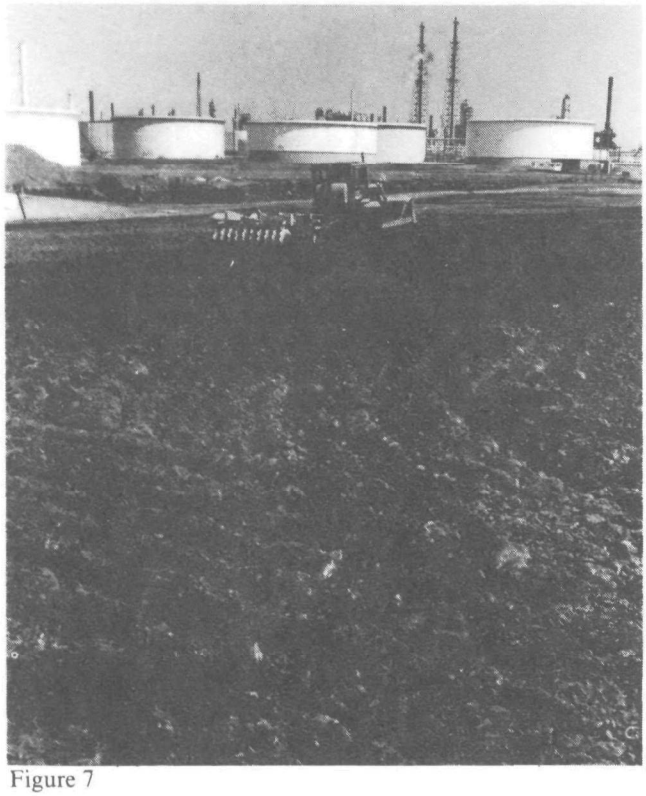

Figure 7

The actual performance and health of the farm is readily determined by visual inspection of the color and consistency of the soil. When sludges are first applied, the soil is black and tends to clump. As the oil decomposes the soil turns gray and then brown as well as becoming looser or powdery. We have also recently begun monitoring temperatures of the soil. Indications are that during the process, the temperature of the soil rises ~10–15°F above ambient and then drops off as the oxidation rate decreases.

The farm soil is sampled and analyzed every two months for the parameters shown in Figure 8. Typical soil analysis and guidelines are discussed below:

pH: The target for pH is 7.0–7.5 in order to keep the metals immobilized as insoluble salts. In order to maintain a high pH, lime is applied to the farm as needed (2 times/yr).

Nutrients: Nitrates and phosphates are both nutrients for the bacteria and are necessary for good oxidation. Our guidelines for nitrates and phosphates are 20–30 mg/kgm. Application of a commercial fertilizer 2–3 times per year is necessary to maintain these levels.

Oil and Grease; After an application of sludges the oil content of the top six inches of the soil is 8–9%. The oil content is allowed to decrease to 2–4% before the next application of sludge is made.

Metals: Heavy metals such as lead and zinc have accumulated in the soil of the farm. This should cause no problems with leaching as long as a high pH is maintained to immobilize the metals. We understand that some researchers have found zinc contents as high as 20,000 ppm with no adverse effects, provided crops are not grown. As mentioned before no crops are grown. Experimental work by others has shown that there is no downward movement of the metals through the soil.

pH	-	7.0 - 7.8
Oil & Grease	-	2 - 9%
Ammonia	-	0.3 - 3.0 mg/kgm
Nitrate	-	2.0 - 25 mg/kgm
Phosphate	-	<1.0 - 600 mg/kgm
Cadmium	-	2.0 mg/kgm
Lead	-	150 mg/kgm
Zinc	-	1000-1500 mg/kgm

Figure 8: Typical Soil Analysis

Runoff from the farm is controlled by discing frequently, contouring to the slope of the land. This enables the soil to absorb the maximum amount of water. Dikes have also been provided at the low points of the farm to pond the runoff until it evaporates. Figure 9 shows this ponding effect. It should be noted that sludge is not applied to these ponding areas since the wetness inhibits oxidation.

Leaching is controlled, as mentioned before, through maintenance of the proper pH. In addition the 3 monitoring wells located around the site are sampled quarterly. Figure 10 shows one of our engineers sampling a monitoring well. The

Figure 9

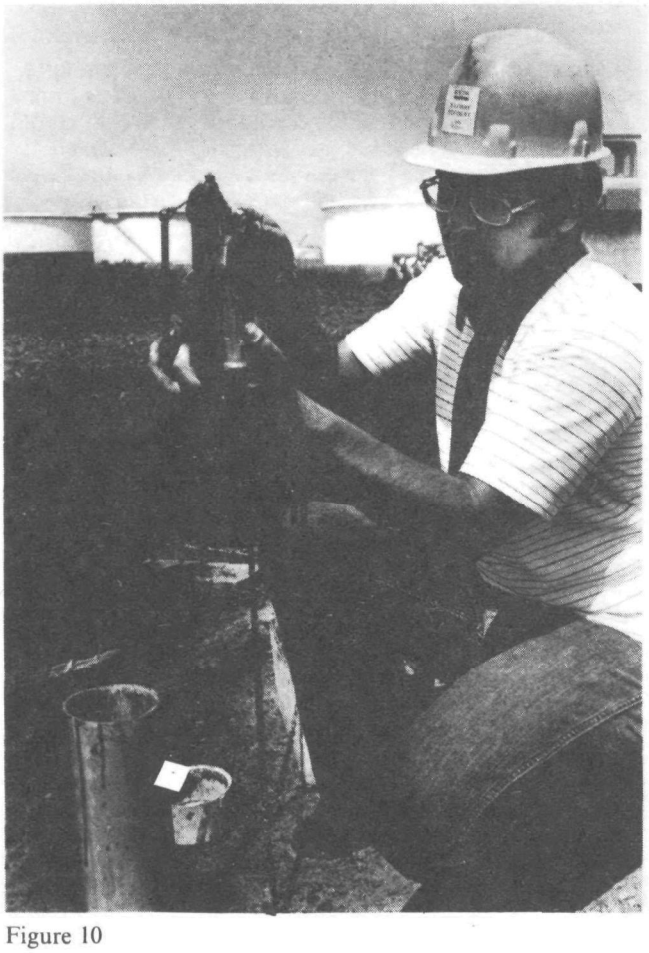

Figure 10

(1) PARAMETERS

- pH
- TOC
- OIL
- COD
- NITRATES
- SULFATES
- METALS
- CHLORIDES

(2) DIFFICULT TO INTERPRET DATA

- EFFECT OF FORMER LANDFILL OPERATION?
- EFFECT OF MORSES CREEK?
- NO BACKGROUND DATA?
- EFFECT OF DRILLING WELLS?
- SAMPLING TECHNIQUES?
- ACCEPTABLE LEVELS?

Figure 11: Leachate Testing (Quarterly)

samples are analyzed for the parameters shown on Figure 11, namely—pH, TOC, Oil, COD, Nitrates, Sulfates, Metals, Chlorides. In general the quality of the water has been similar to that of Morses Creek and thus indicates no problem. The data have been difficult to interpret since no background data are available and we don't know what effect the former landfill operation has had. Initially, the actual drilling of the wells and sampling techniques caused variability in the results but the results have since stabilized. In addition, acceptable contaminate concentrations for this type of ground water have not been established. We have plans to run a test program to collect leachate ~1' below the surface to better understand the leaching characteristics of our operation.

COSTS

- CAPITAL COSTS
  - + LAND VALUE
  - + EQUIPMENT - HARROW, BULLDOZER
  - + MONITORING WELLS
- OPERATING COSTS
  - + REGISTRATION FEES
  - + SAMPLING & ANALYSIS
  - + BULLDOZER OPERATOR
  - + SUPERVISION, TECHNICAL SUPPORT
  - + FERTILIZER & LIME
  - + AREA MAINTENANCE

COST/TON: ~$3.00/TON VS. $10-30/TON

OTHER ADVANTAGES:

- CONTROL OF WASTE DISPOSAL
- LOWER CONTRACTOR CLEANING COSTS

Figure 12: Economic Factors

Economic Factors

The final items to be covered are the economic factors of landfarming. Figure 12 shows some of the cost items for the sludge farming operation. Capital costs for our operation include the value of the land (very low), the farming equipment (bulldozer and disc harrow) and the installation of the monitoring wells. Future regulations could require leachate collection facilities. The operating costs include registration fees, sampling and analysis, the bulldozer operator, technical support, fertilizer and lime, and area maintenance. For our operation it costs ~$3/ ton for disposal of these sludges versus a cost of $10–30/ton for outside landfill disposal. The time a contractor spends dumping on the site has not been included in the $3/ton cost because it is included in the cleaning operation. If the sludge is stored and then farmed later the double handling raises the cost to ~$8/ton. In addition, sludge farming onsite assures us better control over the disposal of these wastes.

SUMMARY

Landfarming at Exxon's Bayway Refinery and Chemical Plant has been shown to be a reliable, practical disposal process for oily wastes such as tank cleanings and separator bottoms. It has proven to be both more economical and more environmentally sound than other available disposal methods. In light of potential environmental regulations additional research and development work is needed; indeed it is being done by Exxon, the API, and others across the country. We are confident (as witnessed by the interest in this conference) that Sludge Farming is a viable and sound disposal method which will gain regulatory acceptance.

Radioactivity Uptake by Plants

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INTRODUCTION

The potentially wide distribution of radioactive wastes in the environment has led to much research on their uptake by plants. This research deals with many, if not most, of the chemical elements. In this review, the great differences in plant uptake of different chemical elements will be stressed. Soil properties affecting plant uptake of certain elements will be pointed out. Finally, the tendency of a few plant species to concentrate specific elements will be discussed.

Much of the data were presented in an earlier review.[80] Uptake data for a few more elements, including some actinides, have been added.

Relative Concentrations in Soils and Plants

After radioactive nuclides are added to a soil, their uptake by plants may result in plant concentrations that are much greater or lower than their soil concentrations. Estimates of this concentration factor for 49 elements have been derived from the experimental data of many greenhouse and field experiments (Table I). To compare elements I established certain rules to govern the selection of experimental data and the calculation of concentration factors.

(1) The elements are added to the soil in water-soluble forms and mixed with the volume of soil under consideration. In small pot experiments, the entire volume of soil is included. In lysimeter or field experiments, only the surface 6 or 7 in is included (2,000,000 lb/acre of mineral soil).
(2) The amount of element added does not change the growth of plants appreciably.
(3) The concentration is measured in plant material harvested within 6 months after the element is added to the soil.
(4) Soil concentrations are based on dry weight of soil. Only the amount of element added to the soil is included in calculating this concentration.
(5) Plant concentrations are based on total dry weight of above-ground plant parts. Only that amount of the element estimated to have originated from its addition to the soil is included in calculating this concentration.

Concentration factors for each element vary over a wide range with changing soil and plant combinations. The ranges given in Table I are not absolute limits, but include most observations for each element. Concentration factors for elements in adjacent columns of the table overlap considerably. Those elements tending to have higher concentration factors are listed first in each column.

Data for calculating concentration factors have been drawn from many sources, including experiments done without isotopic tracers. In experiments made with no tracer, the concentration of element derived from the soil addition was determined by subtracting the concentration in plant material grown in the same soil without addition of that element. A detailed comparison has been made of isotopic and total-uptake methods for determining P derived from fertilizer applications.[81] As long as the condition was met for little growth response, the methods agreed closely. The same agreement was found for several other elements, including Ca, Mn and Zn. The isotopic method is more precise, but within the ranges defined in Table I, the total-uptake method is satisfactory.

Elements Strongly Concentrated

The elements that are strongly concentrated in plants are alkali metals, halides, or essential nutrient elements. Most of the salts of these elements are very soluble in water, and their solubilities do not change much with pH of the solution. Some of the phosphates and sulfates are not very soluble, particularly in combination with the cations Ca, Al and Fe that are abundant in soils. However, phosphate and sulfate are involved in important metabolic processes in plants and may be highly concentrated in cell nuclei and rapidly dividing plant tissues.

To illustrate the concentration factors observed with these elements, let us consider a hypothetical soil solution transferred into a green plant without changing the solution composition. The soil solution would amount to about one-fifth of the dry weight of a mineral soil. The solution in the plant amounts to about 10 times its dry weight. The resulting concentration factor, according to the conditions stated above, is about 50. The correspondence between this concentration factor and that observed for the alkali metals, chloride and bromide, is not accidental, but results from the permeability of plant tissues to these ions.[82]

Elements Slightly Concentrated

Elements that are slightly more concentrated in plant tissues than in the soil are the lighter alkaline earths, Se, Te, and certain micronutrients. Calcium and strontium, which have been extensively studied in fission product investigations, are in this group.

Increasing the supply of available Ca in the soil reduces the uptake of Sr by plants grown on that soil. The Sr/Ca ratio in plants is nearly proportional to the ratio of these cations in soil solution.[83] Analogous behavior has been noted for the similar anions, selenate and sulfate.[84]

Elements Not Concentrated

Elements that are neither more nor less concentrated in the

plant than in the soil are the remaining alkaline earths and halides, Si, Cd and some micronutrients. As compared with elements that are concentrated, these elements are either more strongly adsorbed on soil materials or have less-soluble hydroxides.

Both Ba and Ra are more strongly absorbed in soils than are the more common alkaline earth cations.[85,86] Fluoride may react with silicates to become largely unavailable, and iodide may react with soil organic matter.[87]

Table I: Relative Concentrations of Elements in the First Crop Plants Grown After the Elements Have Been Applied in Water-Soluble Form and Mixed Into Surface Soil.

Relative concentration factor ($\frac{\text{ppm in dry plant material}}{\text{ppm in dry soil}}$)				
10-1000 Strongly Concentrated	1-100 Slightly Concentrated	0.1-10 Not Concentrated	0.01-1 Slightly Excluded	<0.1 Strongly Excluded
Potassium K(1-6)*	Magnesium Mg(26-29)	†Iodine I(22,35,50,76)	†Cesium Cs(8,31-33,61)	†Uranium U(79)
Rubidium Rb(7,8)	Calcium Ca(29,30)	†Barium Ba(8,35)	Iron Fe(62)	Yttrium Y(31,33,35,63)
Nitrogen N(9-12)	†Strontium Sr(8,31-35)	Silicon Si(51)	†Ruthenium Ru(32,33,35,63)	Scandium Sc(69,70)
Phosphorus P(13-16)	Boron B(26,36-38)	Fluorine F(52)	Mercury Hg(64)	Tantalum Ta(69,70)
Sulphur S(17-20)	Selenium Se(39-40)	Cadmium Cd(53-55)	Arsenic As(107)	†Zirconium Zr(32,35)
Chlorine Cl(18,20-22)	Tellurium Te(41)	†Radium Ra(56)	Beryllium Be(65)	†Cerium Ce(32,33,35,63,79)
Bromine Br(23)	Manganese Mn(42)	Cobalt Co(57,98)	Chromium Cr(66,67)	†Promethium Pm(35,63,79)
Sodium Na(1-3,24)	Zinc Zn(31,42-46,66)	Nickel Ni(58)	Vanadium V(68)	Tin Sn(73)
Lithium Li(25)	Molybdenum Mo(19,47-49)	Copper Cu(59,60)	Antimony Sb(69,70)	†Lead Pb(72,74,75)
			Tungsten W(69-72)	†Curium Cm(77)
				†Americium Am(79)
				†Plutonium Pu(35,72,78,79)

*Numbers in parentheses refer to literature references. No suitable data were found for the remaining elements.

†Element has radioactive nuclides significant in plant growth.

Elements Slightly Excluded

The elements that are less-concentrated in plants than in soils include the essential nutrient, Fe, and the important fission product, Cs.

Availability of Fe for plant growth is a problem on many calcareous soils.[88] The availability is affected by valence state and chelation of Fe, as well as by pH. Nevertheless, it is difficult to greatly affect the availability by adding ferrous or chelated iron, since the form changes when these materials are added to calcareous soils.

Cesium is strongly fixed on clay minerals[89] which accounts for its lower concentration in plants than in soils.

Elements Strongly Excluded

The elements that are strongly excluded are very limited in solubility. No data were found for uptake of Al, Ti and many other elements. Likely these would also be slightly or strongly excluded.

Effect of Soil Conditions on Uptake

Soil conditions can modify plant uptake of some elements. In this regard, the most important soil properties are exchange capacity, pH, and redox potential.

It is not possible to entirely separate the effect of exchange capacity from that of competing ions on plant uptake of radioactive elements. A soil with a high exchange capacity will have more available Ca, K, etc., than a soil with low exchange capacity. Soils with high exchange capacity generally sorb a greater proportion of dissolved radioactive elements than do those with low exchange capacity.[90,91] The situation is similar for both cations and anions, except that soil organic matter plays a more important role in sorption of iodide and bromide. Whether the reduced uptake is an effect of exchange capacity or of competing ions may be immaterial. The reduction seldom exceeds a factor of 10, which is small as compared with the differences between elements noted in Table I.

The pH of soils has a similar effect, seldom exceeding a factor of 10, on the uptake of certain elements. The uptake of Mn, Zn and Mo is strongly influenced by pH.[92] Low pH increases plant uptake of elements with slightly soluble hydroxides, like Mn and Zn. However, high pH increases plant uptake of slightly soluble anions, like molybdate and dichromate.

The redox potential of soils may vary enough to change the oxidation state of a few elements, and thus may markedly affect their plant uptake. Generally, the oxidized state will show greater plant uptake for anion forms, and the reduced state will show greater plant uptake for cation forms. Some examples are Mn, Fe, Ru, and Cr.

Submerged soils have lower redox potentials and less-extreme pH values than aerated soils.[93] The uptake of radioactive elements would be affected accordingly. Uptakes of Fe and Mn, for example, would tend to be increased by reduction to their lower valence state, but would be limited by the nearly neutral pH. The net result of flooding is usually to increase uptake of Fe and Mn naturally present in soils.[94] However, few experimenters have measured the effect of flooding on uptake of soluble Fe or Mn added to soils. In one case[95] it was uncertain whether or not flooding increased uptake of added Fe and Mn by rice.

Flooding may affect plant uptake of other metallic elements through solubilizing Fe and Mn oxides.[96] This was possibly the mechanism by which the concentration factor for uptake of applied Zn doubled when rice was grown under flooded as compared with unflooded conditions.[97]

Uptake of Cs and I are increased in unique ways from submerged soils. The fixation of Cs on soil clays is much reduced by the prevalence of the ammonium form of N in submerged soils.[61] Because of this, rice sorbed 20 times more radioactive Cs when grown under flooded conditions. Uptake of iodide by rice was also 10-100 times greater from flooded than from unflooded soils, apparently because bound I was released from soil organic matter upon flooding.[76]

Effects of Chelation on Uptake of Radioactivity

The uptake of radioactive elements may be considerably increased by adding chelating agents to the soil. The uptake of certain rare earth elements was increased by two or three orders of magnitude[31,63] which would give them concentration factors similar to those of Sr or Ba. Less-striking changes were found for the uptake of certain micronutrient elements, like Zn, Mg, and Fe.[31,62,65,95]

Recent research shows that plant uptake of actinides is greatly increased by adding chelating agents to soil[99,100] The magnitude is similar to that observed with the rare earth elements, and has led to speculation that natural chelating agents in soils may increase the uptake of actinides, which behave similarly to the rare earths over a long period of time. This effect, if persistent, will be extremely important in determining the permissible concentrations of actinide elements in soils because of their very long life and low permissible intake for humans. The natural distribution of U in plants and soils should include the effects of natural chelating agents for this element. The average concentration in dry plant material is 0.05 times that in dry soil,[106] indicating about the same concentration factor as was observed when soluble U was added to soils.[79]

Uptake of Radioactivity by Different Plant Species

Various plant species are known as accumulators of certain elements. This subject was thoroughly reviewed recently by Peterson,[101] who cited as the most extreme example the accumulation of Se by some Astragalus species. Although the concentration factors have not been documented according to the criteria established for this paper, plant uptake of insoluble and native soil Se may be 100 times greater for accumulator species than for most crop species.[102,103] Among crop plants, the legumes are generally known as accumulators of alkaline earth elements, and the grasses and cereals as accumulators of Si and alkali elements. However, concentration factors for different species do not generally differ by more than a factor of 10.

There may be significant accumulator species for the actinides. Brazil nuts are known to accumulate Ba and rare earths.[104] Tea and wormwood are reported to accumulate Th and rare earths.[105]

CONCLUSIONS

Plant concentrations of various radioactive elements, after they have been added to soils in water-soluble form, may be several orders of magnitude higher or lower than concentrations in soil. The concentration factor depends mainly on chemical properties of the elements, but it may vary one or two orders of magnitude, depending on soil properties or plant species. Important soil properties include exchange capacity, pH, redox potential, and presence of chelating agents in the soil solution.

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Factors Affecting Plant Uptake of Heavy Metals From Land Application of Residuals

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Pressure induced by population density has given soil the dubious honor of being a convenient waste depository. The waste products, when placed in soil, have four fates: (1) decomposition of organic material, (2) leaching of soluble products, (3) volatilization of gaseous products, and (4) accumulation of the remaining residue as part of the soil matrix. This residuals management approach is a simple disposal process for some waste products. For other waste products it can be considered a recycling process when some of the components of the waste are utilized. For example, numerous experiments have shown that municipal sewage sludge has significant fertilizer value (Lunt,[31],[32] Croker, [11] Braids, et al.,[7] Hinesly et al.,[21] King and Morris,[27] Kelling et al.,[16] and Cunningham, et al.[12]) and the application of this material to soil is considered to be a recycling process. However, sewage sludge may contain, in addition to those elements utilized by plants, relatively large amounts of elements that are not essential to plants or are essential at low concentration but may be phytotoxic at higher concentrations in the soil (Le Riche,[28] Berrow and Webber,[4] Hinesly et al.,[21] Chaney,[8] and Cunningham et al.[12],[13],[14]). This paradox confronts the agronomist and dictates that when sewage sludge is utilized as a fertilizer there must be consideration given to the accumulation of residues in the soil matrix which may result in undesirable accumulation of elements in the crop and/or impair crop growth.

The method used to define plant uptake of elements from waste additions to soil is the classical approach which has been used by the agronomist to solve problems associated with plant nutrition. Emphasis is placed on plant analysis for determining the effects of waste addition on plant growth and quality. To attack the problem various fractions of the plant (leaf, grain, root, stem, and entire plant) are used for analysis. These analyses are then correlated with the chemical properties of the waste amended soil (total soil analysis, strong and weak acid extractions, extractions with chelating agents, analysis of exchangeable ions and fractional analysis of organic and inorganic compounds) in search of the key parameters controlling plant uptake and accumulation.

As would be anticipated, the data collected have resulted in controversial and contradictory explanations and hypothesis. Many of the interrelationships between elements in the soil and in the plant will be controversial for some time. However, as the data base is expanded, analytical capability increased, and control of environmental conditions reported, a better understanding of the problem will develop and these interactions will begin to be more clearly comprehended.

Plant uptake (entry into the above-ground portions of plants, excluding aerial contamination) of an element is a function of four processes and their interrelationships. These processes include availability of the element in the soil, movement of the element to the root, absorption of the element by the root (roots absorb only ionic forms of elements) and translocation of the element in the plant. For a given system, any one of the factors may be rate limiting and thus control the uptake of an element. In order to understand the system, each of these processes and their interactions must be understood.

Metals in Soil

The chemical matrix of soil consists of numerous primary and secondary minerals in various stages of weathering. Because of the amorphous nature and lack of knowledge of the solid phases in soils, we tend to discount their importance and consider exchange reactions (cation exchange) of added constituents as the major reaction in soils. Recent advances in soil chemistry have demonstrated, however, that consideration must be granted to the specific ionic species in the soil solution and the many precipitation and dissolution reactions that are involved. The effects of metal waste additions take on new meaning when the stability of metal complexes, solid phase precipitates, and metal chelates are considered.

A general overview of the reactions of metals in soil indicates the complexity of the problem (Figure 1). Mechanisms for removal of the metals from the soil include plant uptake, leaching with soil water and volatilization of gaseous products. With time the added compounds are broken down into soluble constituents which become part of the soil solution. The soluble compounds can be exchanged for other ions on the soil exchange complex. When the limit of ions in solution exceeds the solubility of solid phase compounds and minerals, these compounds can precipitate. The inverse is also true that as the soil solution becomes unsaturated to any element of the solid phase or mineral that is present, that solid phase or mineral can dissolve. The ions in soil solution are subject to ingestion by soil microorganisms which then incorporate the ion into soil organic matter and/or chelation with soil organic matter.

The soil solution is affected by all the reactions that occur as the various constituents are added or taken from it. As such, its composition is ultimately controlled by the solubility of the various mineral phases. Since the rates of precipitation and dissolution for many of the reactions are slow, both kinetic and thermodynamic factors must be considered.

From these considerations two facts become apparent: (1) The total amount of an element in a soil is not indicative of the environmental risk associated with further additions of that element, (2) The cation exchange capacity (CEC) of a soil is not the controlling factor in determining the fate of elements added to soil. This is not to say that these are not important considerations for determining the amount of an element which can be

added, but that other factors may be more important. Our knowledge of these factors is only general and thus confidence in the factors is lacking. This indicates the dire need for basic research to evaluate the chemistry of elements in the soil.

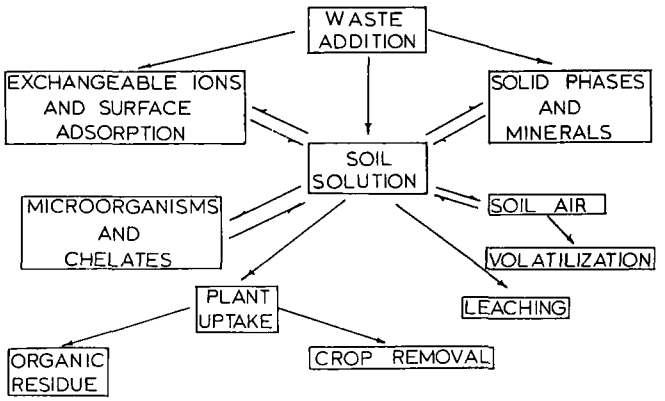

Figure 1: Transformations of Inorganics in Soil

Factors Controlling Metal Solubility in Soil

Numerous reviews of metal reactions in soil are available (Hodgson,[22] Jenne,[24], Ellis and Knezek, [18] Lindsay,[29],[30] Stevenson and Ardakani,[42].) From these reviews it is apparent that many soil components (clays, organic matter, hydrous metal oxides, carbonates, and inorganic compounds of the individual elements) have the ability to bind metals in soil and thus reduce the amount of soluble metal present. Superimposed are the pH and oxidation state of the soil.

The form of metal added (sulfide, hydroxide, carbonate, phosphate, etc.) will have a significant effect on its initial solubility in soil and therefore its initial impact on plant growth (Figure 1). Cunningham et al.,[14] showed that yield was more adversely affected by inorganic metal additions than the addition of an equivalent amount of metals by a sewage sludge which was first equilibrated with the inorganic metals (Table I). These results show only the initial response to the total metal content while the real questions are: "What is the difference in soluble metals added by the two systems?" and "Did the addition of sewage sludge add a sink for metals which was not present in the soil initially?" At least from Figure 1 it would seem logical to assume that, given sufficient time (weeks, months, years), the amount of metals in the soluble fraction would be dependent upon the amount added and not on the initial form. This may not be true, however, if the waste product added a sink for metals which was not as important in the soil initially. For example, sewage sludge adds organic material which reduces the availability of the metals.

The form of metal added would be a function of the waste product. In the case of anaerobically digested sewage sludge the metals are in a reduced form whereas with some waste products they could be in an oxidized form. Each waste and metal will have to be evaluated independently. Chromium is a good example of a metal where form is important. The hexavalent ion is more phytotoxic than the trivalent ion. With time however the hexavalent form is reduced to the trivalent form since it is more stable, and thus after this conversion the phytotoxicity of the two would be the same.

The total metal content added may not be significant in an initial evaluation of the impact of the added waste product. However, it has a significant impact on the ability of a soil to maintain a specific solution concentration. This can be illustrated by looking at the equilibrium between the insoluble and soluble forms of metals in soil. This reaction can generally be characterized by Langmuir or Freundlich isotherms which imply that there is an inverse relationship between bonding strength and amount of metal bound. Therefore, as the total amount of metal increases the equilibrium soil solution concentration will increase.

Table I: Dry Matter Yield as Affected by Inorganic or Sludge Sources of Heavy Metals (Cunningham, Keeney, and Ryan, 1975)

Treatment No.	Metal added* Cr	Cu	Zn	Ni	Crop Corn(1)	Rye(2)	Corn(3)
					yield, g/container		
	Inorganic source						
1	700	75	300	15	1.7	1.5	1.6
2	350	150	300	15	2.6	1.6	1.6
3	350	75	600	15	2.2	1.1	1.2
4	350	75	300	30	3.5	2.0	2.0
	Sludge source						
5	697	88	327	22	4.9	1.9	2.1
6	358	160	327	22	4.7	2.0	2.0
7	358	88	618	22	5.0	1.7	1.5
8	358	88	327	36	3.6	3.2	2.6
	Untreated sludge control						
9	58	46	113	22	13.4	5.5	3.4
	No sludge control						
10	0	0	0	0	8.0	2.8	4.1
			L.S.D.	0.05	1.7	0.8	0.6

*ppm on a soil basis.

Soil cation exchange capacity (CEC) is a measure of the net negative charge and is expressed as milligram equivalents (meq) per 100 g of soil. Soil CEC has been proposed as a controlling factor in metal retention in soil, but this would seem unlikely because it is a non-specific sorption reaction and the general consensus is that only a small proportion of the metals (Cd, Cr, Cu, Pb, Hg, Ni, and Zn) are exchangeable with neutral salts. Additionally, sorption studies with intact soils and soil components indicate that sorption sites with higher activation energies are involved. Further, it has been shown that sorption of metals by soil materials in greater quantities than the CEC does occur (DeMumbrum and Jackson,[16] and Bingham, et al.[5]). It becomes evident that the CEC is not the controlling factor in metal retention in soil. However, the CEC of the soil may be a first approximation of the soil's ability to retain metals in insoluble forms because the CEC does act as a temporary storage system for soluble ions and it is a rough indicator of the clay and organic matter content of the soil (which are important in precipitation and sorption of metals).

The involvement of clay in sorption of heavy metals by mechanisms other than cation exchange was shown by Elgabaly and Jenny[17] when they demonstrated that all the Zn sorbed by montmorilonite could not be removed by extraction with a neutral salt. It is sufficient to know that amount and type of clay in the soil may have a significant effect on the solubility of the heavy metals. In general, once a site for application of waste products has been selected there is little that can be done to alter the amount or type of clay in the soil unless these components in the waste can be changed.

The organic fraction has a significant effect on the solubility of heavy metals in soils. This conclusion is the result of the observations that (1) humic and fulvic acids (the complex heterogeneous mixture which is the nucleus of soil organic matter) and plant extracts exhibit chelation tendencies; (2) biochemical compounds having chelating characteristics are continuously produced and degraded in soils; and (3) heavy metal sorption is often related to the organic matter content of soils. Mortensen,[34] Hodgson,[22] and Stevenson and Ardakani[42] have published extensive reviews on soil organic matter complex formation with metals.

The management of soil organic matter is important because

of its involvement in metal chemistry of soil. Production practices (crop rotation, manure crops, organic matter addition, etc.) which maintain or add organic matter to soil should reduce the solubility of metals.

Inorganic solid phases which contain heavy metals may be the controlling factor in establishment of solubility limits. For example, the oxides of Fe and Mn play a dominant role in governing their solubility (Lindsay[29]). Solid phase Zn, Cu, Cd, Pb, and Ni in soils have not been greatly explored. Jenne[24] postulated that Zn and Cu were bound as trace constituents in the more abundant hydrous oxides. In fact, Thomas and Swoboda[43]; Stanton and Du T. Burger[41]; and Gadde and Laitinen[19] have shown that artificially prepared Fe oxides sorb Zn. Shuman[38] demonstrated that soil Fe oxides sorbed Zn when he found that the removal of the Fe oxides from clay systems caused a decrease in their sorption capacity (Table II). However, it should be noted that this decrease in sorption capacity was not true for all the clay materials tested and in fact for some clay materials there was an increase in sorption capacity when Fe oxides were removed. This increased sorption capacity appeared to be a result of the change in surface area and CEC of the clay when the Fe oxides were removed. This interaction between sorption capacity and Fe oxide content and clay content indicates that the Fe oxide content must be considered when heavy metals are added to soil and it could be further postulated that the other metal oxides and hydroxides in soils may be important considerations in heavy metal chemistry in soil.

Table II: Langmuir Coefficient, Surface Area, and Cation Exchange Capacity for Soil Clays From Two Horizons With and Without Fe Oxides (Shuman, 1976)

Soil	Horizon	Fe Oxide	Langmuir Coefficient Adsorptive Capacity(b) mg/g	Surface Area m^2/g	Cation Exchange Capacity Meq/100g
Decatur	A	with	4.30	264	23.8
		without	4.29	287	27.4
	B2t	with	3.78	162	13.7
		without	1.86	204	17.6
Cecil	A	with	2.27	111	6.4
		without	4.12	71	10.1
	B2t	with	1.85	156	15.7
		without	1.91	517	19.1
Norfolk	A	with	1.39	132	17.8
		without	1.15	124	13.9
	B2t	with	1.96	150	14.8
		without	2.16	504	18.2
Leefield	A	with	3.74	223	25.8
		without	4.70	220	23.1
	B2t	with	4.82	256	--
		without	5.69	232	28.5

Superimposed on the aforementioned soil variables is the pH variable. Superimposed means that the variable has a significant effect on the other variables. It has been demonstrated numerous times that soil pH has a significant effect on heavy metal uptake (Chaney,[8] and Chaney, et al.[9]). This pH effect could be the result of the decrease in solubility of metals as the pH increases. Andersson and Nilsson[2] demonstrated the interaction between soil material and pH on sorption of Cd (Figure 2). These data support the observations that the Cd content of crops is a function of pH in that as the pH is increased the concentration of Cd in the plant tissue decreases. The interesting feature is the difference in response between soil material and pH. For example, with Fe oxide there was no sorption of Cd below pH 4.5 but at pH above 6 most of the soluble Cd was sorbed. In contrast, pH had very little effect on the sorption of Cd by the organic soil. It can be concluded that not only is pH important but the importance of pH on sorption of Cd is a function of the soil material responsible for the sorption. Generally, the higher the pH the lower the solubility, regardless of the type of solid phase. This same general conclusion can be reached for most of the heavy metals.

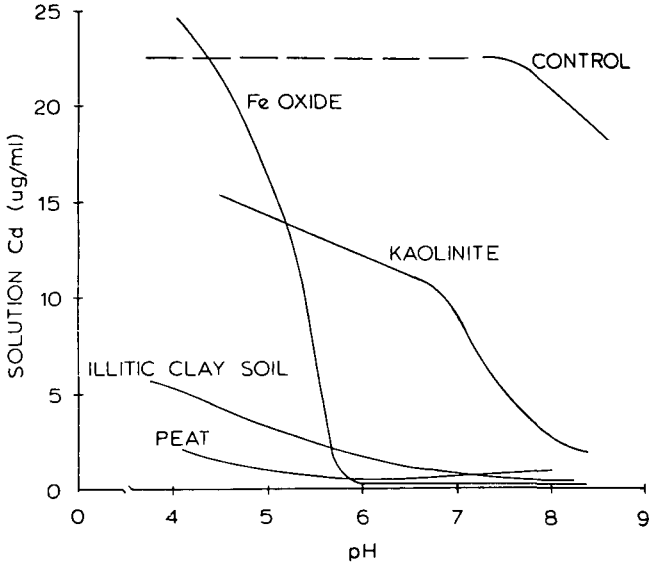

Figure 2: Distribution of Cd Between Soil Material and Equilibrium Solution as a Function of pH (Andersson and Nilsson, 1974)

The oxidation-reduction status of the soil has a great impact on the production of organic complexing agents, the oxidation state of S compounds and the oxidation state of the hydrous oxides of Fe and Mn. Therefore, it should have an effect on the sorption of heavy metals by these compounds. The net result of forming reduced conditions in the soil should be to increase the solubility of Co and Cu (Mitchell[33]) and Mo (Jenne[24]); and a decrease in the solubility of Zn and Cd (Bingham et al.[6]).

Movement to Root Surface

Even when the element is in solution it is not subject to uptake by the plant root unless it first reaches the region of the roots where the ions are absorbed. The general mechanisms to accomplish this have been described by Barber[3] and have been classified as mass flow, diffusion and root interception. Barber[3] defined mass flow as the movement of dissolved nutrients in the water to the root. Water moves to the roots as a result of water absorption by the roots which is induced by transpiration. If mass flow does not supply as much nutrient to the root as is absorbed by the root, the solution concentration at the root surface is lowered and a concentration gradient between the bulk of the soil solution and the soil solution in contact with the root is developed. Movement of nutrients to the root surface as a result of this gradient has been defined as diffusion.

Root interception (contact exchange) is perhaps the least important of the three mechanisms and has been defined as the interception of the nutrients by the root as it grows through the soil. Olsen and Kemper[35] questioned the relevance of root interception as a separate process, but there is no question that the intensity of root growth will have a large influence on the amounts of nutrients which can be moved to the root surface as a result of mass flow and diffusion.

The plant stimulates nutrient movement to the root by the growth of roots in a region (contact exchange), movement by mass flow as a result of transpiration, and movement by diffusion if its rate of nutrient absorption is greater than the rate of movement of ions to the root by mass flow. It is evident then that

any factors which alter the concentration of ions in solution, the ability of the soil to maintain the solution concentration, the amount of root developed by the plant, the plant's ability to accumulate ions, or the rate of transpiration of the plant can affect the movement of ions to the root surface.

The knowledge about movement of ions to roots is at best qualitative. The data which are available to develop a quantitative concept have been developed under conditions where the element under study was limiting plant growth. Thus the application of this knowledge to systems where the element is in excess is tenuous. It would seem logical to assume that when excessive amounts of an element have been applied to the system the rate of movement to the root would not be a rate limiting step. However, where the element is in the upper layer (0-6") of a soil profile and the uptake of nutrients is below this depth, it may be that movement to the root is the rate limiting step and thus should not be ignored. For example, it is known that plant root development is strongly influenced by soil pH with a neutral pH being favorable. Thus, if the pH of the lower soil profile was neutral and the 0-6 inch layer was acid, root development and plant uptake could be from the lower portions of the profile.

It can be argued that movement to the root is a function of the concentration of ion in solution and the ability of the soil to maintain the solution concentration and thus the chemistry of the element in the soil is the most important consideration. However, given the same growth medium the plant species and variety become important because of their impact on the rooting and growth characteristics of the plants.

Absorption of Elements by Roots

The plant is able to take up only those elements that exist either as cations or as anions. For this reason, nutrient uptake is commonly referred to as ion uptake. Probable form in which they are absorbed by roots is shown in Table III. Plants maintain nutrients in their tissue at concentrations much higher than exist in the soil solution. For example, K in the soil solution amounts to about 5 ppm, whereas within the plant the K content is 1,000 to 3,000 ppm. This phenomenon is referred to as ion accumulation.

Table III: Ionic Form of Ions Absorbed by Plants

Element	Absorbed Form
Arsenic	$AsO_4^{=}$
Cadmium	Cd^{++}
Chromium	$CrO_4^{=}$
Copper	Cu^{++}
Iron	Fe^{++}
Mercury	Hg^{++}
Nickel	Ni^{++}
Lead	Pb^{++}
Molybdenum	$MoO_4^{=}$
Selenium	$SeO_4^{=}$
Zinc	Zn^{++}

Ion accumulation occurs with all the nutrients and cannot be explained by the "soaking up" of nutrients from the solution surrounding the roots. A sponge or dead root will soak up nutrients from a solution, but the concentration within the sponge or dead root will never exceed the concentration in the nutrient solution. Therefore, the phenomenon of ion accumulation is dependent upon living tissue. Obviously any factor which affects the metabolic activity of the plant will influence ion absorption. Such factors as temperature, O_2, and metabolic inhibitors affect metabolism and thus ion uptake (Rains[36]).

The pH of the solution has a marked effect on both cation and anion absorption. Cation absorption reaches its maximum rate at pH 5 to 7, and maintains that rate of absorption up to pH 10. Anion absorption is less affected by low pH, but as the pH is increased above 6 the rate of absorption decreases. Changes in the pH of the solution have been observed to occur when anion-cation absorption is not balanced (Hiatt[23]). Thus, there is a release of H^+ to the solution when cation uptake exceeds anion uptake and a release of OH^- or HCO^-_3 when the reverse occurs. These changes in solution pH will be most drastic in the region of the root (rhizosphere) and the chemistry of the soil solution may be radically different in the rhizosphere as compared to the bulk of the soil solution.

For a number of ions and tissues it has been shown that as the concentration in solution increases the absorption by tissue increases. This increase in absorption rate levels off at 0.1 mM and remains essentially constant up to 1 mM. A second plateau is reached at 10 mM. This has been interpreted to show there are two mechanisms of absorption, one at low concentrations and one at high concentrations.

Phytotoxicity from heavy metals has been observed to cause Fe deficiencies which suggest that the heavy metals compete with Fe at the absorption step. Schmid, et al.[37] showed that Cu strongly inhibited the absorption of Zn whereas Mn had no effect. This has led to the hypothesis that there may be nutritional interactions involved in the absorption of heavy metals. Thus, not only is the concentration of the metal ion under study important, but the concentration of other ions in solution is important.

High phosphate concentration has been associated with elimination of metal toxicities (Spencer[40]). Smilde, et al.[39] studied additions of P to soil which contained phytotoxic concentrations of Zn. For some crops, P alleviated Zn toxicity and reduced Zn uptake. The involvement of P could be in soil solution chemistry, ion uptake by roots or in translocation from roots to shoots.

Translocation of Elements Within the Plant

In the early seedling stage stored nutrients are moved from the seed to the roots and shoot. In the vegetative stage there is movement from roots to leaves, leaves to roots, and leaf to leaf. Finally, roots and leaves of the maturing plant translocate nutrients to new seed.

The process of upward ion movement in xylem tissue appears to require metabolic energy even though within the nonliving xylem channels nutrients apparently move passively in transpiration and root pressure streams. Metabolic energy is involved in the release of nutrients into the root xylem and in their release from the xylem into surrounding leaf tissue. Movement of ions in the phloem tissue appears to be related to metabolism. This requirement of metabolic energy for the transport of elements within plants indicates that any factor which influences plant growth and development will influence the translocation of ions within plants.

The transport of ions can be influenced by competing metal ions, particularly where the extraneous metals at high concentrations preempt ligands or displace metals normally chelated in crucial reactions. For example, it has been shown the P can disrupt the Fe nutrition of plants even though the Fe concentration seems adequate for normal growth. It is clear that high P will cause deranged transport and metabolism of Fe and Zn and it is presumed that it will alter the translocation of other heavy metal cations as well.

CONCLUSION

From the above discussion of factors controlling the entry of an element into the above-ground portion of a plant it becomes apparent that any number of variables (soil properties, waste properties, and plant properties) can be the controlling factor for a given experiment. However, in general it appears that movement to the root will be controlled by solution concentration if all the ions moved to the root are absorbed by the root. Further, from the data on ion uptake by roots from solution culture (at least for the major nutrient ions) it appears that the concentration in soil solution would be 1 to 2 orders of magnitude less than the concentration in solution cultures where absorption by roots reaches the first plateau. Therefore, it becomes evident that the chemistry of metals in soil as related to the soluble fraction of metals is a major controlling factor in absorption of ions by the roots and thus lends validity to the relationship between soil composition and plant uptake. However, one must not fail to recognize the importance of the other processes involved and their potential impact on the analysis of the data.

What Elements Should Be Considered?

Any element can be toxic to plants and/or animals if it is present in sufficient quantities. Therefore, the obvious question is what are sufficient quantities? The answer lies in knowing what is in the material to be placed on the soil and what is the normal concentration of the elements in the soil. With this information it can be ascertained if the waste product will have a significant impact on the concentration of the element in the soil. Table IV gives the ranges and common concentrations of trace metals found in soils.

Table IV: Total Concentration of Trace Elements Typically Fo-nd in Soils and Plants (Allaway, 1968)

Element	Conc. in Soils (µg/g) Common	Range	Conc. in Plant Diagnostic Tissue (µg/g) Normal	Toxic*
As	6	0.1 -40	0.1 -5	
B	10	2 -100	30 -75	>75
Cd	0.06	0.01 -7	0.2 -0.8	
Cr	100	5 -3000	0.2 -1.0	
Co	8	1 -40	0.05 -0.5	
Cu	20	2 -100	4 -15	>20
Pb	10	2 -200	0.1 -10	
Mn	850	100 -4000	15 -100	
Mo	2	0.2 -5	1 -100	
Ni	40	10 -1000	1	>50
Se	0.5	0.1 -2.0	0.02 -2.0	50-100
V	100	20 -500	0.1 -10	>10
Zn	50	10 -300	15 -200	>200

*Toxicities listed do not apply to certain accumulator plant species.

Assuming that the waste product has a greater concentration of one or more of the metals than is typically found in the soil, then the movement of the element through the soil to crop to man becomes an issue and has to be examined to determine whether toxic or undesirable concentrations are produced.

From this point the discussion will center around one waste product (anaerobically digested sewage sludge), but the same general approach can be used for other waste materials.

The first question to be answered concerns the value of the material to agriculture production. As has been shown numerous times, sewage sludge has significant quantities of the major plant nutrients (N, P, and K) and thus land application can benefit crop production as well as being a disposal operation. The point at which land application stops being a utilization process and becomes a disposal process will not be discussed. It will be assumed that the material is used as an N or P fertilizer and yearly application rates adjusted accordingly.

From a comparison of Tables IV and V, it becomes apparent that for a given sewage sludge any metal can be in concentrations greater than that normally found in the soil. In general, it has been found that Cd, Cu, Pb, Zn, Cr, Hg, and Ni will be the metals which increase the greatest from sludge application. From Table VI it can be seen that Cu and Ni are more phytotoxic than Zn and Cd and that Pb, Hg and Cr are the least phytotoxic. Therefore, for crop production Cu, Ni, Zn, and Cd become the most important considerations. However, if the impact of this practice results in increased levels of Cd and Pb in the crop then the concern shifts from effects on crops to effects on animals that consume the crops because of the cumulative effects of Cd and Pb on the animal system. Thus, the concentration of Cd and Pb in the crop can impose limits on the utilization of the crop and thus on the amounts of these materials applied.

Table V: Total Concentrations of Trace Elements Typically Found in Sewage Sludge[1]

Element	Conc. in Anaerobically Digested Sewage Sludge Median	Mean	Range
	mg/kg		
As	10	43	6 230
B	36	97	12 760
Cd	16	106	3 3,400
Cr	1,350	2,070	24 28,800
Co	7	8.8	3 18
Cu	1,000	1,420	85 - 10,100
Hg	5	1,100	.5 10,600
Pb	540	1,640	58 19,730
Mn	280	400	58 7,100
Mo	30	29	24 30
Ni	85	400	2 3,520
Zn	1,890	3,380	108 27,800

(1) From L. E. Sommers, Personal communication based on data provided by members of Regional Research Committee NC-118.

Table VI: Potential Toxicity of Heavy Metals

Element	Essentially Plant	Animal	Toxicity Plant*	Animal**	Animal***
Cd	NO	NO	MODERATE	HIGH****	HIGH****
Cr	NO	YES	LOW	LOW	LOW
Cu	YES	YES	HIGH	MODERATE	SLIGHT
Hg	NO	NO	LOW	HIGH****	LOW****
Ni	NO	YES	HIGH	MODERATE	LOW
Pb	NO	NO	LOW	HIGH****	LOW****
Mo	YES	YES	LOW	HIGH	MODERATE
Se	NO	YES	LOW	HIGH	MODERATE
Zn	YES	YES	MODERATE	LOW	LOW

*When metal is applied to soil on which crop is grown
**When metal is fed to animal
***When animal is fed crop which is grown on contaminated soil.
****Cumulate effects

In greenhouse experiments to evaluate source and rate of anaerobically digested sewage sludge on crop growth, it was found that source of anaerobically digested sewage sludge, application rate of anaerobically digested sewage sludge, and their interaction all had significant effects on yield (Table VII).

In general, there was an increase in yield up to the 125 or 251 mT/ha rate and then a decrease in yield with higher rates of application. Multiple regression analysis using yield as the dependent variable, and the amount of N, P, K added by O, 63, and 125 mT/ha rates of the four anaerobically digested sewage sludges as the independent variable, indicated that these variables explained 63 percent of the yield increases.

Table VII: Effect of Source and Rate of Anaerobically Digest Sewage Sludge Application on Yield of Corn (Cunningham, Keeney, and Ryan, 1975a)

RATE	SOURCE			
	JANESVILLE	FOND DU LAC	WISC.RAPIDS	WAUKESHA
metric tons/ha	yield, g/pot			
0	8.0	8.0	8.0	8.0
63	13.4	10.6	13.4	13.2
125	15.2	13.6	15.7	12.2
251	1.3	11.9	15.9	13.1
502	1.0	1.1	1.3	6.6
LSD 0.05	1.4	1.6	1.6	4.9

Regression estimates to explain the decreases in yield using yield as the dependent variable and amount of metals added by the 125, 251 and 502 mT/ha rates of anaerobically digested sewage sludge as the independent variable, suggested that Cu, Zn, and Ni were important but there were significant interactions between these metals and other metals added which complicated the interpretation.

In further experiments to evaluate the interaction between metals, a 3^4 factorial experiment using four metals (Cr, Cu, Zn, Ni) at three rates were equilibrated with anaerobically digested sewage sludge. The anaerobically digested sewage sludge was added to soil at a rate of 63 mT/ha and the metal loading was comparable to the previous experiment.

The findings of this experiment are presented in detail in Cunningham et al.[13] All treatments had adverse effects on plant yields with phytotoxicity being due to Cu and Zn. Rates of Ni addition were relatively low and Ni had no adverse effect, while Cr increased yield (decreased the phytotoxicity of Cu and Zn).

Statistical analysis of the tissue concentration of metals showed that a number of interactions, including increases in the Zn and Cd concentration of plants tissue, occurred when more Cu was added (Table VIII). This resulted in changes in the Cd:Zn ratio of the plant tissue (Table IX). Since Cd was added at a constant rate (4.5 kg/ha) from the anaerobically digested sewage sludge, the increase in Cd:Zn observed with increasing Cu indicates that complex interactions occurred.

Table VIII: Cadmium and Zn in Plant Tissue at Varying Levels of Cu and Zn (Cunningham, Ryan and Keeney, 1975b)

Zn Added	Tissue Zn			Tissue Cd		
	120 Cu	194 Cu	343 Cu	120 Cu	194 Cu	349 Cu
ppm	ppm of plant tissue*					
410	343	356	478	3.6	6.2	9.7
707	520	422	744	5.2	5.3	8.4

*First corn crop

Table IX: Cd:Zn Ratio in Plant Tissue as Affected by Cu Additions (Cunningham, Ryan, and Keeney, 1975b)

Metal Added, ppm of Soil		Crop		
		Corn	Rye	Corn
Cu	120	0.88	0.57	0.57
	194	1.10	0.66	0.81
	343	1.47	0.97	1.31

The effect of soil pH on crop yield and ion uptake cannot be ignored. In a study of sites where sludge had been applied over long periods of time. Chaney et al.[10] demonstrated the importance of soil pH (Table X). It should also be noted that plant species and plant part has a significant effect on the concentration of Cd in the tissue. From similar studies it has been found that even though there was considerable increase in the Cd content of the soil there was minimal increase in Cd content of corn grain (Table XI). It has also been found that the metals of concern (Cu, Ni, Zn, Cd, and Pb) have remained in the upper horizons of the profile where tillage has occurred.

Table X: Cd Content of Crop Tissues as Influenced by Soil Cd Content and pH (Chaney, Hornick and Simon, 1976)

Treatment	Soil Cd DTPH Extraction	Soil pH	Chard Leaf	Soybean Leaf	Soybean Grain
	ppm in Soil		--- ppm in Tissue ---		
Control	.13	5.3	3.6	1.04	0.36
	.10	6.7	1.2	0.55	0.28
Sludged	1.13	4.8	73.0	10.7	3.70
	1.19	6.6	5.5	1.87	1.51

Table XI: Cd Content of Soil in Relation to Cd Content of Plant Tissue (Ryan Old Site Studies)

Soil pH	Soil Cd Total	Soil Cd .1N HCl Extractable	Plant Cd Chard Leaf	Plant Cd Corn Leaf	Plant Cd Corn Grain
	ppm				
6.4	35	32	--	--	.20
7.0	7.56	7.32	--	--	.38
6.8	9.55	9.20	--	--	.22
6.8	6.14	5.82	--	2.06	.36
6.5	4.32	4.31	--	2.52	.10
6.5	4.33	4.30	1.51	3.15	--
6.5	.40	.30	.50	1.96	--

Field experiments involving use of anaerobically digested sewage sludge for production of corn have led to conflicting results (Table XII). Kelling et al.[26] found that applications of 4.3 kg Cd/ha did not cause a change in the Cd content of the corn grain. Hinesly et al.[21] found that applications of 88 kg Cd/ha caused an order of magnitude increase in the Cd content of corn grain (0.06 to 0.59 ppm). In contrast Decker et al.[15] have reported that applications of 2 kg Cd/ha have caused a fivefold increase in Cd content of corn (0.12-0.68). Simlar findings have been reported by Giordano et al.[20]

The resolution of these results is extremely difficult and indicates our lack of complete knowledge about the systems. The difference could be a result of:

Varietal differences—The variety of corn used by Decker et al.[15] may translocate more Cd to the grain than the varieties used by Kelling et al.[26] and Hinesly.[21] The differences between sweet corn and field corn are unknown (i.e., data of Giordano et al.[20] vs. others).

Forms of metals—The sewage sludges used by Decker et al.[15] and Giordano et al.[20] may have contained Cd in a much more available form than the sewage sludges used by Kelling et al.[26] and Hinesly.[21]

Table XII: Field Studies on Zn and Cd Content of Corn

Sludge Rate MT/ha	Soil pH	Zn Soil Kg/ha	Zn Grain ppm	Cd Soil Kg/ha	Cd Grain ppm
0	6.0		20.1		0.09
3.7		11.2	20.3	0.26	0.08
7.5		22.5	20.6	0.53	0.10
15		45	22.0	1.07	0.09
30		90	26.3	2.15	0.09
60		180	26.9	4.30	0.10
0			28.9		0.06
92,9		510	38.4	21	0.17
184.3		1011	47.6	41	0.33
386.6		2122	60.0	88	0.59
0	4.9		35		0.3
50	5.3	90	47	2.5	0.7
100	5.3	180	48	5	0.8
200	5.6	360	52	10	1.0
400		720	61	20	1.0
0	5.2		22		0.12
55	5.4	64	34	.5	0.41
110	5.3	129	49	1.0	0.59
220	5.3	258	60	2.0	0.68

Data from Kelling et al. (1976), Hinesley (personal communication), Giordano, Mortvedt and Mays (1975) and Decker, Chaney and Wohf (1975)

Soils—There could be completely different complexing agents involved in the chemistry of Cd in the soils. It would seem that the pH difference could explain part of the results. This could be a direct influence on the soil chemistry of Cd or it could be an indirect effect (i.e., root distribution of the plant). There may also be plowpans or fragipans in the soil which influenced root distribution and thus the zone in the soil where ion uptake occurred.

Results such as these are to be expected until we have sufficient knowledge to completely define the variables involved. This does not imply that the practice is bad and should not be allowed to continue, but that there can be problems and one must be aware of the potential problems and concerned about their impact on the practice.

Limitations

As has been demonstrated, our knowledge about the chemistry of metals in soils and its impact on crops is not complete, but we do know enough to make some rational judgments. For example, we know the crop (species as well as variety) have significant differences in their tolerance to metals and thus we should grow crops which are least affected by metals. If the crop is to be a general agriculture crop, then corn grain appears to be the logical choice. Grass may be the choice where one is not concerned about a marketable crop. Because of their ability to accumulate metals, the growth of vegetable crops, particularly leafy vegetables, should be discouraged. However, if the material is to be applied to farmer-owned land then consideration should be given to the types of crops normally grown in the area. If the farmer grew a crop which accumulated the metals then there should be an effort to reduce the metal content of the waste product being applied to the land.

The soil pH is perhaps the most important soil variable and should be maintained at pH≥6.5. The impact of pH difference with depth in the profile is unknown but it would seem logical to assume that a soil with a neutral profile would be a better choice than a soil which had an acid profile.

The soil properties which are involved in the removal of metals from solution are diverse and the impact of each is not conclusive. Therefore, it would seem logical to use soil CEC as a method of grading soils on their affinity for metals until more is known about the chemistry of metals in soils. The land grant universities and the USDA-ARS have proposed interim limits on metal application to agriculture soils (Table XIII). These limits seem appropriate and should give sufficient lead time for development of the basic information required to develop a more rational basis for land application.

Table XIII: Maximum Accumulative Amount of Metal Which Can Be Added to Privately-Owned Farmland

Element	Soil CEC 0-5	Soil CEC 5-15	Soil CEC > 15
	--------- kg/ha ------		
Zn	250	500	1000
Cu	125	250	500
Ni	50	100	200
Cd	5	10	20
Pb	500	1000	2000

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Heavy Metal Uptake and Control Strategies Associated with Sewage Sludge Fertilized Crops

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INTRODUCTION

The use of human and animal waste products for plant nutrition is a very old practice. However, during the last decade there was been a renewed interest in the use of municipal sewage sludge for its nutrient value. Concurrent with this interest in the nutrient value of municipal sludges is a growing interest in their metals content—particularly, for those sludges produced in highly industrialized areas. Quite frequently the drawback cited with using sewage sludges from industrialized areas is that they might be high in non-plant essential heavy metals. It is true that many metals from industry are discharged to municipal sewer systems; and as the wastewater treatment plants improve their treatment of those wastes, the more metals can be expected to accumulate in the resulting sewage sludges. It is true also that metals are present in varying amounts in all sewages, and sometimes in relatively high concentrations in situations where industrial discharges are not the prime source, as was demonstrated by Klein[13], for New York City.

A review of the more recent literature leads to the conclusion that the current strong interest in the metals content of municipal sewage sludges is generated in great part by the belief of some workers that the applications of sewage sludges for productive agricultural purposes, is undesirable. By productive agriculture here is meant the production of crops such as corn, soybeans, wheat and barley, and fodder for cattle and swine production.

While the proposals for controlling sludge-borne metals may vary in their specifics, they usually fall into two general categories. One category aims at controlling the discharge of metal-bearing industrial wastes to municipal sewer systems, which in turn would reduce the metals content of the resulting sludges. The other category aims at "protecting the land from additional heavy metals" by restricting the application of sludges to only the lowest metal-content sludges available from small residential communities which have no industrial activities.

This latter approach is at best extreme and could be interpreted to prohibit the use of rock phosphate which has been shown to range as high as 100 μg CD/g (Williams and David, 1976). In a study of 21 commercial fertilizers used in Sweden the Cd concentration was found to range from 0.1 to 225μg/g and the Pb from<0.1 to 225μg/g.[21] These authors concluded that "for Swedish conditions and with application of present Swedish recommendations, commercial fertilizers will probably in the long run have an appreciably greater influence on the cadmium contents of agricultural products and food than will sewage sludge."

To further illustrate this point, the work of Furr et al.[8] is also germane. They analyzed the sludges of 16 American cities for 68 elements, dieldrin, and polychlorinated biphenyls (PCB's), and selected the sludge of Cayuga Heights, N.Y., as an example of a domestic sludge. Of the 16 sludges reported this domestic sludge was in the upper 50 percentile in concentrations of Hg, Pr, Pt, Re, Y and Ca.

There is little doubt that industrial control is feasible and effective. This topic will be discussed later. However, the second type of control defeats the very concept of sludge utilization for productive purposes since the bulk of municipal sludges is produced in the nation's large industrial urban areas. Studies by Zenz et al.[23] and Konrad et al.[14] show that approximately 85% of the nation's municipal sludges is produced in the large urban industrial centers.

After many years of successful use of sludge in England, Paris, Berlin, the United States, and other places, the question of phytotoxicity has been satisfactorily addressed. Unless the soil itself simultaneously has very high metal levels and low pH, phytotoxicity is not a significant cause for concern.

Control Strategies

The United States Environmental Protection Agency (EPA) during the last three years has released various drafts of a policy statement which proposed guidelines for the utilization and disposal of sludges for publicly-owned treatment works. The drafts released before the most recent version, which appeared in the June 3, 1976 Federal Register (EPA, 1976) contained limitations on the levels of heavy metals in sludges applied to land, and also presented an equation which limited the total application of sludge based upon its Zn, Cu, and Ni content, or based upon its Zn equivalent toxicity with respect to the combined concentrations of Zn, Cu, and Ni. This concept of Zn equivalent toxicity was introduced by Chumbley[5] in Great Britain, picked up and recommended by Chaney[4] to the U.S. scientific community in 1973. This concept has since been attributed to the United States Department of Agriculture (USDA). As of this writing, neither Chaney nor Chumbley nor the USDA has presented any acceptable scientific data to support this concept. In fact, it has recently been concluded that the Zn equivalent equation was based upon inadequate information and that data currently available show that the toxicity of these elements is not additive, and that the use of the equation greatly underestimates the amounts of sludge-borne metals which can be safely applied to near neutral, neutral and calcareous soils. Furthermore, the equation does not apply uniformly over a broad spectrum of plant species (CAST 1976).

The early response of the interested scientific community to Chaney's 1973 recommendations was very disappointing. For example, only a very few individuals thought it necessary to question the scientific basis for the recommendations or to inquire into the availability or existence of data in support of these concepts. Instead, the interested scientific community was asked to prove the recommendations and concepts wrong while they were rapidly being incorporated into guideline documents of the USEPA (1974) and the States of Ohio (1975) and Wisconsin (1975), and more recently, the State of California (1976).

Although the most recent version of the EPA (June 3, 1976) guidelines does not contain specific limitations on heavy metals or the above mentioned equation, the document implies that the USDA and FDA are now preparing guidelines and recommendations to reintroduce these limitations and also the "sludge" equation. Although the early EPA drafts which did contain such limitations were never published nor proposed officially, they nevertheless have had a pronounced adverse impact on state agencies formulating their own guidelines. Several states which felt the need of national direction to establish their own policy on agricultural use of municipal sludges immediately incorporated the USEPA endorsed Zn equivalent concept, the loading formula, and the Zn:Cd ratio concept, proposed by Chaney, into their respective state guidelines.

Wisconsin Guidelines

The Wisconsin Department of Natural Resources in Technical bulletin No. 88 (Kenney et al.,[11]) has published guidelines on sludge application to land. The "guidelines can be used for screening the land application alternative, evaluation of environmental effects . . . and for developing a land application program. . . ." The guidelines restrict total applications of sludge by limiting the total "metal equivalent" applications on a pounds-per-acre basis to not more than 65 times the soil cation exchange capacity (CEC) in meg/100 g of soil. Metal equivalents of a specific sludge are calculated using the following formula:

$$\frac{\text{Metal equivalents}}{\text{ton sludge}} \quad \frac{\text{(ppm Zn)} + 2\,\text{(ppm Cu)} + 4\,\text{ppm (Ni)}}{500}$$

In addition, yearly applications are limited to a maximum of 2 lbs/A/yr of cadmium with a total application site lifetime maximum of 20 lbs/A. The lifetime limitation which calculates to be shorter either by the above equivalent methods or the maximum application of 20 lb/A of cadmium takes precedence.

Ohio Guidelines

A task force appointed by Roy M. Kottman, Director of the Ohio Agricultural Research and Development Center, published in July of 1975.[15] The guideline was designed "to assist landowners in making decisions as they consider the application of sludge to their land."

The Ohio guide quotes drafts of USEPA guidelines published prior to June 3, 1976 and suggests that the following equation "should be used for situations of slightly acid to neutral soils where pH can be maintained at 6.5 or higher at all times."

$$\text{Total amount of sludge (dry tons/acre)} = \frac{\text{CEC} \times 32{,}700}{\text{ppm Zn} + 2\,\text{(ppm Cu)} + \text{(ppm Ni)} - 200}$$

CEC = Cation exchange capacity of soil before sludge application (meg/100 g)
ppm = Parts per million or mg metal/kg dry weight of sludge

For soils with a pH below 6.5, the 32,700 figure is changed to 16,350 to calculate maximum total loading while for forest soils with a pH below 6.5, this figure is reduced to 8,175.

Zenz et al.[23] presented a study of the impact on municipal agencies of various drafts of EPA regulations or guidelines concerning heavy metal levels in sludges applied to land. He concluded that most cities could not meet the guidelines while the restrictive loading rates would virtually eliminate the land utilization option. For example, it was concluded from a 30-city survey that only 14.7% of the sewered population of Illinois could apply sludge to land if sludge with a Zn/Cd ratio of less than 100 was not allowed to be applied. Even if the Zn/Cd ratio limitation were not applied, sludge application rates to land would be limited to a lifetime total of 100 dry tons/acre for 50% of the Illinois communities surveyed with soils having a cation exchange capacity (CEC) of 10 meg/100 g.

Although the most recent guideline of the EPA regarding sludge application to land (EPA, 1976) does not have limitations on heavy metals contained in sludge applied to land, it does call for review of all sludge application projects by the United States Dept. of Agriculture (USDA). The USDA has also formulated drafts of regulations or guidelines regarding sludge application, but these have not been officially released.

USDA Regulations/Guidelines

Here we will discuss the USDA regulations or guidelines and their impact on municipal wastewater treatment agencies.

Basically, the various drafts of USDA regulations contain the following limitations regarding the heavy metals content of municipal sludges applied to land:

[No greater amount of sludge-borne metals (kg/Ha) may be applied than shown in the Table below.]

Table I

METAL	Soil Cation Exchange Capacity (meq/100 g) 0-5	5-15	15
	kg/ha		
Zn	250	500	1000
Cu	125	250	500
Ni	50	100	200
Cd	5	10	20
Pb	500	1000	2000

The USDA documents recommend the following:

(1) That sludges with a cadmium content>25 mg/kg (dry wt.) should not be applied to privately owned land unless their Cd/Zn is≤0.015.
(2) Cadmium loadings on land should not exceed 1 kg/ha/yr from liquid sludge and not more than 2 kg/ha/yr from dewatered sludge.
(3) Sludge having a cadmium content>1.5 percent of its zinc content should not be applied on a continuing basis unless there is an abatement program to reduce cadmium in the sludge to an acceptable level.

As mentioned earlier, the USDA has offered no direct scientific data to support these recommendations.

Zenz et al.[23] did an extensive survey of the metal levels in the sludges from 30 communities in Illinois. Presented in Figure 1 is a cumulative frequency plot of the allowable loadings for these 30 Illinois communities for the USDA limitations of 5, 10, and 20 kg Cd/ha. As can be seen, 50% of the communities in Illinois could not apply over 150 dry tons per acre of sludge to soils with a CEC of 5 meq/100 g. Since most crops require 10-20 tons of

sludge per acre to supply nitrogen requirements, this means that application sites would have only a 7.5 to 15 year life span.

Of these 30 Illinois communities, only 8.3% of those with a sludge cadmium content of over 25 ppm had a Cd/Zn of less than .015, while 36% of the sludge had Cd contents greater than 1.5% of the zinc content.

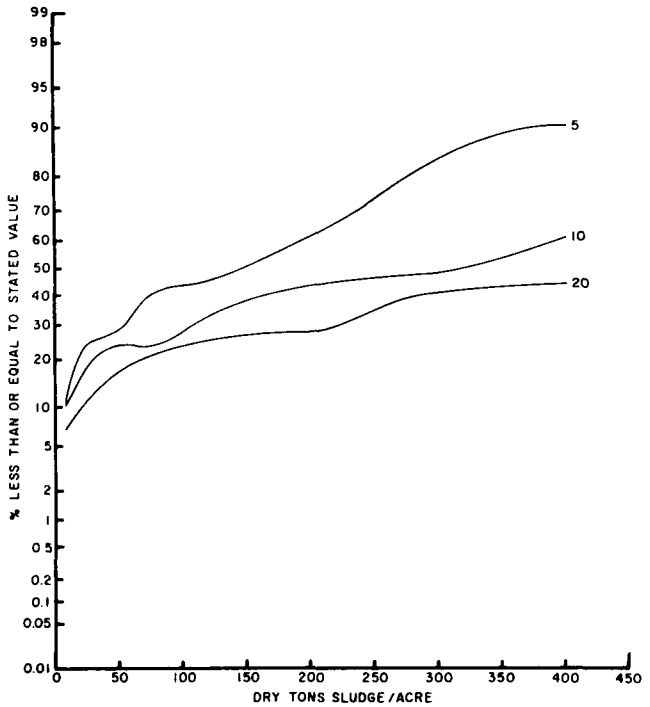

Figure 1: Cumulative Frequency Distribution for Sludge Loading Necessary to Achieve 5, 10, and 20 kg Cd/ha—Illinois

Zenz et al.[23] also presented data on the heavy metal levels of sludges from five midwestern states and two eastern states of the United States. These data were collected by the North-Central Regional Agricultural Experiment Stations Committee on Utilization and Disposal of Municipal, Industrial and Agricultural Processing Wastes on Land. The seven states studied were Wisconsin, Michigan, Indiana, New Jersey, Minnesota, New Hampshire and Ohio.

Figure 2 contains a cumulative frequency graph of the allowable loadings for the sludges from these seven states for the USDA limitations of 5, 10, and 20 kg Cd/ha. In contrast to the Illinois data, 50% of the sludges from these seven states could not be applied at rates exceeding 30 dry tons of sludge to soils with a CEC of 5 meq/100 g over the life of the site. Even soils with CEC values of 20 would be restricted to total sludge applications of 120 dry tons or less for sludges from 50% of the cities in the States surveyed.

Table II contains a listing of the annual application rates permissible by the USDA regulations for liquid sludge (1 kg Cd/ha) and dewatered sludge (2 kg Cd/ha) for the seven States mentioned above. As can be seen, only two States could apply over 7 dry tons per acre of sludge to land in any given year. Again, since most crops will require about 10-20 dry tons of sludge to supply nitrogen needs, this limitation would virtually eliminate the option of land utilization.

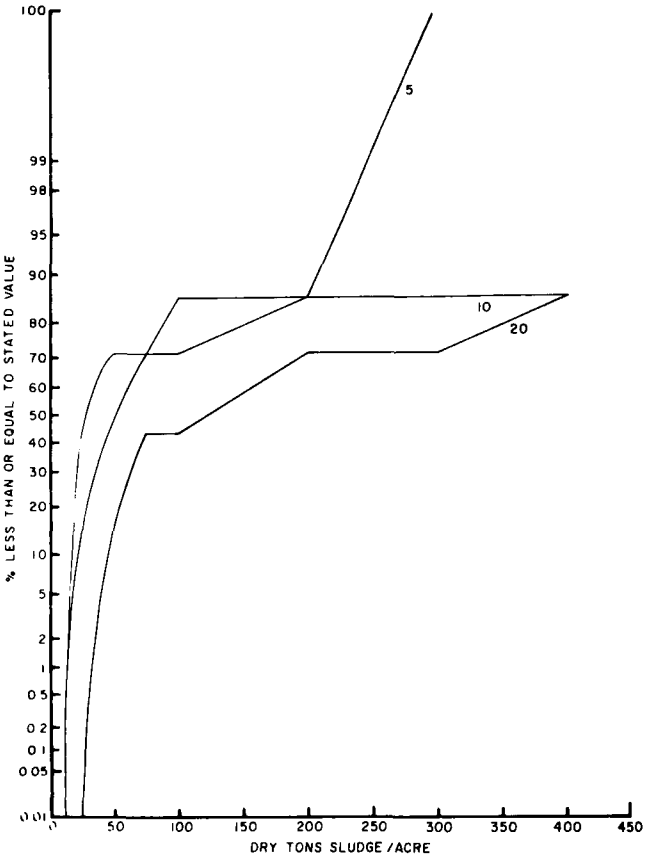

Figure 2: Cumulative Frequency Distribution for Sludge Loading Necessary to Achieve 5, 10, and 20 kg Cd/ha—Seven States

Table II: Effects of Sludge Application Limitations (dry tons/acre). Proposed by U.S.D.A. on the Annual Application Rates of Seven States

STATE	Annual Sludge Application Limit* *Annual Loading Limit for Cadmium* 2 kg/ha	1 kg/ha
	-------dry tons per acre------	
Wisconsin	11.6	5.8
Michigan	5.48	2.8
New Jersey	30.4	15.2
New Hampshire	86.6	43.3
Indiana	5.5	2.74
Minnesota	13.8	6.91
Ohio	4.5	2.3

* To determine the life of a site, the CEC of the soil must be known. For example, if the soil has a CEC of 10 meq/100g and an annual application rate of 2 kg Cd/ha, the life of this site is 5 years.

Case Histories of Large-Scale and Long-Term Projects

While long-term data may not be readily available on many older projects for review and analysis, there is evidence that sludge utilization in agriculture has been practiced in the United States for many decades, particularly in the midwestern region. However, during the last decade, interest at the federal, state and local levels has generated several large-scale projects which have produced very valuable data. The following are brief summa-

ries of long-term projects, all of which are ongoing with the exception of that of the city of Dayton, Ohio.

Hanover Park Experimental Corn Plots

The most extensive demonstration study undertaken within Metropolitan Chicago is the MSDGC's Hanover Park experimental corn plots.

In 1968, a 7-acre field at the Hanover Park Water Reclamation Plant was selected for the development of experimental corn plots for furrow irrigation, the topsoil was stripped, the sub-soil graded to desired slope, and the topsoil was replaced.

Table III: Average Chemical Concentration of the Liquid Digested Sludge Applied at the Hanover Park Plots from 1968 to 1975 and at the Fulton County Site in 1975.

CONSTITUENT	HANOVER PARK	FULTON CO.
	% DRY BASIS	
KJELDAHL N	4.8	5.7
NH_3-N	2.8	2.5
P TOTAL	2.0	3.8
K	0.40	0.39
CA	3.4	2.8
MG	1.3	1.2
FE	2.0	4.7
ZN	0.075	0.39
MN	0.048	0.038
NI	0.022	0.042
CU	0.070	0.18
NA	0.46	0.23
PB	0.028	0.093
CR	0.026	0.38
CD	0.0056	0.030
HG (µG/G)	--	6.95

The soil is a disturbed Drummer silty clay loam with poor natural drainage. The original experimental design was a randomized block with five replications having grades of 0.5, 1.5, and 2.5% confounded in the replications.

Methods

Soil samples were taken in spring and were composites of 20 cores, 0-6 inches deep. The samples were air-dried and then analyzed for pH (Peech[17]) and electrical conductivity (Bower and Wilcox[2]); 1/3 bar moisture content (Richards[19]); organic carbon content (Allison[1]); cation exchange capacity and exchangeable K, Na, Ca, Mg (Chapman, 1965); 0.1*N* HCl extractable Zn, Cd, Cu, Cr, Fe, Ni, Pb, Mn, and Al (1:10 soil to 0.1*N* HCl solution); and available P (Olsen & Dean[16]).

Corn grain analysis for trace metal content began with the 1973 corn crop. Grain subsamples were taken during corn yield determinations. Grain was dry-ashed at 450°C, taken up in 0.1*N* HCl, and analyzed by atomic absorption spectroscopy.

Each spring the plots were plowed and harrowed. Ridges and furrows were formed parallel to field slope. Sludge was applied from gated irrigation pipes at the upper end of the plots and allowed to flow down the furrows.

The plots have been fertilized with sludge every year beginning in 1968. Sludge application has not been replicated according to the original design. Most of the sludge applied came directly from heated anaerobic digesters at the Hanover Park Water Reclamation Plant. In a few instances, lagooned digested sludge was also applied. The average analyses of the digested sludge applied is presented in Table III.

Effect of Sludge Application on Soil

Analyses of the soil samples in 1970, 1973, and 1975 are presented in Table IV. The control plot showed a depletion of some major nutrients and organic carbon over this time period. No nitrogen or phosphorus fertilizer has been applied to the control plots. Potash fertilizer was applied to all plots in 1968 and 1972–1975. There was no influence on soil pH from the sludge application.

Table IV: Chemical and Physical Properties of a Disturbed Drummer Silty Clay Loam Collected in 1970, 1973 and 1975 from the Hanover Park Experimental Corn Plots. These Plots have Received Liquid Sludge from 1968–1975.

Parameter	1970			1973			1975		
	Sludge Applied to Date (T/A)								
	0	15	25	0	37	62	0	52	91
pH	7.9	7.7	7.7	7.3	7.1	7.1	7.8	7.5	7.6
CEC meq/100g	33.4	34.0	32.2	33.9	33.7	33.3	31.4	34.5	32.3
1/3 bar H_2O %	38.0	38.0	36.8	32.2	33.1	32.2	32.0	34.7	33.8
C-organic %	3.08	3.21	3.15	2.61	3.37	3.33	2.66	3.35	3.01
P-available µg/g	N.A.*	N.A.	N.A.	9.8	51.5	79.8	31.3	102.9	113.9
Exchangeable									
K µg/g	138	158	153	126	149	126	106	122	117
Na µg/g	95	131	117	25	30	44	22	84	78
Ca µg/g	5440	5660	5530	5140	6300	5650	4300	4680	4590
Mg µg/g	1520	1600	1600	1660	1700	1690	1060	1100	1060
0.1 N HCl Extractable									
Fe µg/g	813	827	835	301	339	346	247	409	412
Mn µg/g	253	281	290	198	200	195	211	222	235
Zn µg/g	30.5	39.0	37.5	24.4	23.4	27.6	22.9	50.0	51.7
Cd µg/g	0.7	0.7	0.5	0.68	0.58	0.61	0.39	0.49	0.50
Cu µg/g	18.3	66.6	33.8	6.72	13.3	15.8	9.3	23.2	30.2
Cr µg/g	1.7	2.30	5.2	0.93	1.26	1.47	0.42	1.02	1.46
Ni µg/g	11.3	10.9	10.9	8.60	9.11	8.93	6.78	8.15	7.39
Pb µg/g	16.2	11.8	13.3	8.25	9.21	9.68	9.1	12.0	13.9

*NA = No Analysis

The 1975 soil analysis showed that Zn, Cd, Fe, available P, NO_2 + NO_3 = N, organic carbon, and 1/3 bar water holding capacity all increased with the increase in the levels of applied sludge. The level of NI and cation exchange capacity (CEC) indicates that if higher levels of sludge application were to be used that the NI and CEC level would not increase any further. The soil concentration of Cu, Pb and Cr increased with increased sludge application.

Effect of Sludge Application on Corn

Metal uptake in the grain was determined in the 1973 and 1975 crops. These data are presented in Table V.

The only significant increases in metal content in 1973 were with K and Ca. These increases occurred with the 52 T/A sludge application, and the reasons for these increases are not apparent. The 1975 grain crop showed significant increases in Zn, Cd, Cu, and Fe content with the addition of sludge. The Fe increase was linear in behavior for the sludge application rates used, while the Cu response appears to be approaching a maximum.

The Cd concentration of the grain grown in 1975 on the 85 and 110 T/A total sludge applications were 0.091 and 0.096 μg/g, respectively.

A survey conducted by Pietz, Peterson, Lue-Hing and Welch (Unpublished Data, 1976) on 15 corn fields located throughout Illinois, where all fields were fertilized with inorganic fertilizer, yielded a mean Cd concentration of 0.038 μg/g and a range of 0.001 to 0.294 μg/g in the grain. A summary of this survey is presented in Table VI. The concentrations of Zn, Cu, Cd and Fe at the Hanover Park farm were all within the range reported by Pietz et al.[18]

The corn yields in 1973 were 29, 78, and 99 bushels per acre for the 0, 52, and 79 T/A (accumulative) of sludge applications, respectively. In 1975 the corn yields were 49, 102, and 82 bushels per acre for 0, 85 and 110 T/A of sludge applications, respectively.

Using the USDA guidelines or the Wisconsin guidelines maximum lifetime allowable sludge application at the Hanover Park site is 89 dry T/A. This application limit is due to the Cd content of the sludge which was 56 μg/g dry sludge.

Table VI: Elemental Analysis of Corn Grain from Fifteen Locations in Illinois (243 Samples)

ELEMENT	MEAN ± SD†	RANGE		COEFFICIENT OF VARIATION
	..... µg/g			..... % .....
Ca	50.6 ± 8.4	33.3	98.5	16.6
Fe	20.3 ± 9.4	10.4	84.0	42.2
K	2,970 ± 954	1,930	4,000	32.1
Mg	1,080 ± 105	617	1,480	9.77
Mn	5.60 ± 1.01	2.00	9.26	18.1
Na	7.80 ± 5.44	1.24	35.5	69.7
Cd	0.038 ± 0.030	0.001	- 0.294	81.3
Cr	0.087 ± 0.059	0.002	0.429	68.9
Cu	2.62 ± 0.88	1.32	6.31	33.5
Ni	0.87 ± 0.34	0.17	2.50	39.6
Pb	0.168 ± 0.065	0.033	0.519	38.5
Zn	19.6 ± 3.2	13.0	32.6	16.6

†STANDARD DEVIATION OF THE SAMPLE

Table V: Chemical Concentration of 1973 and 1975 Corn Grain Grown at the Hanover Park Experimental Corn Plots which Have Received Liquid Sludge from 1968-1975.

Sludge Applied to Date	Zn	Cd	Cu	Cr	Fe	Ni	Pb	K	Na	Ca	Mg	Mn
T/A	µg/g dry basis											
1973												
0	25.0	<0.5	1.74	0.77	39.2	<0.5	0.81	3030	26.2	57.9	1330	5.07
52	25.8	<0.5	2.01	0.76	34.4	<0.5	0.83	3600	27.2	70.6	1340	5.51
79	23.8	<0.5	1.70	0.71	36.9	<0.5	0.79	3158	32.1	55.0	1240	5.65
1975												
0	18.2*	0.067**	1.81**	0.076	23.6**	0.63	0.54	3260	9.71	61.4	1070	5.70
85	25.8	0.091	2.32	0.058	29.8	0.43	0.53	3490	2.78	57.8	1140	6.52
110	25.8	0.096	2.29	0.067	30.3	0.48	0.51	3380	3.39	54.2	1160	6.52

*Values in a column are significant at the 0.05 level of probability for that year.
**Values in a column are significant at the 0.01 level of probability for that year.

Dayton, Ohio Sewage Treatment Plant Farm

At Dayton, Ohio, the sewage sludge has been spread on Warsaw silt loam for 35 years. The annual sludge application rate has been calculated at 28 metric tons/ha (12.5 T/A). A study of the trace metals in the corn grown on this land was conducted by Kirkham[12] in 1973. She reported the total concentration of metals in the 0-30 centimeters depth of soil was increased by the following factors: Cd, 35; Cu, 16.5; Ni, 2; Pb, 16.5; and Zn, 13. Even with these large increases in the metals present in the soil, these metals did not accumulate appreciably in the corn plants when compared to unsludged corn plants. For example, the Cd content of corn grains was 0.9 and 0.8 ppm dry wt. for sludge-grown and control corn, respectively.

The Dayton, Ohio, sludge contained from 800-830 mg Cd/kg, 4,100-6,020 mg Cu/kg, 400 mg Ni/kg, 4,000-6,940 mg Pb/kg, and 8,390-10,500 mg Zn/kg dry wt. basis. This calculates to a total 35 year per hectare application of approximately 780 kg Cd, 4,020 kg Cu, 390 kg Ni, 3,800 kg Pb, and 8,200 kg Zn.

These loadings for Cu, Ni, Pb, and Zn, as reported by Kirkham, are about 40-50 times higher, and loadings of Cd about 100 times higher than those proposed by Chaney in 1973. However, it is clear that the Cd uptake in the sludge amended corn grain is very small. Using the Wisconsin guidelines where the total sludge application is limited by the lifetime maximum of 20 lb Cd/A (22.4 kg/ha). The Dayton sludge which contained 0.8 kg Cd/metric ton of solids would be limited in Wisconsin to a lifetime application of 28 metric tons/ha (12.5 T/A), or field operational life of 1 year per field.

Kirkham estimated the total application at Dayton, Ohio, to be 980 metric tons/ha over the 35 year period of record.

University of Illinois Experimental Field Plots—Soybeans

Except for the 1975 data, most of the results reported in Table VII were presented previously by Hinesly et al.[9] By regression analyses they concluded that sludge-borne Cd incorporated into soil just prior to planting soybeans was more efficiently assimilated than sludge-borne Cd applied in years previous to the crop year. Results of their analyses suggested that if annual sludge applications were terminated, Cd contents in plant tissues would be drastically reduced. To further test the hypothesis, annual sludge applications were continued on one-half and terminated on the other half of split plots, beginning in 1973. Another reason for making the split was because soybeans growing on maximum sludge-treated plots had suffered from P toxicity in 1972. The P toxicity was not observed in 1973, when sludge was not applied to any plots after 2 applications in the early part of the 1972 growing season until after harvesting operations in 1973. In 1974, on split-plots where maximum sludge applications were resumed in 1973, soybeans had a Cd content of 0.92 μg/g as compared to 0.35 μg/g in soybeans grown on plots where no further applications were made. Also, it may be noted that where sludge applications were terminated, Cd contents of soybeans from plots previously treated with 1/4-maximum sludge applications were not significantly different from Cd contents in soybeans from control plots. In 1975, Cd contents of soybeans from plots where sludge applications were terminated were similar to those of soybeans in 1974. But in 1975, Cd contents in beans from previously treated 1/4-maximum and 1/2-maximum treated plots were not significantly different from contents of soybeans from control plots. Soybeans growing on

Table VII: Mean Dry Weight Cd Contents of Soil Samples from 0- to 6-Inch Depths and Soybean Samples Collected from Blount Silt Loam Plots[9]

		SLUDGE APPLICATION RATES (inches)						
YEAR	Cumm. Solids mt/ha	0	1/4	1/2		1		
		Cd µg/g Soil 0.1 N HCl Extractable						LSD
1969	43							
1970	102							
1971	237	<.10	2.94	8.11		13.33		2.29**
1972	242	0.19	3.63	9.53		15.24		1.43**
1973	255	0.16	3.86	8.51		13.66		1.38**
1974(A)	314	0.20	4.03	8.14		14.69		4.53**
1974(B)	255	0.15	4.43	8.74		14.13		4.45**
		SOYBEANS						
					Soil pH		Cumm. Cd kg/ha	
1970		.06	.32	.54	5.7	1.02	34.7	0.30**
1971		.27	.41	.90	5.4	1.55	58.5	0.30**
1972		.29	.49	.94	5.2	3.00	59.4	0.93**
1973		.18	.31	.55	5.8	0.75	62.0	0.13**
1974(A)		.31	.31	.57	6.0	0.92	77.6	0.39**
1974(B)		.13	.23	.35	6.1	0.35	62.0	0.15*
1975(A)		.07	.34	.72	6.0	1.69	89.2	0.31**
1975(B)		.12	.18	.34	6.3	0.46	62.0	0.29**

A--Sludge applications were resumed after harvest in 1973.
B--Sludge applications were suspended following one application in 1972.
*Significant at the 0.05 level of probability.
**Significant at the 0.01 level of prabability.

maximum sludge-treated plots in 1975 where application had been resumed, suffered from P toxicity again. Cadmium contents were highest in 1972 and 1975 in soybeans harvested from maximum sludge-treated plots where plant growth was adversely affected by P toxicity. Thus, it is concluded that Cd contents in soybeans will decrease with time after sludge applications have been terminated and that Cd contents will be increased in plants subjected to conditions adversely affecting growth.

University of Illinois Experimental Field Plots—Corn

Except for the 1975 results, all of the data presented in Table VII were previously reported by Hinesly et al.[10] Regressing Cd contents of corn grain on annual and accumulative sludge-borne Cd applications, they concluded that application just prior to planting the crop was the main determinant of Cd levels in corn grain. However, even in the absence of results from regression analyses, an examination of the data presented in Table VIII shows that Cd levels in corn grain varied with the amount of sludge-borne Cd applied by furrow irrigation during the previous growing season and incorporated just prior to the crop year of interest. On a per unit basis of annually applied sludge-borne Cd, levels of the metal in corn grain remained fairly constant regardless of amounts incorporated by spring plowing in years previous to a particular crop year. These data suggest that if Cd levels in grain are within acceptable concentrations for a particular annual loading rate of sludge-borne Cd, the situation will not change with accumulative years of sludge applications.

From both the soybean and corn data presented in Tables VII and VIII, it appears that availability of Cd is considerably more important in determining levels in plant tissues than soil pH. Availability of sludge-borne Cd for assimilation by plants is greatest immediately after incorporation into soils and then decreases with time.

These data from Hanover Park, Illinois; Dayton, Ohio; and the University of Illinois prove that the type of restrictions being proposed on heavy metals and on Cd in particular are not necessary. Bodman and Baker (1975) presented evidence that the Cd in the sewage sludge was not readily available to soybean and corn leaves or grain. They also found that the Zn:Cd ratio increased over the check plot with the use of 10 dry T/A/yr of sewage sludge, and they concluded that the Zn:Cd ratio did not provide a reliable index for evaluating the suitability of a sludge for application on cropland. Bodman and Baker did get increased metal concentrations of Zn and Cd in the leaves and grain of corn and soybeans, if the soil was treated with the 10 T/A sludge equivalent level of a Zn- or Cd-salt. Thus showing the higher availability when metals are applied directly as salts rather than in combined forms such as sewage or sludge.

Alternatives to Empirical Sludge Equations—Industrial Waste Control

A very effective way to reduce the level of metals contained in municipal sewage sludges is to limit the industrial input of metals at the source; namely, at the point where industry discharges into the sewer system. While industrial waste control

Table VIII: Mean Dry Weight Cd Contents of Soil Samples from 0- to 6-Inch Depths and Corn Grain Samples Collected from Blount Silt Loam Plots[10]

		SLUDGE APPLICATION RATES (inches)						
YEAR		0	1/4	1/2		1		
		Cd µg/g						
		Soil 0.1 N HCl Extractable						LSD
1971		<0.25	1.3	3.6		6.8		4.0**
1972		0.27	3.1	4.7		12.1		3.3**
1973		0.29	3.3	6.7		12.9		3.6**
1974		0.58	3.8	7.3		16.4		4.9**
		CORN GRAIN						
	Cumm. Solids mt/ha				Soil pH		Cumm. Cd kg/ha	
1970	152.5	0.30	0.60	0.79	4.9	1.00	48	0.20**
1971	280.9	0.14	0.70	0.65	5.2	0.92	77	0.40**
1972	306.5	0.14	0.45	0.83	5.0	1.10	81	0.52**
1973	368.6	0.08	0.15	0.35	5.3	0.61	88	0.06**
1974	417.4	0.09	0.18	0.40	6.2	0.81	101	0.22**
1975	449.9	0.06	0.17	0.28	6.6	0.51	108	0.08**

A--Sludge applications were resumed after harvest in 1973.
**Significant at the 0.01 level of probability.

has been shown to be effective, it may be emphasized here that metals including cadmium and mercury will always be present in sewage sludges as a result of their natural content in food and human wastes, and from surface runoff, etc.

A successful case in point is the experience of the Metropolitan Sanitary District of Greater Chicago, where an industrial waste control ordinance has been in effect since 1969. To evaluate the effects of this ordinance, the metal content of anaerobically digested sludges from the Calumet plant which were placed in storage lagoons before 1969 were compared with sludges from this same plant through the summer of 1974, as shown in Table IX. It is clear from the data that the metal content of the sludge was lower after passage of the ordinance than before. The concentrations of metals of greatest environmental concern (nickel, copper, lead, and cadmium) were reduced in the digested sludges by 92, 81, 73, and 72%, respectively, during the period from 1969 to 1974. Data for 1976 are similar to those for 1974, which indicates that industrial waste control has reached its limits of effectiveness for this plant with respect to sludge metals levels.

Although an industrial waste control program can effect substantial reductions in the metal content of sludges in industrial areas, it must be emphasized that each sewage treatment plant or the area served by one has an indigenous concentration for all metals which may not be further reduced by more stringent industrial pretreatment. For example, Chicago's industrial waste control ordinance has had no appreciable effect on the metal content of sludge from the Hanover Park plant, which is subject to the same ordinance and which serves a nonindustrial area. Digested sludges from this plant had a cadmium content of 60 ppm in 1969 and 56 ppm in 1975. The cadmium content of the Hanover Park sludge before and after the 1969 ordinance is similar to that of the Calumet sludge in 1974.

A successful industrial pretreatment program implies the existence of effective monitoring and enforcement procedures. In view of the political ramifications of these procedures, the effectiveness of an industrial pretreatment program cannot be generalized from one area to another until such time that the commitment becomes national.

Genetic Modification

There is ample data that the soil-root barrier restricts the passage of metals into the leaves, stems and reproductive parts of plants; and that metals taken up by roots accumulate preferentially in the stems and leaves rather than being translocated to the fruits or grains as is typified by the cereals. These natural characteristics of the cereal plants, particularly corn with its high nitrogen demand, makes it a prime candidate for possible genetic modification of hybrids to reduce the accumulation of metals in the grain.

This type of plant genetics research is currently being conducted at the University of Illinois. Preliminary results of greenhouse studies using 6 inbred lines and 2 crosses of corn have indicated that some lines are capable of greatly reducing the Cd uptake to the grain.

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Table IX: Effect of Industrial Waste Control Ordinance on Metals Content of the Calumet Sewage Treatment Plant's Sludge

METAL	MAX. LIMIT BY ORDINANCE	SLUDGE SOURCE			METAL REDUCTION BEFORE 1969/1974	
		LAGOONS BEFORE 1969*	ANAEROBIC DIGESTER 1972†	1974±	RATIO	PERCENTAGE
	mg/ℓ	·····*μg/g dry weight basis*·····				
Cd	2.0	190	100	54	3.51	72
Cr (Tot.)	25.0	2100	1100	790	2.66	62
Cu	3.0	1500	900	282	5.32	81
Fe	50.0	53700	36800	24200	2.22	55
Hg	0.0005	3.3	3.0	2.15	1.53	34
Ni	10.0	1000	290	77	12.99	92
Pb	0.5	1300	1800	486	3.70	73
Zn	15.0	5500	3500	2800	1.96	49

*Mean of 10 samples from the MSDGC Calumet Sewage Treatment Plant sludge lagoon

†Mean of 22 samples from June to October 1972 (Peterson, Lue-Hing, and Zenz, 1973)

±Mean of 6 samples from the MSDGC Calumet Sewage Treatment Plant anaerobic digesters from June to October 1974

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General Technology on Soil-Salt Chemistry and Saline Subsurface Irrigation Return Flows

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INTRODUCTION

There has been considerable interest in recent years regarding water quality problems resulting from irrigated agriculture. Most everyone involved with agriculture in the West is keenly aware of EPA's efforts to include irrigation return flows in the permit program under the National Pollutant Discharge Elimination System (NPDES).

This paper discusses the most prevalent water quality problem resulting from irrigation—namely salinity—which results from subsurface irrigation return flows. These subsurface flows, consisting of seepage losses from canals and laterals along with deep percolation losses from over-irrigation of croplands, result in increased ground-water salinity concentrations which frequently reach downstream river channels. Generally, subsurface saline irrigation return flows must be considered as a non-point source of pollution.

That portion of the water supply which has been diverted for irrigation but lost by evapotranspiration (consumed) is essentially salt-free. Therefore, the irrigation return flow will contain most of the salts originally in the water supply. The surface irrigation return flows will usually contain only slightly higher salt concentrations than the original water supply. Thus, the water percolating through the soil profile contains the majority of salt left behind by the water returned to the atmosphere as vapor through the phenomena of evaporation and transpiration. Consequently, the percolating soil water contains a higher concentration of salts. This is referred to as the "concentrating" effect.

As the water moves through the soil profile, it may pick up additional salts by dissolution. In addition, some salts may be precipitated in the soil, while there will be an exchange between some salt ions in the water and in the soil. The salts picked up by the water in addition to the salts which were in the water applied to the land are termed salt "pickup." The total salt load is the sum of the original mass of salt in the applied water as the result of the concentrating effect plus the salt pickup.

The *most significant improvements* in reducing downstream salinity problems will potentially come *from improved on-farm water management.* This will be particularly true for areas containing large quantities of natural pollutants, such as salts, in the soil profile. In such situations, the *key is to minimize* the *subsurface return flows,* thereby minimizing the quantity of salt pickup. Poor irrigation practices on the farm are the primary cause of overly large water diversions, as well as being the primary source of present return flow quality problems. Due to the nature of irrigated agriculture, whereby salts must be leached from the root zone, an optimum solution will, in most cases, require improvements in on-farm water management.

A term frequently used to characterize irrigated agriculture is "site specific", which means that each irrigated area has its own unique physical characteristics, that in turn require a unique set of solutions for alleviating the irrigation return flow quality problems peculiar to that area. In order to arrive at the unique set of technological solutions to reducing salt loads from a particular irrigated area requires a process of: (a) using an inflow-outflow analysis to determine if there is a salinity problem, and if so, its magnitude; (b) determining the sources of salinity by developing a hydro-salinity model of the area; (c) determining the soil chemistry characteristics of the area including the development of a predictive soil chemistry model; (d) developing cost-effectiveness relationships for a variety of technological alternatives, as well as combinations of appropriate technologies; and (e) assessing the cost-effectiveness relationships in an optimizational format in order to arrive at the least cost combination for achieving a desired salinity reduction.

Inflow-Outflow Analysis

An inflow-outflow analysis is usually the first step in analyzing water management and salinity problems. A schematic example of irrigated tracts is shown in Figure 1 wherein an inflow-outflow analysis is represented by the difference in the two stream gaging stations, A and B. The well-known hydrologic equation,

$$I - O = \Delta S \qquad (1)$$

where I is the inflow, O is the outflow, and Δ S is the change in storage, can be used.

Representing the volume of salts passing Stream Gaging Station A over any desired period of time as A_s,

$$A_s - B_s - \Delta S \qquad (2)$$

Initially, the analysis is undertaken using annual data over the time length of available data for the two stream gaging stations. (A word of caution—unmeasured subsurface flows underneath the two stream gaging stations could have a significant effect on

the analysis.) If ΔS is positive, then salts are being accumulated in the soil profile of the irrigated lands. If $\Delta S = O$, a salt balance is being maintained. A long-term (e.g., 10, 20 . . . 50 years) salt balance is necessary for irrigated lands in order to maintain agricultural productivity.

If ΔS is negative in Eq. 2 ($B_s > A_s$), then salt pickup is occurring and the difficulty comes in determining the source of this salt pickup. Also, this would indicate that at least the shallow groundwater flows would be expected to be highly saline. A long-term annual time history of salt pickup will disclose (provided sufficient data are available) whether or not the salt pickup rate is increasing, remaining fairly constant, or declining. A declining salt pickup rate indicates that the natural salts in the soil profile (either irrigated lands or watershed lands) are being taken into solution and conveyed into the groundwater reservoir, and then returned to the river. A relatively constant salt pickup rate indicates a large source of salts in comparison with the amount of water percolating through the soil profile and moving through the groundwater reservoir; however, additional analysis (e.g., hydro-salinity modeling) will be required to determine how much of this salt pickup is the result of irrigated agriculture and how much occurs from natural runoff. Also, mineralized springs could be a significant contributor of salts. An increasing salt pickup rate indicates man-made activities (e.g., increasing irrigated acreages or poorer water management on existing irrigated lands).

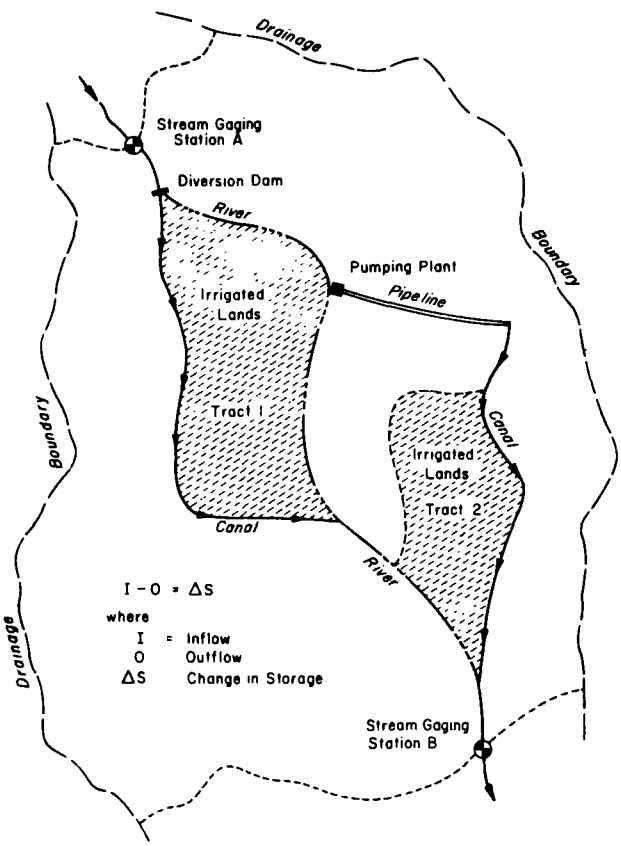

Figure 1: Schematic Example of Inflow-Outflow Analysis

The schematic in Figure 1 shows two tracts of irrigated lands. Thus, an inflow-outflow analysis between stream gaging stations A and B does not yield any information regarding the differences between the two tracts. The installation of an additional stream gaging station on the river between the two tracts may allow an inflow-outflow analysis which has only one tract of irrigated land inside the natural surface boundary, but this depends upon the geology and its effects upon subsurface return flows.

An *inflow-outflow analysis* is primarily useful for identifying which areas are contributing salts to a river, or whether or not an area is maintaining a salt balance. This analysis *will not provide* the *solutions* to indicated problems, but will disclose which areas require additional study in order to arrive at necessary technological solutions.

Hydro-Salinity Model

Salinity problems from irrigated agriculture are the result of subsurface return flows. Therefore, it becomes highly important to model subsurface, or groundwater, flows. The capability of a *hydro-salinity model* to provide the necessary information for arriving at technological solutions is *highly dependent* upon the accuracy of the *ground-water* field *data* and *analysis.*

A difficulty often encountered while preparing water and salt budgets is the variability in the accuracy and reliability with which the hydrologic and salinity parameters are measured. Usually, the measurement precision varies with the scope of the investigation and the area of the study.

Since the hydrologic system is difficult to monitor and predict, it is impractical to expect models to operate without applying some adjustments in order that all components will be in balance. In short, the budgeting procedure is usually the adjustment of the segments in the water and salt flows according to a weighting of the most reliable data until all parameters represent the closest approximation of the area that can be achieved with the input data being used. The vast and lengthy computation procedure of calculating budgets is facilitated by a mathematical model programmed for a digital computer. A schematic diagram of a general hydro-salinity model is shown in Figure 2.

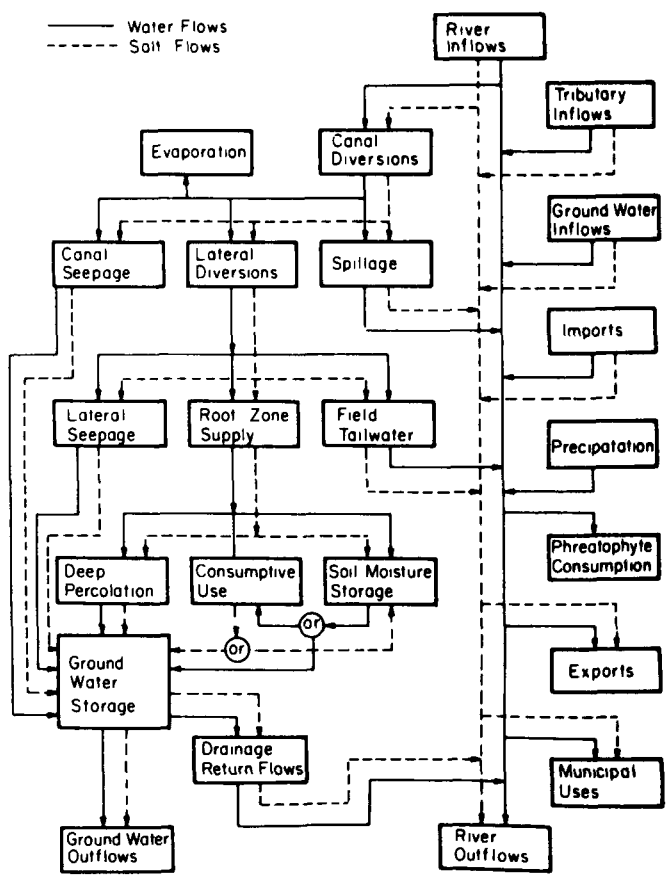

Figure 2: Schematic of Generalized Hydro-Salinity Model

The model was developed in three general sections:

1. All diversions from the canals through small turnouts into the lateral network are distributed onto the farmland after taking into account lateral seepage losses;
2. Flow within the root zone including evapotranspiration, tailwater runoff, and deep percolation losses; and
3. Groundwater return flows resulting from seepage and deep percolation return to the river system with their salt loads through both surface and subsurface drainage routes.

The details of the computer program are listed by Walker.[3] (Note that the hydro-salinity model between sections 2 and 3 does not make any computations between the root zone and the underlying groundwater, which must be analyzed using the soil chemistry modeling techniques that will be discussed later.)

The mathematical model attempts to simulate the hydrologic conditions of an agricultural system. The concepts are general and can be extended to many areas with some modifications likely required for each area. The program is written in individual but interconnected subroutines that provide a measure of flexibility during operations by separating the calculation phase from either input or output phases. Thus, several of the subroutines become optional if their functions can be replaced by input data, or if certain outputs are not desired.

The main portion of the program is used to read necessary input data and to control the order of water and salt budget calculations. There are certain advantages in separating the input, output and computational stages of a program including:

1. Input order is not important as the data are completely available at all stages of computation.
2. Variable sets of data can be utilized in the model when several budgets are desired, or when some form of integration is desired. This is especially useful when an area can be broken down into smaller dependent areas (e.g., Tracts 1 and 2 in Figure 1).
3. The functions of the subroutines are independent of input, thereby making each subroutine a unit that can be implemented in other programs.
4. Corrections and adjustments are easily made without detailed consideration to other segments of the program.

In controlling the computational order of the program, the main program separates the calculation of the water and salt budgets. Consequently, the modeling procedure involves only the water phase of the flow system. This is possible when sufficient field data have been collected. Once the water flow system has been simulated, the individual flows are multiplied by measured salinity concentrations and converted to units of tons per month. At this point in the formation of the budgets, careful attention must be given to the salt flow system since irregularities may be present, thereby necessitating further model adjustments. Thus, when the final budgets have been generated, the salt system, groundwater system, and surface flow system must be reasonably coordinated and additional reliability is assured.

Soil Chemistry Modeling

The hydro-salinity model describes the present situation in an agricultural area regarding water and salt flows. However, the only method for predicting the reduction in salts returning to the groundwater and river through implementation of any salinity control measure(s) is by assuming a one-to-one relationship between water (reduction in subsurface return flows) and salt pickup. That is, if the subsurface return flow is reduced by 50%, the salt pickup is also reduced by 50%.

The primary objective is to model the transport of salts through the soils. (See Ayars[1] for a more thorough discussion.) The first portion of the flow of water and consequent transport of salts is through the root zone, which is usually a zone of partial saturation. A numerical model of the moisture flow and chemical and biological reactions occurring in the root zone has been developed by Dutt, et al.[2] (This reference contains a complete listing of the computer program.) This is the basic model which will be used to describe salt transport.

The model consists of three separate programs. The first program describes the soil moisture movement and distribution with time. The second program interfaces the soil moisture movements with the chemical-biological model. This is needed because the horizons used in the calculations of soil moisture and chemistry differ. The third program computes the chemical and biological activity occurring in the soil profile. Figure 3 is a block diagram of the overall model. A brief description of the moisture flow and chemical-biological models is included to serve as a basis for understanding the data collection requirements.

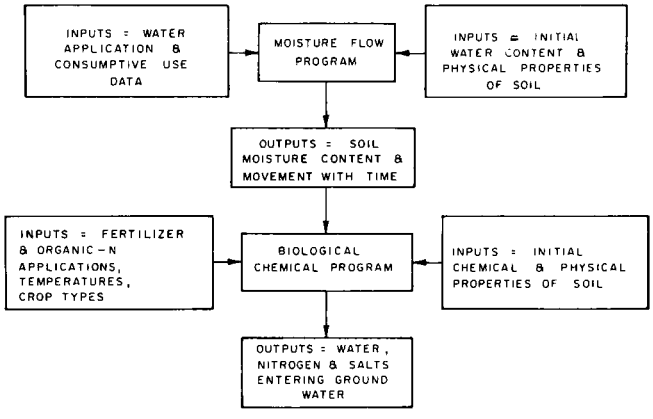

Figure 3: Generalized Block Diagram of the Model

The flow is one dimensional and was developed using the Richards equation with a sink term. Schematically, the model is given in Figure 4. Mathematically, the flow is described using Richards equation in the form:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left(\frac{D\partial \theta}{\partial x} - K\right) - S \qquad (3)$$

where

θ = volumetric water content

t = time

x = length

K = hydraulic conductivity

S = sink term

D = diffusivity

This is the diffusivity form of the equation which means that only flow in the partially saturated zone of the soil profile can be described. The sink term, S, is computed using the Blaney-Criddle equations for evapotranspiration (other equations could be adapted to the model) with the loss due to evapotranspiration being distributed through the soil profile by assuming a specific root distribution for the crop. The root distribution and coefficients for the Blaney-Criddle equations are supplied by the user. Actual values of evapotranspiration can be used in the sink term when they are known.

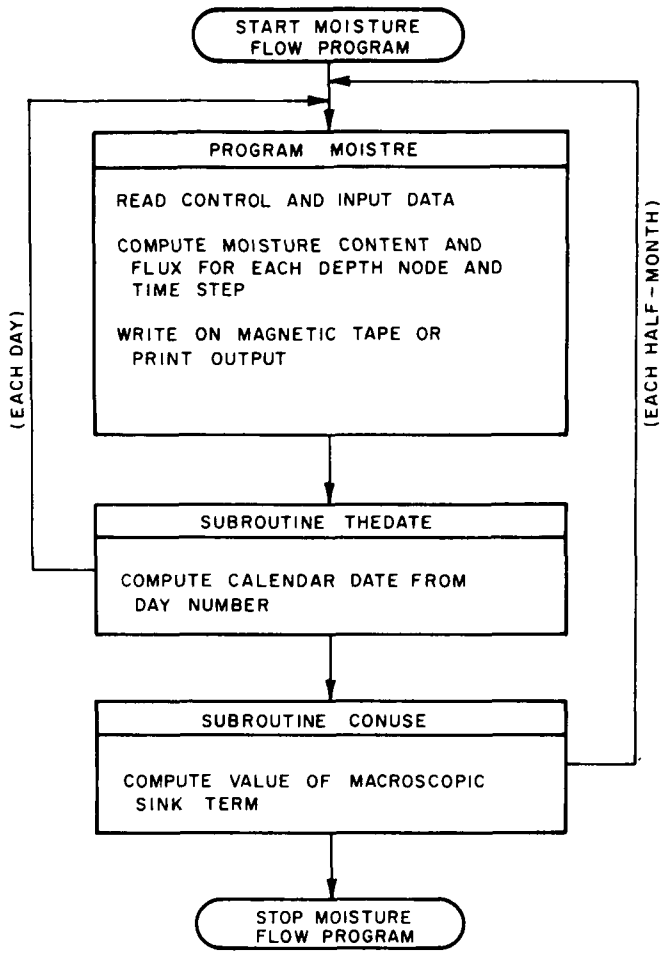

Figure 4: Generalized Block Diagram of Moisture Flow Program

Salt transport is described by the following equation in one dimension.

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left(D\frac{\partial c}{\partial z}\right) - \nu\frac{c}{z} \qquad (4)$$

where

c = solute concentration

t = time

D = dispersion coefficient

z = depth

ν = flux or darcy velocity

By assuming the term $\partial/\partial z$ (D $\partial c/\partial z$) is negligible compared to ν $\partial c/\partial z$ the equation reduces to $\partial c/\partial t = -\nu\ \partial c/\partial z$. This assumption implies that transport due to dispersion in partially saturated soils is negligible compared to the convective transport which occurs. This is generally a good assumption.

The model computes the moisture flow (ν) and couples the flow with the chemical changes $\partial c/\partial z$ computed in the biological-chemical program to give the salt transport. This technique is the basis for the mixing cell concept.

The chemical exchange model computes the equilibrium chemistry concentrations for calcium, magnesium, gypsum, sodium, bicarbonates, carbonates, chlorides, and sulfates. The nitrogen chemistry including ammonium, nitrates, and urea-nitrogen uses a kinetic instead of an equilibrium approach. The kinetic approach is needed since microbial activity involved in nitrogen transformation occurs over a period of weeks and days instead of minutes and seconds. The equilibrium chemistry for inorganic salts is a good approximation since the reactions describing their chemistry occur in a matter of minutes or seconds in a flow regime which is changing very slowly. A block diagram of the biological-chemical model is given in Figure 5. A block diagram illustrating the chemical reactions that are considered in one of the subroutines is shown in Figure 6.

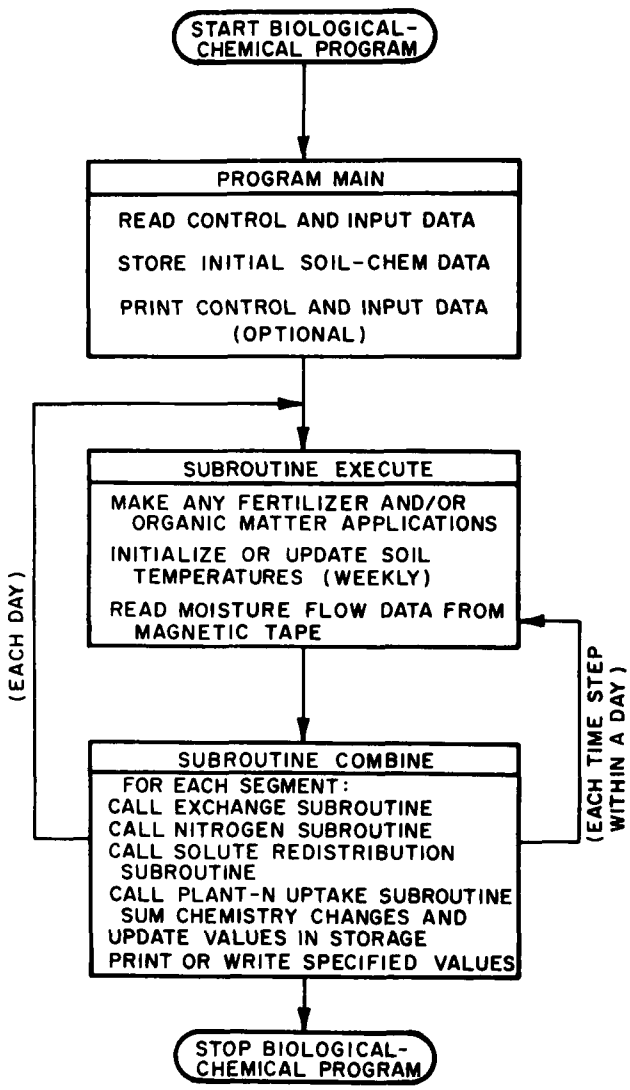

Figure 5: Generalized Block Diagram of Biological-Chemical Program

Once the necessary field data have been collected, equations can be developed to predict the variation in chemical quality (including ionic constituents) of the moisture movement through the soil profile, as well as the salt pickup (or salt precipitation) resulting from movement of subsurface irrigation return flows. These results, when combined with the hydro-salinity model, will allow an evaluation of various salinity control measures upon salinity reaching the groundwater and returning to the river.

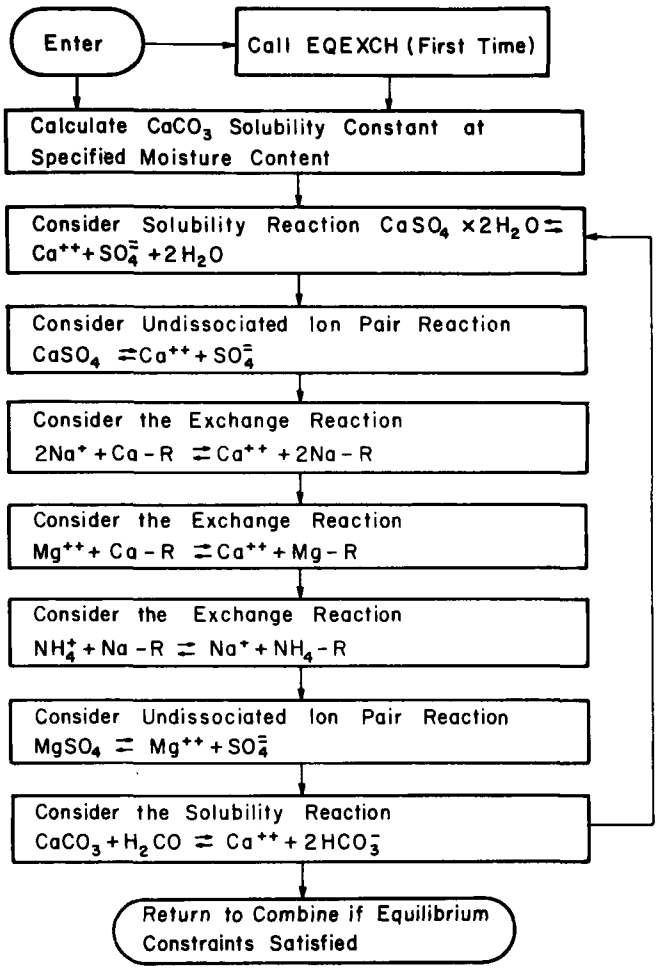

Figure 6: Generalized Block Diagram of Subroutine Exchange

Cost-Effectiveness of Technological Solutions

The results from the hydro-salinity model will provide considerable insight as to which technologies might be most appropriate in order to reduce subsurface return flows (since salinity is a problem associated with subsurface return flows). The goal in reducing subsurface return flows might be: (a) to lower groundwater levels in order to alleviate waterlogging, thereby allowing the leaching of salts in the root zone, which in turn facilitates increased crop production; (b) reducing downstream water quality degradation resulting from salt pickup; (c) improved on-farm water management to increase crop production; or (d) any combination of the above three goals.

Field studies must be undertaken to evaluate the effectiveness of any particular technology, or combination of technologies, in achieving the desired goal(s). An example will be used to illustrate the development of cost-effectiveness functions. If seepage loss measurements are made along many sections of each canal in an irrigated area, there will usually be a considerable variation in seepage loss rates. If the cost of canal lining is compared with seepage loss reduction, then the greater benefits accrue by first lining those sections of canal which have the least cost per unit of seepage loss reduction. Finally, the last sections of canal lining may be quite costly per unit of seepage loss reduction. This concept is illustrated in Figure 7a. The maximum seepage loss reduction shown on the ordinate in Figure 7a represents the total seepage loss from all canals; but, since canal linings still have some seepage losses, there will still be some seepage losses after lining all canals. The lowering of groundwater levels resulting from canal lining is illustrated in Figure 7b. In order to compute the downstream salt load reduction resulting from various levels of seepage loss reduction, the chemical-biological model described in the previous section must be utilized. This same model can be utilized to determine the reduction in ionic constituents making up the total salt load reduction, thereby allowing the prediction of downstream ionic chemical quality. The analysis could be carried forward another step if data are available regarding the effect of groundwater levels on production of various crops.

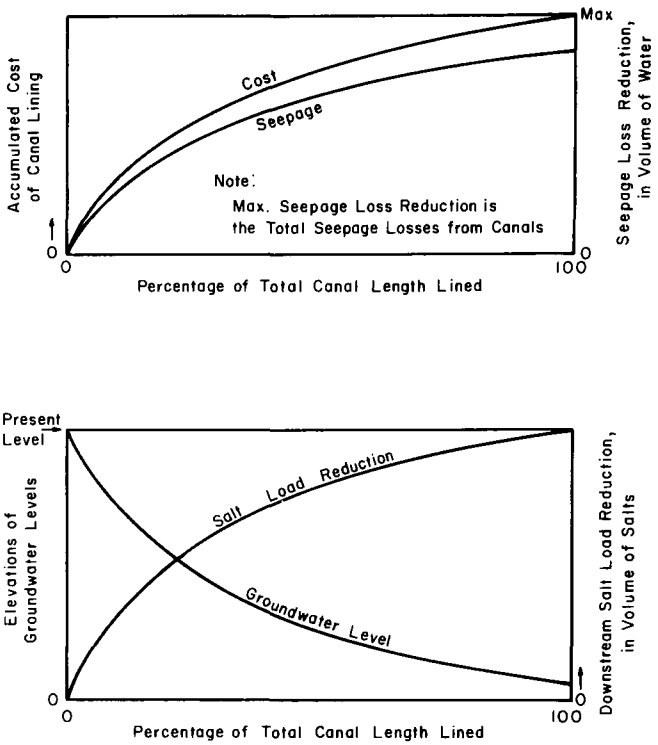

Figure 7: Illustrative Example of Development of Cost-Effectiveness Function for Canal Lining

The above example illustrates one of the simpler technologies for developing a cost-effectiveness function. Lateral lining becomes somewhat more complex because of the combined effects of seepage loss reduction and providing water control, which may be highly effective in improving irrigation application efficiencies, which in turn reduces deep percolation losses and increases crop production. The addition of flow measuring devices at all junctions in laterals, as well as at farm inlets, can prove highly effective in achieving improved water management. The development of improved on-farm water management technologies can require considerable field data collection. One of the most appropriate on-farm technologies is "tuning up" the present irrigation practices.

Cost-effectiveness functions should be developed for each appropriate technology that can be identified. Then, cost-effectiveness functions should be developed for each combination of appropriate technologies. These cost-effectiveness functions, which relate subsurface return flow reductions to the desired goal(s) resulting from a specified investment, would then be assessed in an optimizational format to arrive at the least cost combination for achieving a desired level of the stated goal(s). Thus, this analysis details the optimal strategy for implementing various levels of individual technological improvements into a comprehensive technology package. An example of such an analysis considering only the lining of farm head ditches, lining laterals, and lining specific canals in Grand Valley is shown in Figure 8.[4]

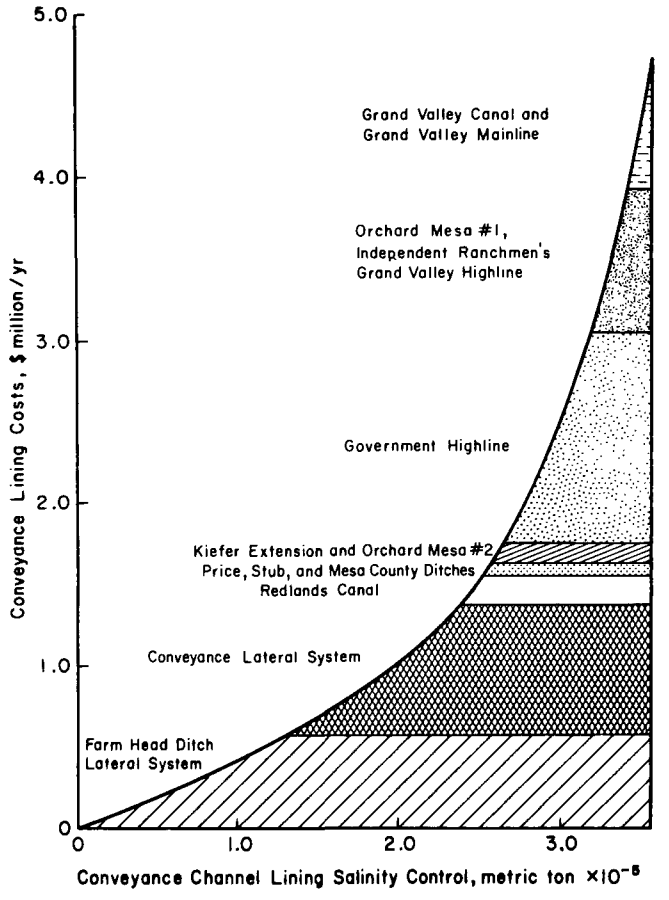

Figure 8: Optimal Conveyance Channel Lining Policy for Irrigation System in the Grand Valley, Colorado

CONCLUSIONS

Much emphasis will be given in the future towards improved irrigation water management to reduce downstream water quality degradation and minimize diversions in order to provide water supplies for new demands. In most cases, the key will be improved on-farm water management. However, technology alone will not usually bring about the necessary improvements. A combination of technological changes and institutional modifications will usually be required to effectively alleviate salinity problems resulting from irrigated agriculture.

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Tracing Leachate from Landfills A Conceptual Approach

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INTRODUCTION

Of the 60 million tons of fly ash produced annually in the United States, only about 8 percent is utilized. The other 55 million tons are discarded; 80 percent of the discarded material is being sluiced. Add to that the SO_2 scrubber sludge that is being and is expected to be generated and we are confronted with one of our biggest residual disposal problems. All of this material will be deposited in landfills, either by sluicing or dry placement. The environmental impact of such landfills is, therefore, a major concern. How to determine the potential impact of such residue before it is placed in a landfill is critical. A great deal of work is being done in this area and the purpose of this paper is to point out how some of the data that are being developed can be misleading and to offer a concept that we believe can better determine the true impact of landfilled residues.

There is nothing very profound or unique about the concept, but we offer it here because we find that some studies of stabilized materials are only partial analyses which lack detailed interpretation and explanation. The results are, therefore, misleading. Simply stated, the concept is to determine:

1. The physical characteristics of the material to be tested.
2. The method of placement and the character of the landfill.
3. The principal mechanisms for water movement through and around the material.
4. The laboratory tests that will best demonstrate the total mass transport of pollutants from the landfill to the water system.

For illustration, we will compare an unstabilized, sluiced SO_2 sludge and our stabilized material, Poz-O-Tec®, which we consider to be at the opposite ends of the spectrum. We acknowledge that there are many variations in between and that no two materials are identical but our purpose is to demonstrate principles, not to make specific comparisons. We have selected Poz-O-Tec because we have a greater knowledge of our own material and can discuss it more freely. However, we believe the concept is generally applicable and should be used to evaluate all landfilled materials.

The Poz-O-Tec Process

The Poz-O-Tec process, as shown in the diagram on Figure 1, is a method of stabilizing SO_2 sludge, fly ash and bottom ash with lime and other additives. The product is environmentally acceptable and its engineering properties can be controlled so that it is highly suitable for landfill, road embankments, mine reclamation, impermeable liners and other similar uses.

The complex pozzolanic reactions of the sludge, fly ash, lime and other additives produce cementitious materials which give Poz-O-Tec its exceptional physical properties and low permeability. These, coupled with precise moisture control, proper placement, compaction and good engineering practices result in a landfill with superior structural integrity which will virtually eliminate all of the environmental problems of the original materials: ash and sludge. However, it is not the purpose here to review the benefits of Poz-O-Tec or the polluting properties of ash and sludge, other papers have covered those subjects thoroughly. Rather, our purpose is to discuss how a completed landfill can and should be evaluated before the fact. How do you determine before placing 5 to 10 million tons of material in a landfill that it will not cause an environmental problem?

Part of our job at Conversion Systems, as suppliers of waste management systems, is to demonstrate to our customers and regulatory agencies that the stabilized material we produce, Poz-O-Tec, is environmentally acceptable, structurally sound and will be of value to them in the future. As in every business, we find part of this job simple and part complex and difficult. The easy part is where there are long established and accepted test methods to demonstrate specific properties. The difficult part is where:

1. There are no standards or established test procedures.
2. A multitude of people, including regulatory agencies and consultants, are testing materials, each with his own test method for determining a specific property without relating it to the final disposal method.
3. Comparisons are made between specific properties without regard to or recognition of the different nature of the materials.

To illustrate this problem, let us make a hypothetical comparison between our stabilized material and unstabilized sludge using the test procedures that we use regularly in our laboratory. A description of these procedures will be given later.

It is conceivable, depending on when the tests are run, that the results could be as follows:

Hypothetical Comparison

	Sludge	*Poz-O-Tec*
permeability	1×10^{-5}	1×10^{-5}*
leachate	3000 ppm	3000 ppm
runoff	1000 ppm	1000 ppm

In the face of such results, stabilization is a waste of time and money.

Those results say that the two materials are environmentally identical. But that conclusion is absolutely erroneous because

the data are incomplete and not related to the physical properties of the materials. A look at some of the properties of the two materials will indicate why the comparison is fallacious.

* Normal range: 5×10^{-6} to 1×10^{-7}

	Sludge	Poz-O-Tec
1.	Settled solids from slurry	Placed dry
2.	Saturated when placed	No surface water
3.	Continuous recharge	Requires years to saturate, probably never
4.	Permeates immediately and continuously	Will not permeate until saturated
5.	Thixotropic	Monolithic mass
6.	Unconfined compressive strength 0	Unconfined compressive strength—50 - 1000 psi
7.	Completed fill useless	Completed fill—valuable land

Obviously, the two materials will act differently in natural environment and the identical results from the initial laboratory tests require explanation and interpretation. The in vitro and in vivo conditions vary drastically and it is the latter with which we are concerned. A valid test program should be designed to evaluate actual field conditions and not for laboratory convenience.

Physical Properties

The demonstration of physical properties of a material, the first requisite of our concept, is straightforward and there are well estabished test methods to determine:

1. Unconfined compressive strength
2. California Bearing Ratio
3. Triaxial shear strength
4. Consolidation
5. Shear strength
6. Slope stability

There is no point in a detailed discussion of these test methods since they are readily available and we find them completely acceptable. We are, therefore, only presenting here comparative results for three different materials.

	Sluiced		*Stabilized*
	fly ash	*sludge*	*ash/sludge*
Unconfined Compressive Strength	0	0	50-1000psi
California Bearing Ratio	0	0	100
Consolidation	High	High	Incompressible

The physical and environmental properties of the Poz-O-Tec material improve with time as the pozzolanic reaction proceeds.

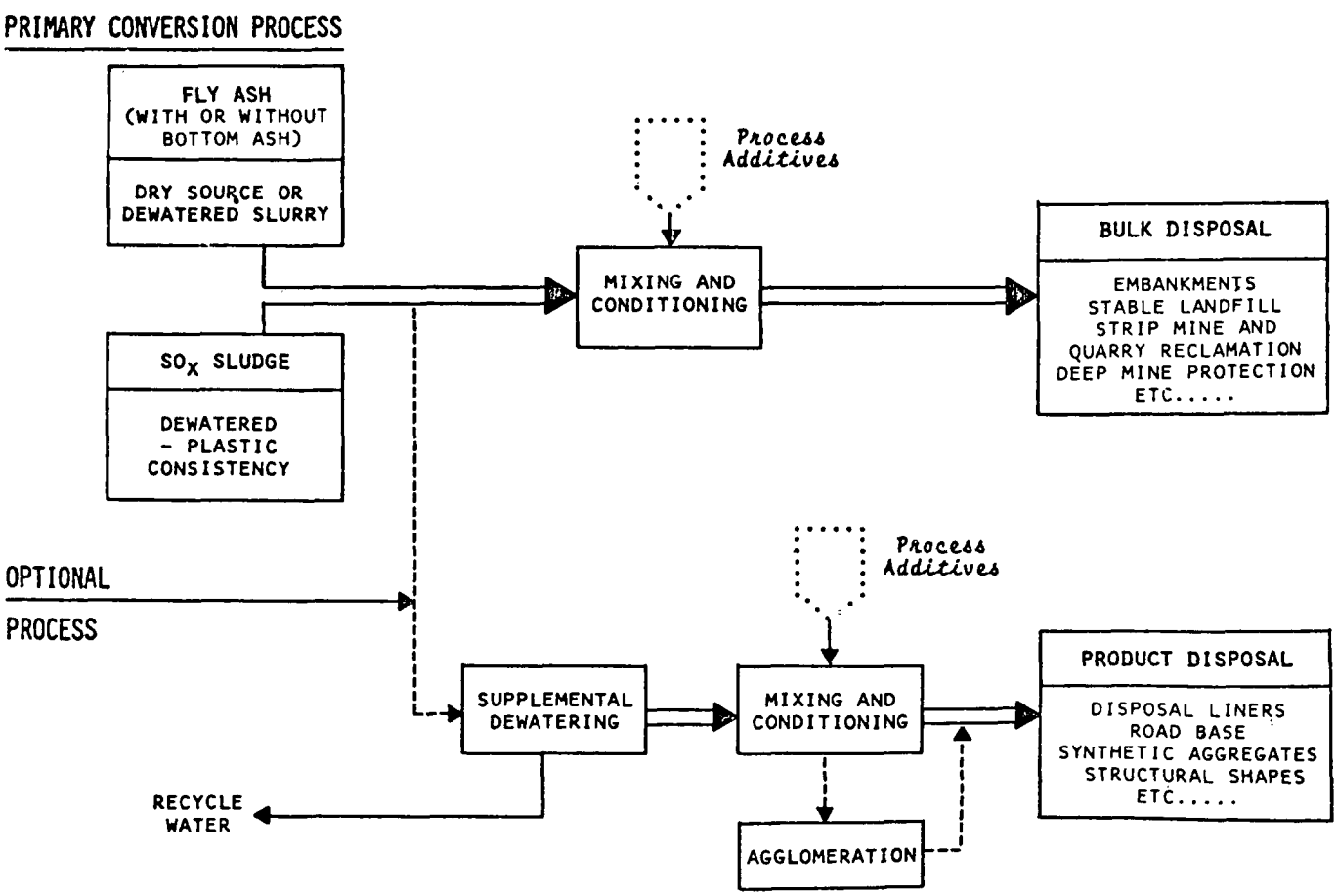

Figure 1: Schematic Diagram of IU Conversion System's Waste Conversion Process

The cementitious nature of the reactions produces a landfill that is monolithic in nature, of low permeability and is subject to leaching from the external surface only. All of the internal surfaces and, therefore, the mass of the potential pollutants are unavailable. Since it is the total mass transport of soluble salts that is of environmental concern and not the concentrations in initial leachate, our test procedures are designed to evaluate that long term mass transport.

Placement

The method of placement, our second requisite, is of extreme importance because it establishes some of the critical properties and conditions of the material and the nature of the completed landfill. A sluiced material, because of its nature, must be ponded. Since it is saturated, all of the internal surfaces are exposed and all of the soluble salts are available for leaching. The leachate will, therefore, always be at the solubility limit or maximum concentration. Untreated sludge will leach indefinitely. The duration of leaching from treated material will depend on the type of treatment. If an impermeable liner is used, you have, in effect, created a perched water table that must some day overflow and is exposed to the hazard of a ruptured liner. If not an immediate problem, it is a permanent potential for pollution.

The characteristics of a material that is placed dry will be entirely different and we cannot use the same parameters to evaluate both.

Mechanisms for Water Movement

Our third requisite is to determine which mechanisms of water movement, considering the type of material and method of placement, are likely to result in sufficient flow to cause a problem. There are six categories of water movement that theoretically could occur. They are hygrometric, capillary, thermal, freeze/thaw pumping, osmotic, gravitational and runoff.

Hygrometric Flow:

Hygrometric flow releases water vapor to the atmosphere as the result of differences in relative humidity. Since only distilled water is produced there is no transport of pollutants.

Capillary Flow:

Capillary action could cause flow of water from Poz-O-Tec to the ground if the ground is unsaturated and contains pores smaller than those of the landfilled material. That, generally means that the permeability of the soil must be below 1×10^{-7}. If so, the soil is impermeable and ground water pollution is unlikely.

Thermal Flow:

Thermal flow is dependent on a temperature gradient with vapor flow from the higher to lower temperature area; a condition that is unlikely to have any significant effect on a landfill.

Freeze/Thaw Pumping:

Freeze/thaw pumping occurs when water in the material expands as it freezes forcing it deeper into the material. When thawing occurs, the surface area is recharged setting the stage for a repetition of the cycle. This condition is easily controlled by proper cover on the completed fill area and expected to have little or no effect on the transport of salts from the fill.

Osmotic Flow:

Osmotic flow occurs when solutions of different concentrations come into contact with each other resulting in the flow of ions from the higher to lower concentration by diffusion. If ground water does contact the bottom of the fill material such flow will occur.

Gravitational Flow:

Gravitational flow or movement of water due to its own weight is considered to obey Darcy's law. As applied to soils, it quantifies flow and establishes permeability coefficients. Whether it can be applied directly, at hydraulic gradients close to one, is a matter of contention. Work done by the Russians indicates that at a permeability of 1×10^{-7}, a gradient of 20 is required to initiate flow. However, that is not a matter for discussion here.

For a sluiced sludge of relatively high permeability and constant recharge, the overriding mechanism is gravitational flow; assuming, of course, that there is no runoff or discharge and the supernatant is returned for transport of fresh material. The permeate will be at the saturation limits and the maximum concentrations of pollutants will be carried to the ground water.

For a material such as Poz-O-Tec, we must consider three conditions that could result in pollution of the water system: permeation, surface runoff and ground water contact.

Permeability:

Permeability by definition can only be measured when there is flow. To have flow, the material must be saturated in some areas, i.e., some of the channels through the pores of the material must be completely filled with water so that pressure exerted at the top by recharge will result in flow from the bottom. In the laboratory, the sample is force saturated and the falling head permeability test is run at a hydraulic gradient of about 10. Those conditions bear no resemblance to what takes place in a commercial landfill. A hydraulic gradient of 10 on a 10 ft. deep landfill requires 90 feet of standing water, a wholly unlikely situation, in the field, unless you are creating a lake and not a landfill. Our landfills are designed for rapid runoff and immediate dissipation of surface water. Recharge, therefore, only occurs during a rain.

Accepting for the moment that the coefficient of permeability measured at a hydraulic gradient of ten is valid at a gradient of one, a simple calculation will indicate the time required to saturate a 10 ft. deep landfill.

Assume:

1. 30 inches of rain/yr.
2. No drying or evaporation between rains
3. Permeability of 1×10^{-6} cm/sec.
4. Average rain 1/4"/24 hrs.

.000001 cm/sec x 60 min x 24 hr x 120 dys = 10.37 cm/yr
or 4.1 inches/yr
or 30 years to saturate

This time will be greatly extended due to loss by evaporation. It would, therefore, appear that we can eliminate permeation as a problem if the permeability is 1×10^{-6} or lower.

Thus, we are left with two mechanisms for the transport of pollutants from Poz-O-Tec; runoff and ground water contact or surface washing and diffusion. We have done a great deal of work to quantify the effects of these phenomena on Poz-O-Tec material and the results demonstrate that it has minimum polluting potential.

Runoff

Surface runoff water can be contaminated by dissolution of the surface salts and diffusion of the subsurface salts to the bulk solution, if there is sufficient contact time. In a properly designed landfill, contact time will be extremely short and diffusion is, therefore, of minor consequence. Hence, it is not considered in our runoff analyses.

Two different test procedures were utilized to determine the quality of runoff from Poz-O-Tec and the effects of repeated washings. Those tests established that:

1. Surface salts wash off rapidly
2. Succeeding runoff contains substantially reduced total dissolved solids
3. The average weight of surface salts available is .05 gr/sq in.

The first series consisted of successive 48 hour shake tests in which a sample of known weight and superficial surface area is placed in a container of distilled water at a ratio of 1 gram of material to 4 milliliters of water (typically 500 gr. to 2000 ml). The container is oscillated (60-70 one inch strikes per hour) for 48 hours. The water is then filtered and analyzed. The results of such tests of Poz-O-Tec from the Shawnee test pond are shown in Table I.

Table I

POZ-O-TEC LEACHATE
FROM
SUCCESSIVE SHAKE TESTS

TDS (PPM)	GRAMS LEACHED	GRAMS/ IN.^{2}
974	1.948	.046
338	.676	.015
268	.536	.012
194	.388	.009
214	.428	.010

SURFACE AREA: 42.4 IN^2

DILUTION RATIO (IN^2/L): 21.2 : 1

As can be seen, after 3 or 4 washings, the TDS reaches an equilibrium of approximately 200 ppm. That equilibrium represents the diffusion controlled leaching process of soluble salts encapsulated below the immediate surface. Thus, diffusion is significant only when water is in contact with the material for extended periods. The washing and diffusion controlled phases are indicated on the curve in Figure 2. The effect of dilution on leachate concentration and mass transport is shown on Table II.

As demonstrated by these data, an average surface loading of .05 gr/in^2 is available for leaching. Applying this to a one acre site, 634 lbs. of leachable material are available for the first washing. For a one inch rain, approximately 208,000 lbs. of water will contact the one acre surface. That would produce a maximum loading of 3000 ppm TDS in the runoff, assuming a 48 hour contact. Subsequent rainfalls will produce lower TDS, with the third approaching 100 ppm for stabilized high sulfite and 500 ppm or less for stabilized high sulfate sludges.

These shake test results have been substantiated by data derived from a runoff test that we have developed. This test is flexible enough to simulate any amount of rainfall over any time period and any length of flow. As shown in Figure 3, the apparatus consists of a box 1 ft. long x 1 ft. deep x ½ ft. wide. Clean, inert material of high permeability is placed in the bottom and the material to be tested is placed on top and compacted as in the field. Water is sprayed on top of the material to simulate any desired rainfall, usually a one inch rain, once a week. The box can be tilted to any angle to conform with the expected slope of the landfill. The runoff is collected for analysis and there are drains in the bottom to remove any permeate for testing. The data that can be gathered by use of this procedure are:

1. Runoff analysis
2. Amount and quality of permeate
3. By weighing, the amount of water absorbed and the loss through evaporation between tests.
4. By introducing water into the bottom, the effect of ground water contact.

The test accurately simulates field conditions and produces a wealth of data. Table III shows some of the comparative results obtained.

Table II

EFFECT OF DILUTION

SURFACE AREA IN^2	DILUTION RATIO IN^2/L	TDS PPM	GRAMS LEACHED	GRAM/IN^2
34.77	307.6	4842	0.547	.0157
34.77	174	3536	0.778	.0288
34.77	84.6	3418	1.442	.0415
34.77	58.2	3282	1.959	.0563
60.78	30.39	1932	3.864	.0636

POZ-O-TEC FROM SHAWNEE-AEROSPACE POND

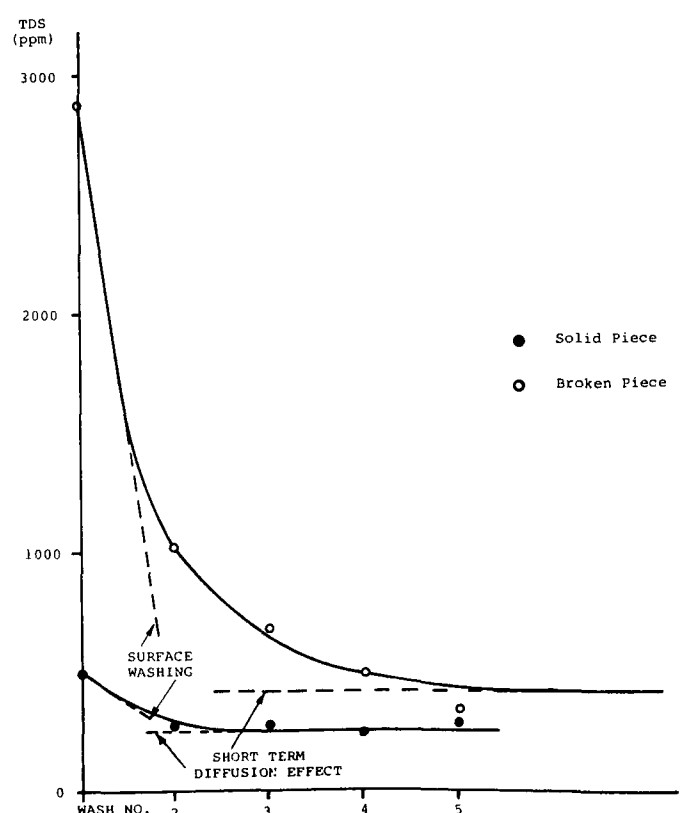

Figure 2: Poz-O-Tec from Aerospace Shawnee Pond (Leachate TDS vs Wash No.)

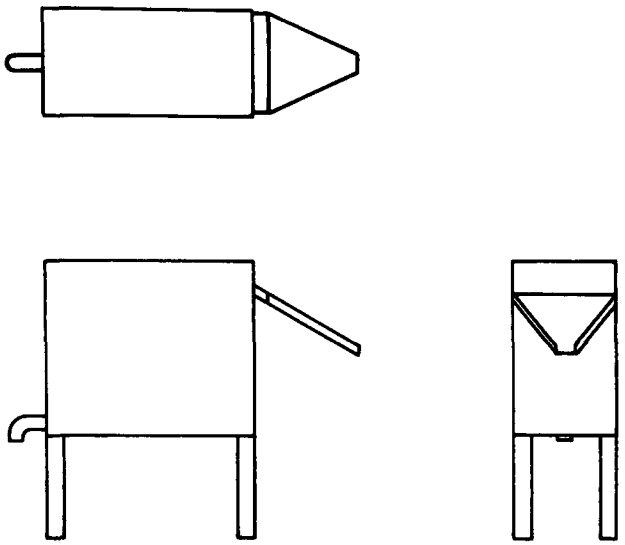

Figure 3A: Leachate Run-off Test Box

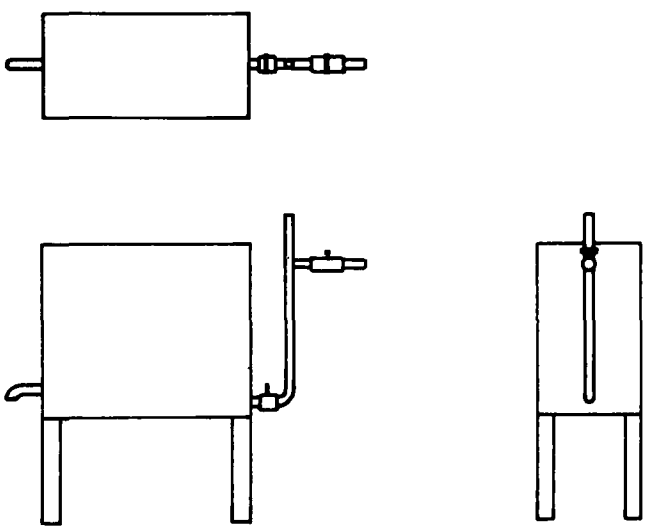

Figure 3B: Ground Water Simulation Test Box

Table III

RUNOFF RESULTS
STABILIZED SULFATE SLUDGE

	FILTER CAKE	FILTER CAKE AND FLY ASH	POZ-O-TEC
IMMEDIATE	2658	2482	2240
7 DAYS	584	2296	588
28 DAYS	2138	1800	439

Ground Water Contact

Before a landfill is started, the site is carefully selected, the hydrology of the area, (height of water table surface flow, etc.) is determined. The site is selected to prevent ground water contact and must be acceptable to the local authorities. Where necessary, a bottom drainage system, consisting of French drains or piping, is installed. In spite of all of that, we must answer the what if question. What if ground water does contact the material?

It is our opinion that for a material of low permeability, such as Poz-O-Tec, the only water movement mechanism that can transport pollutants from the bottom surface to the ground water is diffusion. We have, therefore, performed numerous diffusion tests to determine the effects.

Because ground water moves very slowly and the flow is laminar and not turbulent, we have discounted any mixing effect the flow might have. The tests were, therefore, performed in static water. Specimens were immersed in deionized water and TDS was measured as a function of time and distance. Assuming a maximum TDS of 5000 ppm, the solubility limit, as determined from the shake tests, the diffusion coefficient was calculated to be 2×10^{-5} cm^2/sec. Water must, therefore, be in contact with Poz-O-Tec for extremely long periods of time before enough salts are transported to the ground water to be of concern. This theoretical diffusion coefficient was substantiated by plotting it against long term data obtained from the supernatant on the Poz-O-Tec pond at Shawnee. The results are shown on curves in Figures 4 and 5.

SUMMARY

We believe that it is the mass transport of polluting salts to the water system that is of concern. The magnitude of that problem cannot be determined by the initial leachate or any test of a single property without regard for the physical characteristics of the material, the manner of placement and the pertinent water movement mechanisms. The release of partial data, without explanation or interpretation from programs that are limited in scope, is misleading and a disservice to the industry. An additional problem is the time frame. Some on-going programs will not be completed for one to four years. The problem is now, not four years from now. We need a fast and effective method of evaluating residues to be landfilled. We believe that our concept, coupled with the test procedures we have outlined, offers that capability.

We have spent a great deal of time and effort to develop our test program. We work with it constantly and continuously. It is important to us, because sludge stabilization is our livelihood. We offer our procedures to anyone who is interested and we are receptive to any that can be shown to be better.

With our Poz-O-Tec landfill material and procedures, we have greatly reduced the potential for the transport of pollutants to the water by:

1. Increasing the pH to reduce solubility
2. Placing a dry, unsaturated material.
3. Isolating the internal surfaces by making the material effectively impermeable.
4. Protecting the external surfaces through rapid runoff and good bottom drainage.

It must be remembered that we are talking about landfill operations of 500,000 to 1,000,000 tons per year, and extremes in disposal methods from sluicing untreated sludge and ash to unlined ponds to placing stabilized material in a well-engineered and well-managed landfill. There are many variations in between but proper evaluation shows the Poz-O-Tec system to be an effective, economically viable means of protecting the environment. Our test procedures enable us to develop all of the data necessary to design the most environmentally effective landfill.

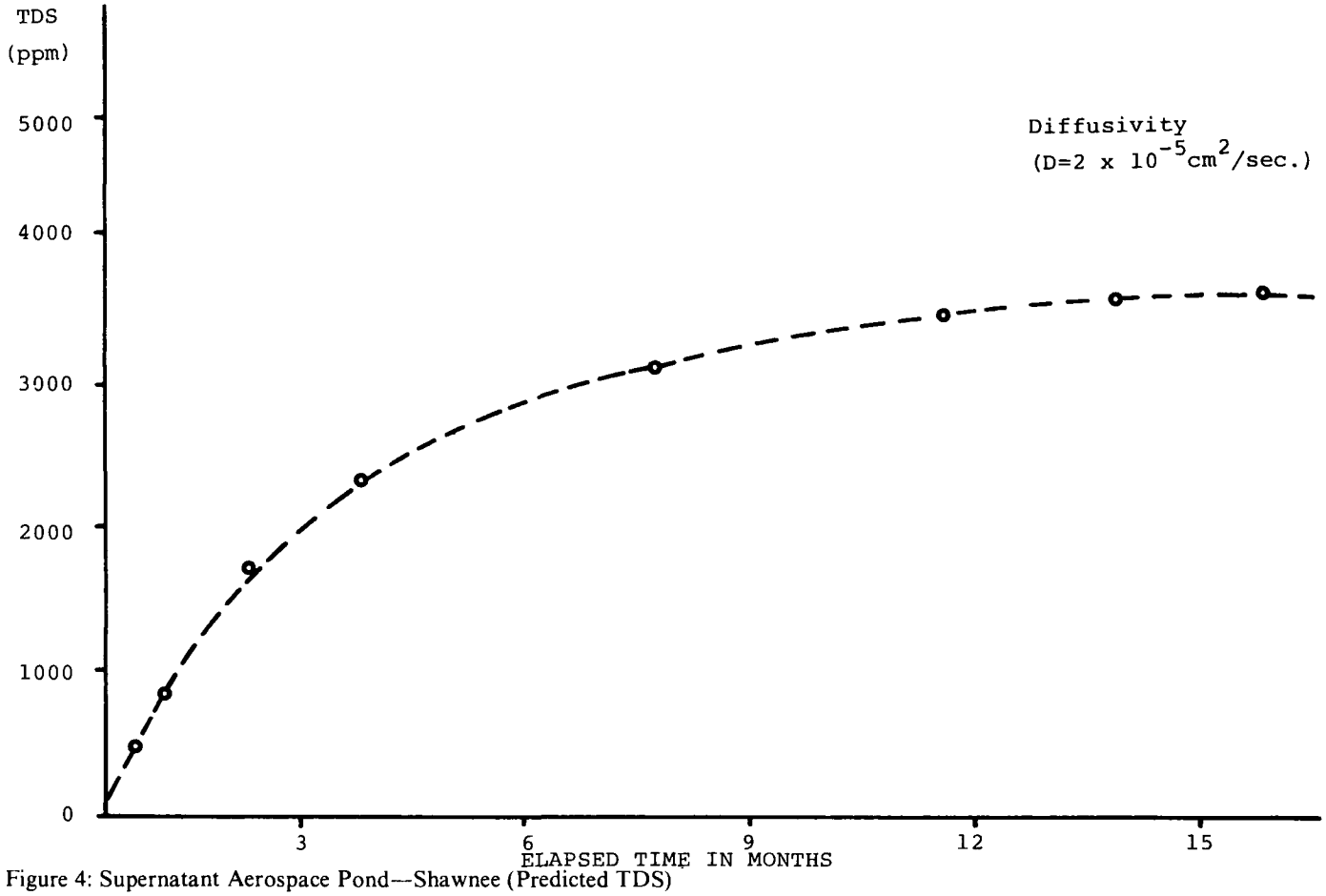

Figure 4: Supernatant Aerospace Pond—Shawnee (Predicted TDS)

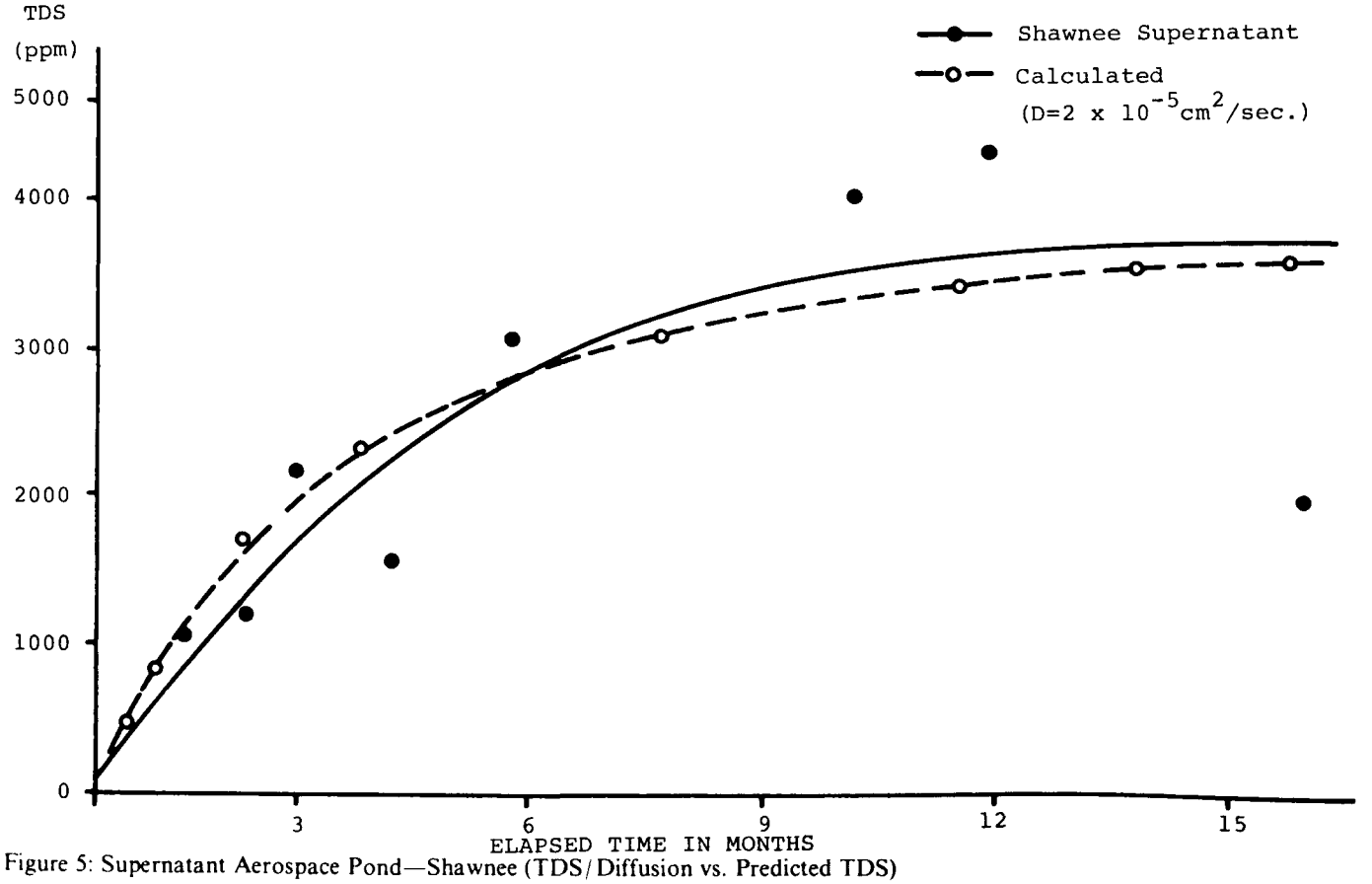

Figure 5: Supernatant Aerospace Pond—Shawnee (TDS/Diffusion vs. Predicted TDS)

Transport of Salts from Disturbed Geologic Formations

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INTRODUCTION

The observed chemical composition of natural runoff is a reflection of combined chemical and hydrologic processes that are highly dependent upon the distribution and physical-chemical characteristics of the geologic material in the watershed. Dissolved solids in watershed drainage result from dissolution of minerals contacted by the water and depend upon both the distribution of soluble minerals and the opportunity for contact of these minerals by precipitation as it moves through the watershed. Therefore, large scale disturbance of geologic strata, particularly those within about 50 meters of the ground surface, provides the potential for significantly modifying the water-quality hydrology of the watershed.

This paper is a discussion of factors effecting the concentration of inorganic dissolved solids in runoff from watersheds that have been partially disturbed by surface mining. Hydrologic factors, including surface runoff, runoff by interflow, and ground water runoff are combined with the corresponding concentrations of dissolved solids to provide a quantitative description of observed water quality in an area disturbed by surface mining. The basis for the material in this paper is the observation of the water-quality hydrology on a surface-mined area in northwestern Colorado.

Study Area and Monitoring Program

The study area is a surface-mined watershed located between the towns of Steamboat Springs and Oak Creek, Colorado. The coal mining operation is near the southeast limit of the Yampa coal field. The disturbed strata are part of the Williams Fork member of the Mesa Verde group, a Late Gretaceous sequence of thin sandstones, shales and sandy shales.[1] The portion of the watershed investigated lies above 7000 feet in elevation and extends to elevations in excess of 8000 feet. Annual precipitation exceeds 20 inches, about half of which occurs as snow. Snowmelt begins in late March and extends into May on the study area. The mined area is located on a relatively uniform slope that dips to the west and northwest (Figure 1). All drainage from the mined area is received by Trout Creek, a perennial stream that flows in a generally northward direction at the base of the mined slope.

The study area was subdivided into four watersheds designated as C 3, C 5, C 9, and C10, the boundaries of which are shown by the heavy lines in Figure 1. Each of these watersheds is drained by a perennial stream tributary to Trout Creek. The shaded areas in Figure 1 represent the disturbed Williams Fork rocks.

A total of thirteen water-quality monitoring stations were established. The location and designation of the most important of these stations are indicated by the black dots in Figure 1. Several of these stations are also gauging stations for the determination of discharge. A description of the monitoring stations is contained in Table I. The two discharge stations (C 2 and C 6) on Trout Creek consisted of rated cross-sections on which the stage was monitored. The stage was monitored at C 2 with an automatic stage recorder, and by reading a staff gauge at C 6. All other discharge stations were equipped with flumes, three of which (C3, C9, and C10) were also equipped with stage recorders.

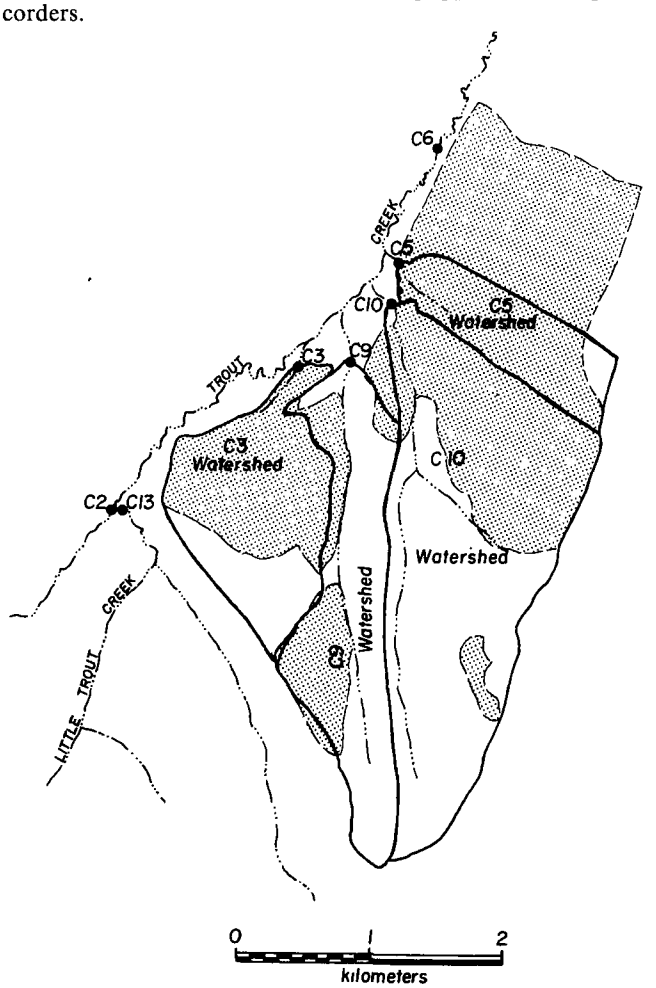

Figure 1: Map of the study area showing monitoring stations, subdivision into watersheds, and disturbed ground.

Table I: Description of Monitoring Stations

Station No.	Type Discharge	Type Quality	Description
C1		X	One mile above mine on Trout Creek
C2	X	X	On Trout Creek immediately above mine
C3	X	X	On mine drainage (interflow & surface water)
C4		X	On Trout Creek
C5	X	X	On mine drainage (interflow & surface water)
C6	X	X	On Trout Creek near downstream limit of mine
C7		X	Ground water seep
C8		X	On Trout Creek near downstream limit of mine
C9	X	X	On mine drainage (interflow & surface water)
C10	X	X	On mine drainage (interflow & surface water)
C11		X	On Trout Creek below downstream limit of mine
C12		X	On ephemeral drainage from undisturbed area
C13	X	X	On Little Trout Creek above mine

Grab samples for the determination of water quality were collected periodically at each of the stations. The frequency of sampling varied from station to station and with the time of year. During the winter months, late summer, and fall, monthly samples were collected. The interval between samples at selected stations was decreased to one or two days during peak runoff. Water samples on which complete chemical analyses were to be performed were handled in accordance with USEPA Standard Methods[2]. On many of the samples temperature, pH, and specific conductance were the only parameters measured, and these measurements were made directly in the field.

Evidence of Salt Pickup

Graphic evidence of salt pickup in the portion of the watershed contributing between stations C2 and C6 on Trout Creek is shown in Figure 2. Monthly averaged (discharged weighted) concentrations of dissolved solids at the downstream station, C6, are substantially greater than at the upstream

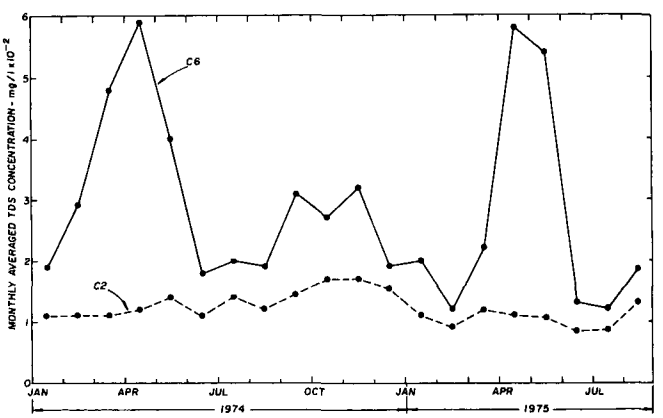

Figure 2: Dissolved solids concentration at C2 and C6 on Trout Creek.

Table II: Monthly Discharge[1], Salt Load[2], and Concentration[3] By Station For 1975

Month	C2 Q	C2 Q_{ds}	C2 P_t	C3 Q	C3 Q_{ds}	C3 P_t	C6 Q	C6 Q_{ds}	C6 P_t	C9 Q	C9 Q_{ds}	C9 P_t	C10 Q	C10 Q_{ds}	C10 P_t
Jan	75.9	83	109	0.444	6.4	1441	136.6	273	200	0.494	3.1	628	0.148	2.7	1824
Feb	71.0	62	87	0.494	7.9	1599	127.7	160	125	0.494	3.1	628	0.148	2.7	1824
March	75.9	91	120	0.494	10.0	2024	136.6	259	190	0.309	4.3	1392	0.494	11.0	2227
April	118.0	137	116	3.555	57.4	1615	204.6	1184	579	3.987	62.6	1570	5.899	145.2	2461
May	479.9	481	100	11.851	233.5	1970	590.1	2061	349	7.962	104.3	1310	9.740	176.1	1808
June	1434.5	876	61	4.481	86.5	1930	1682.4	1888	112	3.074	38.5	1252	4.518	57.2	1266
July	517.9	367	71	1.284	23.2	1807	635.3	689	108	1.901	24.9	1310	0.802	12.5	1559
Aug.	126.0	148	117	0.506	9.9	1957	192.8	345	179	1.358	18.5	1362	0.296	5.9	1993
Sept.	86.5	89	103	0.296	5.9	1993	153.4	249	162	0.506	5.6	1107	0.185	3.2	1730
Oct.	86.5	84	97	0.370	7.3	1973	161.3	282	175	0.704	8.0	1136	0.160	2.8	1750
Nov.	125.9	128	102	0.444	9.3	2095	137.7	298	216	0.704	6.4	909	0.148	2.7	1824
Dec.	98.3	118	120	0.444	9.3	2095	153.4	265	173	0.704	6.4	909	0.148	2.7	1824
TOTALS	3296.3	2664	69	24.664	466.4	1891	4311.8	7953	184	22.195	285.5	1286	22.788	424.7	1864

[1]Q volume of water ($m^3 \times 10^{-4}$) discharged during the month.
[2]Q_{ds} - total weight ($kg \times 10^{-3}$) of salt contained in Q.
[3]P_t average concentration of dissolved solids (mg/ℓ).

station, C2. All of the indicated accumulation of dissolved solids is not attributable to the mined area, however, because the undisturbed portions of the watershed also make a contribution. Estimates of the contribution attributable to mining are discussed subsequently.

Monthly total salt loads, discharges, and dissolved solids concentrations for several stations during 1975 are presented in Table II. The peak concentration at C6 on Trout Creek occurs in April, but the greatest salt loading from C3, C5, C9, and C10 occurs in May. This observation is explained by the time distributions of runoff contributing at station C6. More specifically, the April discharges at stations C3, C5, C9, and C10 are approximately 10 times greater than the corresponding March discharges, indicating a very significant snowmelt on the disturbed watershed. On the other hand, the discharge at C2 in April is only 55 percent greater than in March, indicating a much less significant snowmelt on the high watershed above C2. Thus, the April concentration at C6 reflects the relatively high salt concentrations in the inflow from the C3, C5, C9, and C10 watersheds. In May, however, the discharge at C2 increased by a factor of four, and this influx of water with low concentration was sufficient to reduce the concentration at C6 in spite of more saline inflow from C3, C5, C9, and C10.

The total salt pickup between stations C2 and C6 for 1975 is 5289 metric tons, the large fraction of which is contributed by spring runoff. Similar observations were made in the spring of 1974 and 1976.

Factors Effecting Observed Water Quality

The water at monitoring stations C3, C5, C9, and C10 is a combination of overland flow from both undisturbed and disturbed ground and shallow ground water (interflow) that has returned to the surface at various points along the water courses. The observed water quality at these stations depends upon the concentration of dissolved solids in each contributing component and upon the volumetric contribution from each source. The dependence of the observed water quality on the concentrations and volumes of each component can be estimated by formulating a combination of water and dissolved solids budgets. This approach has been used successfully in hydrograph analysis.[3,4,5]

The Water Budget

The water budget for a watershed can be expressed in terms of the volumes in each budget component over a specified time interval ▲ t. For example.

$$V_p - V_e - V_s - V_g - V_d = \Delta S \qquad (1)$$

where

V_p = volume of precipitation in Δt

V_e = volume of evapotranspiration in Δt

V_s = volume of surface runoff in Δt

V_g = volume of shallow ground water runoff in Δt

V_d = volume of percolation to deep aquifers that do not contribute to stream flow in the watershed under consideration.

ΔS = the change in storage in the watershed in Δt.

Under conditions of dynamic equilibrium, the total inflow equals the total outflow and ▲ S = 0. This condition is approximated over a time interval of one year in some cases and will be assumed to apply in the subsequent developments. It is further assumed that deep percolation is zero. This is a reasonable assumption in the study area because it is underlain by a sequence of shales that are expected to have a small permeability relative to that of the disturbed ground and natural soils. Abundant evidence of a water table perched on the interface between the disturbed material and the underlying shale exists in the study area. For example, many interflow seeps were observed where a mine cut or natural drainage intersected this interface.

With ΔS and V_d equal to zero, Eq. 1 can be rearranged so that

$$V_t = V_p - V_e = V_s + V_g \qquad (2)$$

where V_t is the total volume of watershed drainage. Equation 2 can be rewritten in terms of volumes per unit area for the undisturbed area and the disturbed area. Putting A_m equal to the area of the disturbed ground and A_n equal to the area of the natural ground, Eq. 2 becomes

$$V_t = q_t A_t = q_m A_m + q_n A_n = (q_{pm} - q_{em}) A_m + (q_{pn} - q_{en}) A_n \qquad (3)$$

where q represents volume per unit area, the subscripts m and n refer to disturbed and natural, respectively, and the subscripts p and e refer to precipitation and evapotranspiration, respectively. Rearrangement of Eq. 3 yields

$$q_t = (q_{pm} - q_{em}) F_m + (q_{pn} - q_{en})(1 - F_m) \qquad (4)$$

Where $F_m = A_m/A_t$ and $1 - F_m = A_n/A_t$. In other words, F_m is the fraction of the total watershed area that is mined or otherwise disturbed.

A uniform distribution of precipitation is assumed so that $q_p = q_{pm} = q_{pn}$ and, therefore,

$$\frac{q_t}{q_p} = \left(1 - \frac{q_{em}}{q_p}\right) F_m + \left(1 - \frac{q_{en}}{q_p}\right) (1 - F_m) \qquad (5)$$

Let $f_{em} = q_{em}/q_p$ and $f_{en} = q_{en}/q_p$ so that

$$\frac{q_t}{q_p} = (1 - f_{em}) F_m + (1 - f_{en})(1 - F_m) \qquad (6)$$

The parameter f_{em} represents the fraction of the precipitation that is consumptively used on the disturbed land and f_{en} is the fraction of precipitation that is consumptively used on the natural portion of the watershed. Differences in the physical characteristics of soils, topography, and vegetation make it unlikely that f_{em} is equal to f_{en}.

Dissolved Solids Budget

The dissolved solids budget for a watershed partially disturbed by mining can be written

$$V_t P_t = V_m P_m + V_n P_n \qquad (7)$$

where

P_t = average TDS concentration in the total drainage from the watershed,

P_m = average TDS concentration in drainage from the disturbed area,

P_n = average TDS concentration in drainage from the natural portion.

Equation 7 can be expressed in terms of volumes per unit area to give

$$P_t = \frac{q_m}{q_t} F_m P_m + \frac{q_n}{q_t}(1 - F_m) P_n. \quad (8)$$

But since $q_m = q_p - q_{me}$ and $q_n = q_p - q_{ne}$, then

$$P_t = \frac{q_p}{q_t} [(1 - f_{em}) F_m P_m + (1 - f_{en}) (1 - F_m) P_n]. \quad (9)$$

Data at the study site, both under conditions of natural runoff and runoff induced by rainfall simulators, indicate a large disparity between the TDS in overland flow and in the shallow ground water on the disturbed area. This is explained by the fact that the volume of material contacted by overland flow is very small relative to the volume of surface runoff. Therefore, the surface layer of material is rapidly leached, and overland flow contains a relatively small concentration of dissolved solids. On the other hand, the volume of infiltrated water is quite small compared to the volume of disturbed material through which it must pass before reaching the streams. Therefore, leaching of soluble materials from the bulk of the disturbed ground is a much much less rapid process than in the surface layer, and interflow contains a much greater concentration of dissolved solids. To some degree, the surface runoff from undisturbed areas is also less than the shallow ground water in the same area. The difference is less pronounced, however, because leaching of the bulk of the soil has been occurring for hundreds of years.

Because of the significant difference between the quality of overland flow and interflow on the disturbed area, the variable P_m in Eq. 9 is expressed as the sum of the contributions from surface runoff and interflow:

$$P_m = f_{sm} P_{sm} + (1 - f_{sm}) P_{gm}, \quad (10)$$

wherein f_{sm} is the fraction of the total runoff from the disturbed ground that is surface runoff (overland flow). Substitution of Eq. 10 into Eq. 9 yields the following expression for the dissolved solids budget:

$$P_t = \frac{q_p}{q_t}[(1 - f_{em}) \{f_{sm} P_{sm} + (1 - f_{sm}) P_{gm}\} F_m \quad (11)$$

$$+ (1 - f_{en}) (1 - F_m) P_n].$$

Combined Water and TDS Budgets

Equation 6 from the water budget is substituted into Eq. 11 to yield

$$P_t = \frac{f_{sm} P_{sm} + (1 - f_{sm}) P_{gm}}{1 + \left(\frac{1 - f_{en}}{1 - f_{em}}\right) \left(\frac{1 - F_m}{F_m}\right)} + \frac{P_n}{1 + \left(\frac{1 - f_{em}}{1 - f_{en}}\right) \left(\frac{F_m}{1 - F_m}\right)} \quad (12)$$

after considerable rearrangement. Let

$$K = \frac{1 - f_{en}}{1 - f_{em}} \quad \text{and} \quad R = \frac{1 - F_m}{F_m} \quad (13)$$

which permit Eq. 12 to be written as

$$P_t = \frac{P_n KR + f_{sm} P_{sm} + (1 - f_{sm}) - P_{gm}}{1 + KR} \quad (14)$$

Equation 14 is the final expression for the concentration of dissolved solids in watershed drainage as affected by the volumes and concentrations of overland flow and interflow contributed by the disturbed and natural portions of the watershed. The parameter R is simply the ratio of the undisturbed area to the disturbed area. R is zero for a watershed that is completely disturbed and becomes very large for watersheds that are minimally disturbed. The parameter K is the ratio of the total drainage (including overland flow and interflow) on the natural portion of the watershed to the total drainage on the disturbed portion. K, therefore, is a hydrologic parameter. Likewise, the parameter f_{sm}, being the fraction of the total runoff from the disturbed area that is overland flow, is a hydrologic parameter.

Application of the Budget Equation to Study Area

The application of the foregoing budget equation requires determination of three average dissolved solids concentrations: P_{sm}, P_{gm}, and P_n. The TDS concentration in overland flow on the disturbed ground, P_{sm}, was estimated from samples of natural runoff and from runoff on four experimental plots subjected to simulated precipitation. P_{sm} for the natural runoff averaged 149 mg/ℓ (15 kg/ha-cm) and from the experimental plots 158 mg/ℓ (16 kg/ha-cm). The value of P_{sm} is, therefore, taken as 150 mg/ℓ (15 kg/ha-cm) in the subsequent calculations.

The experimental plots were equipped with subsurface drains at depths ranging from 1.5 m to 2.2 m below the surface of the disturbed ground. The average TDS concentration in 57 samples of water taken from these drains is 3025 mg/ℓ (303 kg/ha-cm). This average concentration agreed closely with the average of 3126 mg/ℓ from 11 water samples extracted from saturated pastes prepared from the disturbed material.[6,7,8] The concentration of dissolved solids in ground water seeps at station C5 also agreed well with the above values. Therefore, the concentration of dissolved solids in the ground water beneath the disturbed ground was taken as 3025 mg/ℓ (303 kg/ha-cm).

The remaining water-quality parameter, P_n, is the TDS concentration in combined overland flow and interflow runoff from the undisturbed watershed. Measurements of concentration in a natural water course draining undisturbed land were used to estimate P_n. During periods of base flow, the concentration averaged 462 mg/ℓ (46 kg/ha-cm) and substantially less when overland flow was contributing. Thus, P_n was written as the sum of a ground water and overland component. It was also assumed that the fraction of total runoff that is overland flow was the same as on the disturbed ground, an assumption that is not required if P_n is measured directly. With the above assumption, P_n is given by

$$P_n = 46 f_{sm} + 15 (1 - f_{sm}), \quad (15)$$

where P_n is in kg/ha-cm.

Substitution of the values for P_n, P_{sm}, and P_{gm} into Eq. 14 yields

$$P_t = \frac{\{46\, f_{sm} + 15(1-f_{sm})\}\, KR + 15\, f_{sm} + 303(1-f_{sm})}{1 + KR} \quad (16)$$

The value of R for each watershed was determined by measuring the disturbed area and the total area of each catchment above the monitoring stations. The values for F_m and R are presented in Table III.

TABLE III: R and Fm For Study Area

Watershed	F_m	R
C3	0.68	0.47
C5	1.00	0.00
C9	0.35	1.86
C10	0.44	1.27

All parameters in the budget equation are now determined, save the two hydrologic parameters f_{sm} and K. It is expected that the values for these hydrologic parameters are different for each of the four watersheds, because the catchments differ in respect to vegetation, topography, etc. However, it was not possible to measure f_{sm} and K for each watershed, nor is it possible to determine f_{sm} and K by fitting Eq. 16 to the data for each individual watershed. The latter statement is true because R is a single value for a particular watershed, causing the situation to be one of a single equation and two unknowns. On the other hand, if it is assumed that K and f_{sm} do not vary appreciably from watershed to watershed, then average values of K and f_{sm} can be calculated by determining the best fit of Eq. 16 to the data from all four watersheds.

The best fit of Eq. 16 to annual data from the four watersheds is shown in Figure 3. The dashed line is the limiting value of observed TDS concentration for an undisturbed watershed. All of the data points for the C3 watershed fall below the curve. This is probably explained by the fact that the disturbance of the strata in C3 occurred some 30 years ago, providing sufficient time for significant leaching to have occurred. All other disturbances are relatively recent. The values for K and f_{sm} determined by fitting Eq. 16 to the observed data are 1.04 and 0.06, respectively. K equal to 1.04 implies that the total drainage from the disturbed portions of the watershed is practically equal to that from the natural portion. A value for f_{sm} of 0.06 means that only 6 percent of the total drainage occurs as overland flow. It has, in fact, been observed that surface runoff is very small. This results from highly permeable materials in the study area, and the fact that most of the water available for runoff is from melting snow and not from high intensity rainfall.

Inspection of Eq. 14 reveals that the observed concentration P_t should vary linearly with the fraction F_m of the watershed that has been disturbed in the special case in which K = 1.0. Because the average value of K as determined above is nearly unity, the measured values of P_t should exhibit a nearly linear relationship to F_m. A plot of P_t versus F_m for the study area is shown in Figure 4. The straight line is a linear regression line. Extrapolation of the regression line to $F_m = 0$ yields $P_t = 450$ mg/ (45 kg/ha-cm), a value that should approximate the annual average TDS concentration in watershed drainage prior to disturbance of the area. It is possible, therefore, to estimate the increase in TDS concentration due to mining. The results are shown in Table IV for 1975.

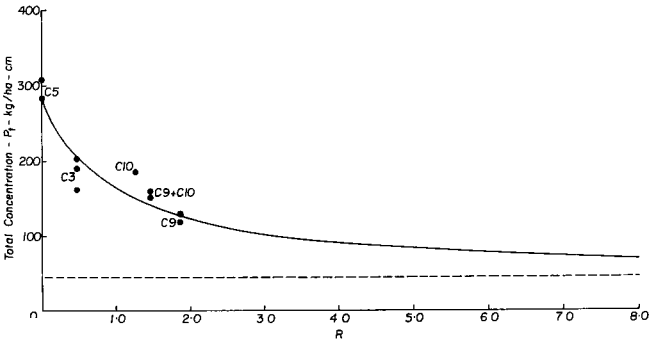

Figure 3: Best fit of the budget equation to observed data - K = 1.04, f_{sm} = 0.06.

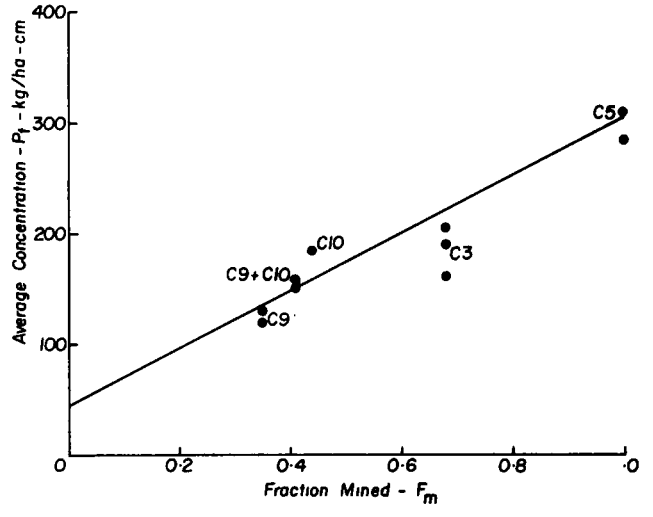

Figure 4: Relationship between observed water quality and the fraction of the watershed that is disturbed.

TABLE IV: Estimated Increase In Average TDS Concentration Attributable to Mining—1975

Watershed	F_m	Percent Increase in TDS
C3	0.68	320
C5	1.00	529
C9	0.35	187
C10	0.44	313

The percentages indicated in Table IV apply to the individual watersheds. The percent increase in the TDS concentration in the receiving waters (Trout Creek), attributable to mining, is much less than that shown in Table IV.

CONCLUSIONS

Three years of monitoring the water-quality hydrology on

four small watersheds, partially disturbed by surface mining operations, have shown that shallow ground water runoff (interflow) from the disturbed lands is the largest contributor to observed dissolved solids concentration in watershed drainage on the study area. Concentrations of dissolved solids in interflow exceed those in overland flow by a factor of approximately 20. Highly permeable materials and the gradual release of water by snowmelt, result in small surface runoff relative to infiltration. The variation of observed average annual TDS concentration from different watersheds is satisfactorily explained by a simple algebraic model derived from material balance considerations. Comparison of the model with annual data from the four watersheds indicates that the percent of the catchment area that is disturbed is the most significant parameter with respect to accounting for the differences in TDS concentration observed from one watershed to another. This was true in the study area, only because the chemical characteristics of the disturbed material were practically the same in all watersheds, with the possible exception of the C3 watershed.

The most important factors influencing the observed water quality in a particular watershed are the chemical characteristics of the disturbed area and the distribution or routes by which percipitation makes its way to the observation point. The material balance model presented herein accounts for differences in the quality of surface and ground water runoff, the division of total drainage into overland flow and interflow on the disturbed and natural portions of the watershed, and the chemical characteristics of the two areas. The model should, therefore, be useful for anticipating, in a quantitative manner, the effects of disturbed areas on water quality prior to the occurrence of the disturbance.

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Disposal of Coal Mining Industry By-Products

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This discussion describes the materials remaining as wastes or process by-products from mining, processing, and utilization of coal. Materials considered include coal washing plant wastes, sludges resulting from acid mine drainage (AMD) neutralization, flyash recovered from precipitators in coal-burning power plants and bottom ash, and solid reaction products recovered from flue gas scrubbers on coal burning power plants.

A study of the geologic formation of coal is the first step in understanding its composition and in handling the drainage from coal wastes. Swamps of the Mesozoic and Paleozoic eras account for most of the Earth's coal reserves. Vegetable material falls into the swamp, is protected from immediate decay by the high water table, and begins to accumulate and form a peat bog. Natural acidity in the vegetation is probably responsible in part for the depressed rate of biological decomposition. In the absence of erosive forces, the bogs are filled, eventually covered by protective layers of sediment, and slowly converted to lignite, bituminous, and anthracite coals.

The conditions required for coal formation are: an interior or coastal swamp environment, little erosion, rapid deposition of material, and subsidence or subsequent flooding to allow further deposition and covering. Considering this type of formation, one can easily visualize layers of silt and other foreign matter periodically flooding into the swamp, covering the vegetable material, and eventually forming partings in the fully developed coal seam.

The vegetable material carries with it various minerals and trace metals accumulated during the growth process. Among these constituents is organic sulphur derived from the swamp water. Studies show that sulphur and pyrite are present in modern peat deposits, as they must have been in the geologic past. According to Simon and Hopkins[11] seawater in the coastal swamps may have been a primary contributor of sulphur in the form of lenses, nodules and bands in the coal seam and adjacent strata. In addition to the impurities formed in the coal during its deposition, mineral impurities are carried by the groundwater into the porous layers of fully developed coal seams.

The composition of the coal, and thereby the composition of washing plant wastes, power plant flyash and bottom ash, and stack scrubber precipitates, is the determining factor in considering which elements may be a pollutional problem with respect to disposal of any of these materials. Materials removed from raw coal during cleaning and washing processes will not be present in flyash, bottomash, or scrubber precipitates. However, washing plant wastes will be enriched in elements removed as contents of unsalable materials. Ruch, et al.[10] presented data suggesting the extent of elemental segregation in cleaned coal, and conversely elements that may be expected to concentrate in the cleaning waste products, based on elemental analyses of over 100 coal samples. Their data showing the composition of various specific gravity fractions show which elements tend to be associated with the organic fraction of coal, which remains after the most intensive heavy-media separation of minerals, and which elements tend to be contained in highest proportions in the highest specific gravity fractions, indicating the composition of the most inorganic or mineral-laden portion of the coal. Data in Table I from analysis of one coal sample illustrate the trend of elemental composition in coal fractions. Other analyses reported by Ruch, et al. [10] follow the same general pattern. The elements germanium, beryllium, and boron consistently appeared in higher amounts in the lightest fractions, suggesting greatest affinity for or association with the organic matrix of coal. Elements with the least affinity for, or association with, the organic coal matrix, and therefore most associated with the mineral portion of coal include cadmium, mercury, lead, zinc, and arsenic. These elements are readily recognized as cations found with sulfides, and therefore an association with the pyritic impurities of coal can be inferred.

Table I: Davis Coal

Clean coal - lightest specific gravity fraction (elements in "organic combination")	B Ge Be Ti Ga P V Cr Sb Se Co Cu Ni Mn Zr Mo Cd
Mineral matter - specific gravity greater than 1.60 (elements in "inorganic combination")	Hg Pb Zn As

Elements within the central part of Table I do not appear to be specifically associated with either the heavy or light portions of coal with any degree of reliability, therefore, they cannot in a general way be assumed to be related to any specific components of coal; likewise, these "central" elements are ones which may not be removed in proportionately greater or lesser amounts by flotation cleaning techniques, and, therefore, also could not be expected to be concentrated in cleaning plant wastes. However, some individual elements may predominate in certain coal fractions in coals from specific geographic and/or geologic environments.

Metallic elements readily associated with sulfide minerals can be assumed to be solubilized into the environment as these minerals oxidize after cleaning plant separation and subsequent exposure. Acid generated through oxidation of the sulfides allows wash water and percolate through coarse refuse disposal piles to dissolve large quantities of other metals contained in the waste. The current emphasis of both the coal cleaning industry and regulatory bodies to produce a zero-discharge of cleaning plant wash waters will tend to negate a significant contamination problem from these elements in slurry waters as closed circuit systems are developed. A long range situation may arise, however, where these elements accumulate in settling ponds, coarse and fine refuse dumps, or other areas around cleaning plants where recycling waters are stored.

Martin[6] has presented data showing the elemental content of some typical coal refuse pile drainages. Silt, heavy metals, and acid constitute the major water pollution hazards of coal refuse. His data tables list the substantial amounts of sodium, aluminum, magnesium, calcium, manganese, iron, zinc, copper, lead, and nickel that were found in many samples. Oxidation of reduced sulfur compounds, mainly pyrite, present in many eastern coals and associated rock strata, contributes to the wide range of acidities contained in waters from coal operations. Table II illustrates the wide variety of water quality emanating from coal refuse areas. The amount of pollutants generated by coal refuse piles can also be related to the compaction of the refuse, angle of side slopes, soil cover or surface water control, in addition to the basic geochemical constitution of the coal.

The EPA currently is funding an active project at the Greene-Sullivan State Forest, where the Indiana Department of Natural Resources is demonstrating an economical method to abate acid mine drainage from surface coal mine refuse. The project area consists of a large pile and adjacent acid lake. The restoration program includes grading, covering, revegetating and permanently inundating a portion of the refuse. These procedures are designed to break the cycle of erosion, exposure of pyritic material, oxidation, acid formation, and erosion. Eventually, the area will be restored to recreational use.

The coal mining industry, under severe pressure from pollution abatement legislation, has in some cases adopted effective measures to deal with large volumes of acid mine drainage waters resulting from various facets of the coal extraction process. Currently, acid mine drainage treatment employs the use of lime or limestone as the neutralizing agent. These neutralizing agents contribute to the production of substantial quantities of sludge or insoluble precipitates. In extreme cases, as much as one-third of the treatment plant inflow can remain as sludge. This precipitated sludge may contain over 99% water, which compounds handling and disposal problems. Currently, sludge is either perpetually stored in ponds, pumped underground into mined-out workings, trucked to abandoned surface mines for disposal, or dumped into drying lagoons.

The chemical composition of AMD neutralization sludge is variable. Lovell[4] reported that sludge is generally composed of hydrated ferrous and/or ferric oxides, gypsum, hydrated aluminum oxide, varying amounts of sulfates, carbonates, bicarbonates, calcium, and trace amounts of silica, phosphate, manganese, titanium, copper and zinc. Akers and Moss[1] provide several sludge analyses, along with their investigations of dewatering techniques. Table III presents the means of analyses of effluents from four AMD neutralization plants discussed in their report.

Table II: Water Quality Data from Selected Refuse Sites

Parameter	Luzerne County, Penna.	Pike County, Ky.	Muhlenburg County, Ky.	Sullivan County, Ind.
pH	3.0	6.9	2.5	2.4
Conductivity*	4400	880	6800	6400
Acidity+	690	7	7020	6500
Alkalinity	-	135	-	-
SO_4	3000	690	7800	9500
Na	100	115	270	200
Mg	250	26	195	285
Al	87	1.8	440	340
K	4.8	8.1	13	3.0
Ca	340	50	300	350
Mn	50	3.5	72	120
Fe	30	6.2	3400	2600
Ni	1.7	-	3.0	1.6
Cu	0.14	-	-	0.16
Zn	2.8	0.1	8	7.2
Pb	-	-	0.12	0.30

* All Values expressed in mg/l except pH in standard units and conductivity in umhos/cm.
\+ Acidity to pH 7.3.

Table III: Average Composition of Four AMD Neutralization Plant Effluents

	Treatment Plant			
	Shannopin Mean	Banning Mean	Norton Mean	Edgell Mean
Ca (ppm)	1,600	860	310	920
Mg (ppm)	190	130	30	75
Al (ppm)	140	45	25	35
Si (ppm)	40	25	10	15
$SO_4^=$ (ppm)	4,600	2,700	790	4,200
Total Fe (ppm)	550	260	90	260
Nonfilterable Solids (ppm)	4,300	2,400	140	2,200

Reports of investigations of land disposal of neutralization sludge have been sparse in the literature. Conrad[3] reported that neutralization sludge was used to neutralize minewaste piles in Illinois. He also reported beneficial effects resulting from application to corn fields. Zaval and Robins[13] proposed application of sludge from the neutralization of acid strip mine pit waters onto acid spoils in western Kentucky. Lovell[4] developed initial design criteria from preliminary studies on the use of drying beds for dewatering of AMD sludge.

The Environmental Protection Agency (EPA) has an active research program currently under way on spray-irrigation and drying bed dewatering of AMD sludge. The studies are being conducted at the EPA Crown Mine Drainage Control Field Site near Morgantown, West Virginia. The sludges for the studies were obtained from pilot plant neutralization of a moderately severe ferrous iron AMD source (e.g., 640 mg/l acidity, 300 mg/l total iron, 270 mg/l ferrous iron, 370 mg/l calcium, 110 mg/l magnesium, 480 mg/l sodium, and 3000 mg/l sulfate). Hydrated lime, rockdust limestone and a combination of limestone/lime were used as the neutralizing reagents at various times throughout the research study. A flow diagram of the EPA neutralization facility is shown in Figure 1.

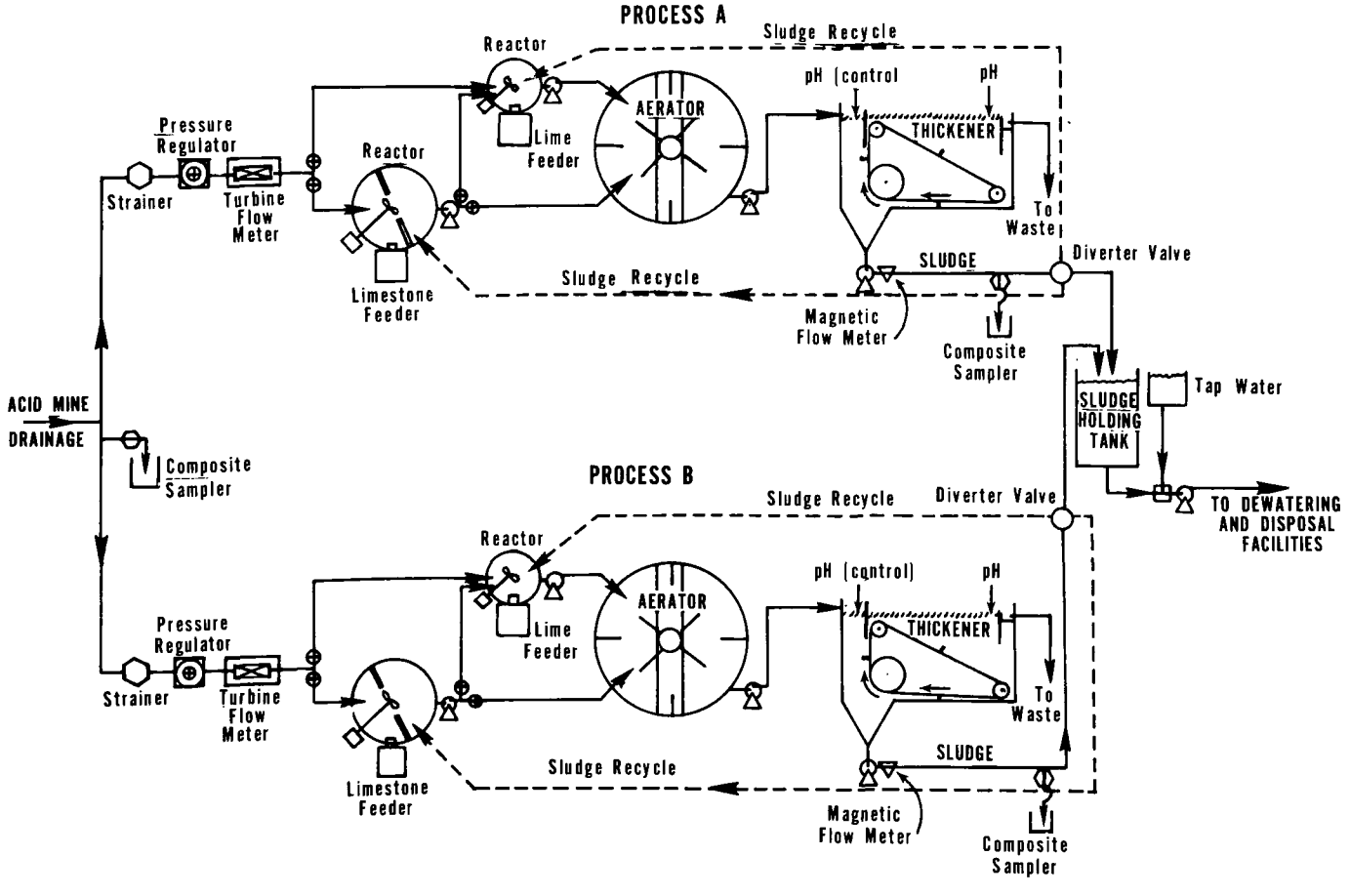

Figure 1: Schematic Flow Diagram for the EPA Neutralization Facility

Sludge produced from neutralization of acid mine water with calcium was spray-irrigated onto a plot area composed of weathering minewaste. Plot runoff water quality, soil moisture status, and soil surface temperature effects were influenced by sludge application. The most significant factors affecting plot runoff water quality were rainfall intensity, vegetative cover, and plot slope.

Several factors appear significant when considering the applicability of spray-irrigation of neutralization sludge:

1) Erosion of the sludge during high and medium intensity rainfall is readily apparent and undesirable.
2) No gross pollution was observed in the runoff from the sludge irrigated areas during mild precipitation events.
3) It appears essential to have virtually flat topography on sites proposed for spray irrigation of neutralization sludge in order to prevent erosive loss of sludge during precipitation events.
4) Sludge application appeared to have a slight beneficial effect upon establishment and maintenance of a vegetative cover. This was difficult to substantiate, however, in this initial study.

Drying bed sludge dewatering was complicated by winter freezing problems. Summer operation using lime-neutralized, coagulant-treated sludge provided the following observations:

1) Approximately 20-percent by volume of the influent sludge quantity (2.5-percent solids) was retained on the sand bed as a 20-percent solids gell-like mass, 50 percent drained through the sand as a clear effluent, and the remaining 30 percent was assumed to be lost to the atmosphere by evaporation.
2) The drainage rate through the sludge and sand averaged 26 liters/day/sq m (0.6 gal/day/sq ft).
3) Sludge solids appeared to stabilize near 20 percent within 20-days drying time.

Plans are under way to landfill the gell-like sludge removed from the drying beds. Casual observations indicate that plants species tolerant of alkaline soils may be successful on sludge landfills.

Several organizations exist whose members have been engaged in research into many aspects of coal ash disposal. The National Ash Association (1819 "H" St. NW, Washington, D.C. 20006) sponsors regular Ash Utilization Symposia within which soil amendments of flyash and bottom ash have been discussed. The Dairyland Power Cooperative (Box 855, LaCrosse, Wisconsin 54601) has sponsored one conference on soil amendments and disposal of flyash, and has also assembled a bibliography on the characterization and utilization of coal ash.

The geographical occurrence of coal, associated processing industries, and the materials involved limit the availability of by-products to the immediate locality where they are generated. Therefore, disposal or utilization of these by-products occurs nearby to the site of formation. The expensive hauling costs of powerplant flyash, primarily because of the tremendous volumes, dictate that flyash disposal be nearby to the powerplant. Current flyash disposal is either by dumping on the floor of nearby surface mines, placement into abandoned underground mines, placement onto large disposal piles in remote (to the public) neighborhoods, or disposal with bottom ash or SO_x scrubber sludge.

Potential soil and groundwater contaminants from disposal of flyash depend upon the specific properties of the local flyash involved. The operating conditions of the powerplant boilers have an effect on the physical nature of the flyash particles, and also on the degree of chemical recombination of elements during the coal burning process. Probably of greater significance, however, is the nature and composition of the particular coal being burned. Chemical analyses of coal samples taken from within and among various seams show tremendous variability; even one seam can vary in composition geographically. However, it is usually found in practice that a particular powerplant has developed a long-term contract with a specific mine, or a few mines, that provides a consistent quality of coal, and the powerplant is then operated in adjustment for the particular feedstock, so that the flyash generated by a specific powerplant can be well characterized. These properties are depended upon as long as the coal supply and plant operation are consistent. Surveys have found that particular powerplants are a source of flyash of distinctive properties that could be selected if needed to accomplish some particular purpose, such as strip mine reclamation where a limey amendment is needed.

Many studies of flyash, such as those of Townsend and Hodgson[12] have expressed concern over the high amounts of boron contained in flyash applied to soil. The boron is considered to be present as a complex glass-like borosilicate, and thus potentially available for soil release over high levels of boron in coal are not universally found, suggesting a regional or depositional variation in coal boron composition. Some workers believe that higher boron levels are a result of coal depositional swamp development under heavy influence of sea water (marine environment) while lower coal boron levels are found where coals formed under continental or less saline conditions.

Martens[5] has extensively reviewed literature on the implications of agricultural use of flyash. Flyash particles are silt or fine-sand sized, and can be considered as amorphous silica with crystalline impurities of many elements in varying amounts. The soluble salt content was found to range between 1 and 3% with pH ranging from below 5 up to 12. Neutralizing capacity ranged up to almost one-fifth that of calcium carbonate. Studies were made of the capability of flyash to supply the plant nutrients boron, molybodenum, phosphorus, and zinc. Results varied with the source of flyash and the type of soil to which it was applied. He concluded that application of flyash may be beneficial for crop production where the material increases the pH of acidic soil, the availability of an essential element in soil, or the the amount of available water in soil. Indiscriminate application of flyash to soil was deemed undesirable because of (a) possible decreased plant growth due to boron toxicity, (b) injury from a high concentration of soluble salt, (c) phosphorus deficiency to plants induced by reaction of soil phosphorus with hydroxides and oxides of aluminum and iron in flyash, (d) possible nutrient deficiencies induced at high levels of soil pH. Monitoring of the elemental composition, including plant-available elements, in flyash prior to incorporation into agricultural soils was considered essential to forestall possible future problems.

Solids generated by stack scrubbers are an increasingly significant waste disposal problem for coal-burning powerplants and other industrial plants that currently exhaust fluegasses unchecked. Rossoff, et al.[9] and Proceedings[7] have presented the most recent review of the status of flue-gas-desulfurization (FGD) product disposal. These volumes contain detailed papers which present industry and regulatory experience to date in this field.

The disposal of scrubber sludges presents a potential water pollution problem and land reclamation problem because of soluble species and sludge dewatering difficulties. Sludges containing leachable chemical pollutants will require containment within the disposal site or chemical fixation to reduce leaching potential. Permeability of the sludge to leachate waters varies tremendously depending on sulfate/sulfite composition, moisture content, compaction, and flyash content. Characterization of input materials such as coal, flyash, make-up water, lime, and limestone showed that most of the constituents of concern, which without scrubbing are discharged in the flyash and flue gas, originate in the coal.

Chemical analysis of five untreated scrubber sludge liquors showed mercury, selenium, boron, chloride, sulfate and TDS considerably in excess of water quality criteria. Each of the sludge liquors exceeded EPA proposed criteria in at least one of the following trace elements: arsenic, cadmium, chromium, lead, mercury, and selenium. Particular excesses existed for chloride, sulfate and TDS. Fluorine is also becoming a major concern. Soil attenuation of selenium, boron, and chloride is known to be ineffective. Mechanical stability of the sludge at a given moisture content is affected by the sulfite content; sludges proportionately higher in sulfite than sulfate tend to be more thixotropic, leading to compaction and stability problems in developing completed landfills for structural or recreational uses.

SUMMARY

Coal mining industry by-products subject to land disposal include washing plant wastes, AMD neutralization sludges, powerplant flyash and bottom ash, and flue-gas-desulfurization sludges. The geochemical composition of the raw coal determines the elements and compounds that are removed in coal cleaning operations, and thus are concentrated in cleaning plant wastes. Likewise, elements carried within the coal itself accumulate in the combustion exhaust products, flyash, bottom ash, and flue-gas-desulfurization sludges. Elements solubilized as groundwater passes through coal seams and associated rock strata contaminate mine drainages, and are found in mine drainage treatment residues.

Ultimate disposal of most of these solid wastes has heretofore been into ponds and dumps for perpetual storage. Recent studies of elemental constitution, leachate water composition, and other environmental aspects of disposal of these materials indicate that greater notice must be taken of the potential reactions between the product, containment medium, and associated waters, in order to prevent long-term degradations to the environment. Various research and demonstration projects are showing short-term improvements; but study efforts must be continued to resolve the long-term problems concerning the leaching and percolation of acid, heavy metals, and other toxic materials associated with coal.

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Phosphate Transport Through Soil

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Phosphorus in water readily reacts with the available calcium or iron and aluminum in soil to form relatively insoluble compounds, and must soils have a large capacity for immobilizing applied phosphorus. The phosphorus concentration in naturally occurring ground waters is low, typically 0.05 mg/l or less. It is, thus, easy to see why designers ignore phosphorus when designing land application wastewater treatment systems. Soils do, however, have a limited capacity for immobilizing applied phosphorus. The objective, herein, is to discuss factors affecting phosphorus transport in relation to land application of wastewater.

Land application of waste material containing phosphorus can be thought of in two different ways. First, the land can be considered a treatment facility where the objective is to remove phosphorus from a waste stream prior to discharge. Secondly, the land can be considered as a media by which phosphorus can be recycled through crop production. When the application rate is low, plant removal can play a significant role in the fate of applied phosphorus; but, as the application rate increases the significance of plant removal is reduced.

Table I gives some typical phosphorus removals which can be expected by plants.[1] The impact of the plant on the treatment system can be seen by following some example calculations using the following simplified balance equation for phosphrous transport

$$L = A - (C + S)$$

where L = Loss of phosphorus from the land treatment facility;
A = application of phosphorus to the treatment facility;
C = crop removal of phosphorus;
S = net gain in storage of phosphorus by the soil profile.

C can be determined from the values in Table I; A can be calculated with a knowledge of the phosphorus concentration in the wastewater being supplied to the treatment system and a knowledge of the wastewater's application rate.

Example 1. If the phosphorus concentration in the applied wastewater is 10 mg/l as phosphorus; the proposed application rate is 1 ft/year; and corn is to be grown at the treatment facility which can be expected to remove 31 pounds of phosphorus per acre per year.

then A (lbs/acre/yr) = 2.7 x concentration of P in wastewater (mg/l) x annual application of wastewater (ft)

A = 27 lbs/acre/yr
L = 27 - (31 + S)
L + S = - 4 pounds/acre/yr.

This would indicate no phosphorus would be lost from the treatment system, and supplemental phosphorus would be required to maintain the level of production.

Example 2. If the phosphorus concentration in the applied wastewater is 10 mg/l as phosphorus; the proposed application rate is 50 ft/yr; and rice is to be grown at the treatment facility which is expected to remove 20 pounds of phosphorus/acre/year, then using equation (1)

L = A - (C + S)
L = 1,350 - (20 + S)
L + S = 1,330 pounds/acre/yr.

Few soils would have a capacity to remove this amount of phosphorus without losing some from the treatment facility.

With this introduction, it is clear that a knowledge of the fate of phosphorus (S) in soils and the transport of phosphorus (L) through soils is desirable when considering the design of a land treatment system.

There is a large variability in a soil's ability to sorb phosphorus. A soil's capacity to sorb phosphorus is a function of pH and the concentration of phosphorus in the applied waste material. In other words, as the applied phosphorus concentration increases, the total capacity of the soil to react with phosphorus also increases. Simultaneously, passing water through the profile reduces the total capacity of the profile to react with phosphorus. This is because the elements which have the potential to react with phosphorus are washed out of the profile.

Figure 1 shows the relative end points of the applied phosphorus as a function of pH; thus, in acidic soils, we can conclude that iron and aluminum play a predominate role in a soil's capacity for sorbing phosphorus. In basic profiles, calcium is the predominate actor, while neutral soils give a confused picture with many compounds influencing the fate of phosphorus.

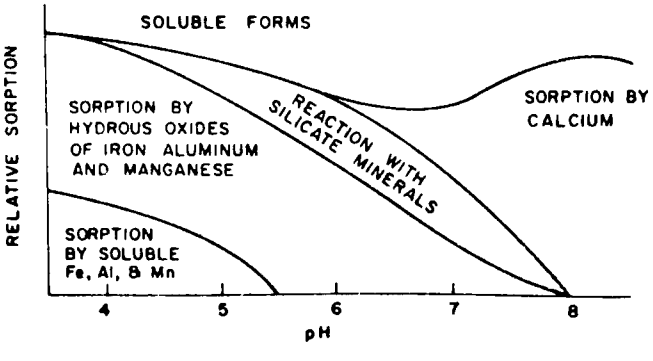

Figure 1. Fate of phosphorus applied to soils.

Table I: Plant Phosphorus Uptake by Group

	Pounds per acre	
	P_2O_5	P
Corn:		
180 bu. grain	70	31
8,000 lbs. stover	30	13
Cotton:		
1,500 lbs. lint and 2,250 lbs. seed	38	17
stalks, leaves, burrs	25	11
Wheat:		
80 bu.	44	20
8,000 lbs. straw	10	4
Oats:		
100 bu.	25	11
straw	15	7
Barley:		
100 bu.	40	18
straw	15	7
Rice:		
7,000 lbs. grain	46	20
7,000 lbs. straw	14	6
Sugar beets:		
30 tons roots	15	7
16 tons tops	25	11
Sugar cane:		
100 tons stalks	90	40
tops and trash	66	29
Tobacco (burley):		
4,000 lbs. leaf	14	6
3,600 lbs. stalks, tops, suckers	16	7
Soybeans:		
60 bu.	49	22
7,000 stalks, leaves, pods	16	7
Peanuts:		
4,000 lbs. nuts	22	10
5,000 lbs. vines	17	8
Apples:		
600 boxes (42 lbs.)	8	3
Grapes:		
12 tons fruit	23	10
vines	12	5
Oranges:		
600 boxes (90 lbs.)	23	10
trees (70/acre)	32	14
Tomatoes:		
40 tons fruit	67	30
4,400 lbs. vines	20	9
Potatoes:		
500 cwt	80	36
vines	34	15
Celery:		
75 tons tops	130	58
roots	35	16
Sweet potatoes:		
400 bu.	26	12
vines	14	6
Cabbage:		
35 tons	35	16
23 tons stem and leaf	28	12
Snap beans:		
4 tons	21	9
plants	12	5
Table beets:		
25 tons roots	30	13
20 tons tops	13	6
Flax:		
30 bu.	20	9
2,100 lbs. straw	5	2
Cucumbers:		
10 tons	14	6
vines	14	6
Peas:		
3 tons	9	4
pods and vines	17	8
Onions:		
30 tons	80	36
Lespedeza:		
3 tons	50	22
Johnson grass:		
12 tons	190	84
Para grass:		
12 tons	98	43
Napier grass:		
12.5 tons	147	65
Guinea grass:		
11.5 tons	101	45
Tall fescue:		
3.5 tons	65	29

The "total capacity" of a soil to react with phosphorus without a knowledge of how fast the reaction can take place is misleading. To illustrate this phenomenon, consider two hypothetical soil profiles, both with the same "total capacity"—one with crushed limestone rock; the other of finely ground limestone. Both profiles, then, are constructed of the same material. If wastewater is applied at the same rate to each profile, phosphorus will be detected at the effluent from the coarse material long before it is eluted from the fine material. If one calculates how much phosphorus should have reacted, it would be observed that both columns elute phosphorus long before their "capacities" are reached.

To obtain a feel of how phosphorus moves through soil, consider some typical laboratory breakthrough curves of phosphorus in short columns. In each of the following examples, the independent variable time will be plotted as a function of the dependent variable phosphorus concentration of the column effluent. In addition, the influent concentration in superimposed on the curve. In these columns (5 cm in length), waste containing 9.2 mg 'P'/l was applied at 88 ft/yr (26.8 m/yr), this would be in a range typical for high-rate infiltration-percolation systems. The first soil (Figure 2) is a Lakeland fine loamy sand from Florida with pH of 7.2. There are three regions of the curve presented. First is an area where phosphorus is being applied. Here, during the first four days of application, essentially no phosphorus passed through the profile. Extrapolating these data one would project that 100 pounds of phosphorus per acre foot of soil could be applied before any measurable phosphorus is detected in the effluent. This compares to 1,500 pounds of phosphorus per acre foot total capacity based on the calcium in the soil sample.* This may be close to correct if the waste is applied continuously with no rest period. Notice in the second region of the curve that when phosphorus is removed from the waste stream and the system is allowed to rest, the capacity to immobilize phosphorus is partially restored. In the second application period, 70 pounds per acre foot of soil were applied before any measurable change was observed in the effluent concentration; thus, 70% of the soil's capacity was "rejuvenated" prior to the second application. The amount of "rejuvenation" will depend not only on the "rest period" but also the amount of water without phosphorus (i.e., rainwater) passing through the profile leaching out excess relatively soluble phosphates.

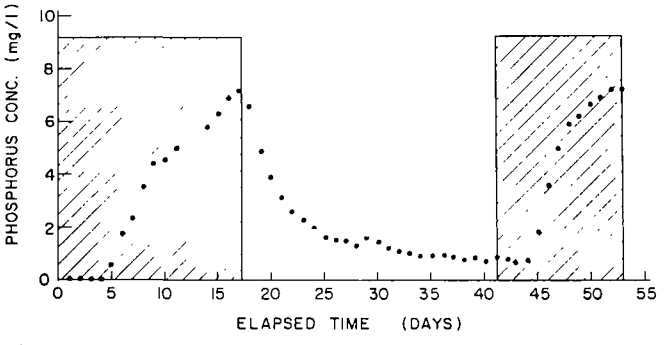

Figure 2. Experimental breakthrough curve for A 5 cm column of Lakeland soil when simulated wastewater, with a phosphorus concentration of 9.2 mg/l, is applied at an application rate of 88 ft/yr. The application rate, 88 ft/yr, remained constant throughout the experiment. Phosphorus was included in the applied water in the shaded areas.

* The "total capacity" in basic soils, pH>7.0, assumes one mole of calcium will fix one mole of phosphorus such as would be the case for the formation of dicalcium phosphate dihydrate, $Ca\ H\ PO_4 \cdot 2H_2O$. It is assumed that the bulk density of the soil is 1.5 g/cc or 93.6 lb/ft.[3] Thus, the "total capacity" in pounds/acre foot of soil can be calculated as 31,600 x (percent calcium in the soil sample.)

The second soil to be considered is from the Maumee series in Indiana. This is an acidic soil, pH 5.3, where the total capacity should be a function of the iron and aluminum. Using breakthrough data, one would estimate under the experimental conditions when wastewaters were continuously applied, an estimated 290 pounds of phosphorus per acre foot of soil could be applied prior to any measurable phosphorus leaving the system. Allowing the system to rest will increase the system's overall apparent detention capacity. A total capacity term for acidic soils is difficult to estimate. If all of the aluminum is considered in the capacity term, it would require dissolving all of the clays in the soil. This would require many centuries. Thus, at the present time, it is not possible to reasonably estimate a total capacity for acidic soils.

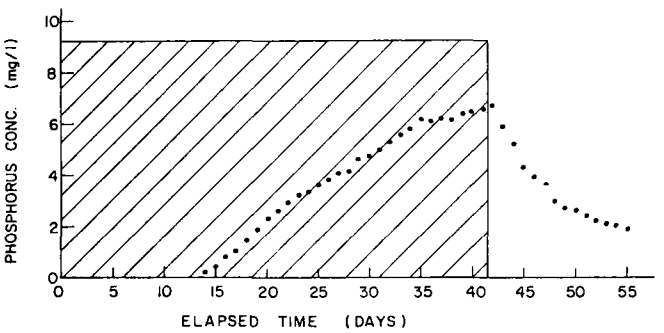

Figure 3. Experimental breakthrough curve for a 5 cm column of Maumee soil when simulated wastewater, with a phosphorus concentration of 9.2 mg/l, is applied at an application rate of 88 ft/yr.

A third soil comes from the Anway soil series of Arizona with a pH of 7.2. This is a finer textured soil than either of the first two samples. The experimental data shown in Figure 4 indicate this soil has a much greater sorption capacity than either of the two precious samples. Here, one would estimate the soil's capacity before any measurable discharge at 670 pounds of phosphorus per acre foot of soil. Based on the calcium in the profile, the capacity is 2,200 pounds of phosphorus per acre foot of soil.

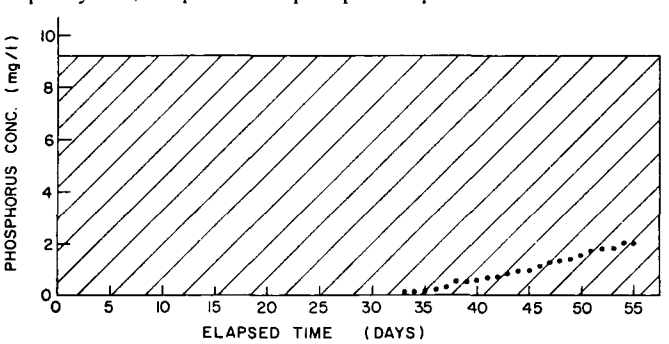

Figure 4. Experimental breakthrough curve for a 5 cm column of Anway soil when simulated wastewater, with a phosphorus concentration of 9.2 mg/l, is applied at an application rate of 88 ft/yr.

In each of the cases discussed thus far, the first detectable phosphorus is considered. If some point other than breakthrough is desired, the situation becomes more complex. Not all breakthrough curves have the same shape. Figure 5 is experimental data from a coarse textured soil from the Chigley soil series of Oklahoma. With a pH of 8.0 one would anticipate a capacity of 240,000 pounds of phosphorus per acre foot of soil because of the calcium in the soil sample. Here, the phosphorus was detectable after about 8 days of application. However, after 54 days of application, the concentration of P leaving the soil was still approximately 1 mg/l. Apparently, this particular soil is capable of releasing calcium at a rate sufficiently fast to form a relatively insoluble phosphorus compound, $Ca\ HPO_4 \bullet 2H_2O$ (dicalcium phosphate dihydrate). This indicates there is more calcium available for "immediate" reaction in this soil than in the other soils tested.

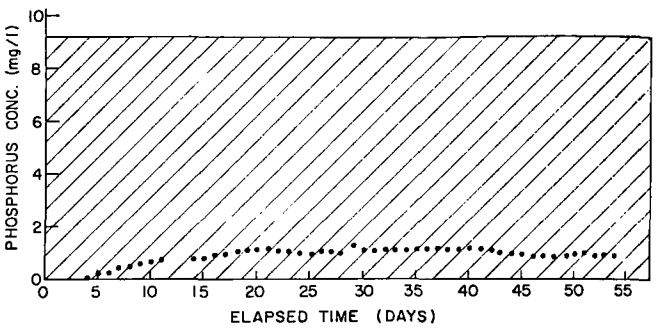

Figure 5. Experimental breakthrough curve for a 5 cm column of Chigley soil when simulated wastewater, with a phorsphorus concentration of 9.2 mg/l, is applied at an application rate of 88 ft/yr.

These examples point out some of the complexities of phosphate chemistry. Before an effective transport model can be developed, a firm understanding of the chemistry involved is required. At the present time, there is no accepted phosphate transport model in the literature. There are several attempts at developing transport models for phosphorus, and with additional work the accuracy and reliability of these models will be improved to an acceptable level.

Phosphate Transport

The dominance of the rate of reaction on the soil's ability to remove phosphorus has created the need for developing transport models capable of predicting how phosphorus will move through soils. In the following paragraphs, three methods based on laboratory sorption data are presented to predict how phosphorus will move through soils. Each of these procedures is compared with the previously discussed experimental breakthrough data to determine the reliability of the procedure.

It was mentioned that the higher the concentration of phosphorus in the applied waste, the greater the capacity for the soil to remove the applied phosphorus. It has been observed by many researchers that if soil is equilibrated with a solution containing phosphorus, experimental data can be generated which follows adsorption isotherm theories. Figure 6 shows experimental data, for the soils previously discussed, plotted as adsorption isotherms. The data and experimental procedures were previously presented by Enfield and Bledsoe.[2]

Adsorption data indicate what level of phosphorus must be supplied to the soil before a given solution concentration can be supported. It is generally easier to use the log transformed data as shown in Figure 7 than the linear form in Figure 6. This permits expanding the lower concentrations and obtaining a more detailed description of the sorption. One can then use these data to project how wastewater might be transformed as it passes through a soil profile. Figure 8 projects a breakthrough curve for the Lakeland soil by calculating the time that would be required for sufficient phosphorus to be applied to the soil to support the effluent concentrations plotted in the figure. These values are based on the flow rate of the applied solution and the concentration of phosphorus in the applied waste. Figures 9, 10, and 11 show the same predictive approach for the other three soils presented. Notice that in each case, this method of predict-

ing phosphate transport underestimates the soil's ability to assimilate phosphorus.

Using the adsorption isotherm approach, just discussed, assumes the soil and the phosphorus in solution were in equilibrium prior to the experimental measurements. Researchers have shown this to be an incorrect assumption. The more time allowed for equilibration, the greater the amount of phosphorus removed by the soil. Figure 12 shows how time plays an important part in the sorption phenomena. Here, the Lakeland isotherm is plotted on log transformed axis for eight different times of equilibration. The equilibration times approximate a geometric progression. This timed series of measurements has made it possible to generate a sorption surface which is a function of (1) equilibrating solution concentration, (2) amount of phosphorus sorbed by the soil, and (3) time allowed for equilibration.

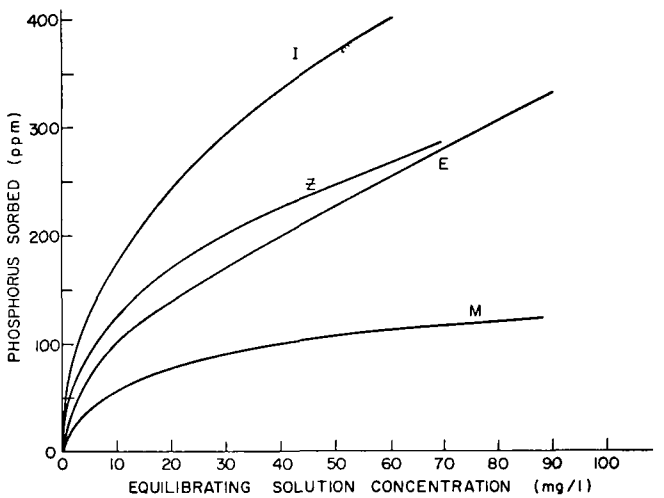

Figure 6. Adsorption isotherms for the four soil samples included in the study. Cruve m is the Lakeland soil, E the Chigley soil, Z the Maumee soil, and I the Anway soil. The time for equilibration is 10 hours. The letter key corresponds to the letter key in reference 2.

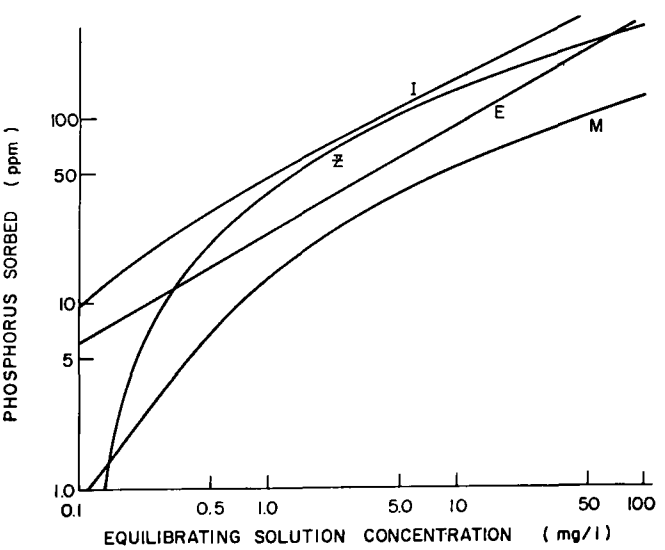

Figure 7. Log transormed adsorption isotherms for the four soil samples included in the study. Curve E is the Chigley soil, I the Anway soil, M the Lakeland soil, and Z the Maumee soil.

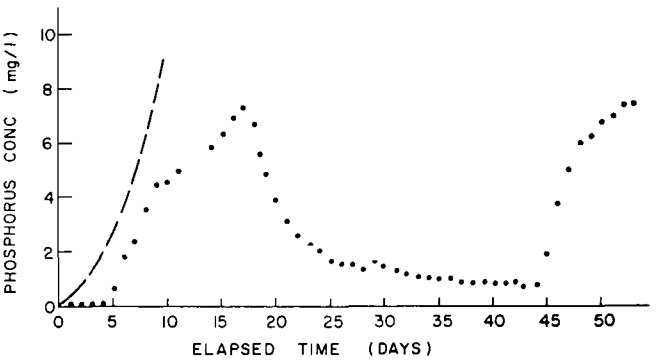

Figure 8. Projected breakthrough curve for the Lakeland soil. This curve is based on the adsorption isotherm curve M in Figures 6 and 7.

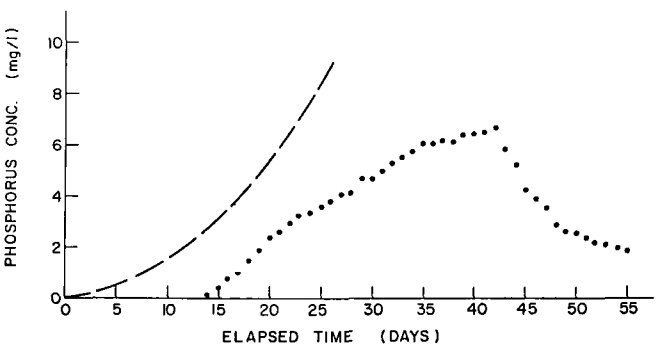

Figure 9. Projected breakthrough curve for the Maumee soil. The breakthrough curve is based on the adsorption isotherm date curve Z in Figures 6 and 7.

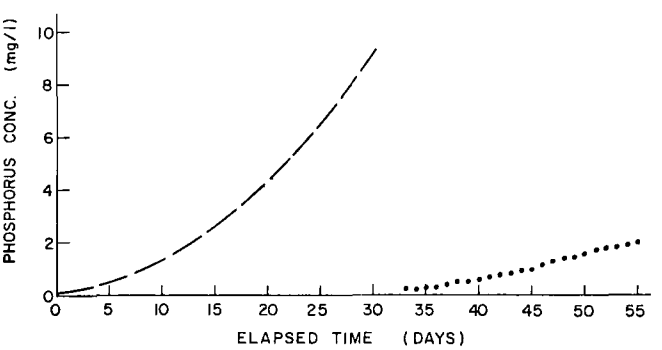

Figure 10. Projected breakthrough curve for the Anway soil. The breakthrough curve is based on the adsorption isotherm data curve I in Figures 6 and 7.

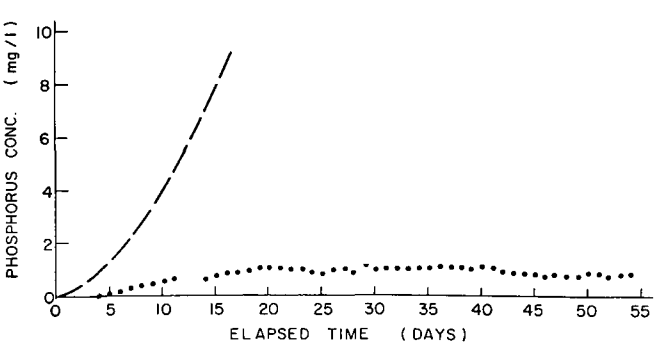

Figure 11. Projected breakthrough curve for the Chigley soil. The breakthrough curve is based on the adsorption isotherm data curve E in Figures 6 and 7.

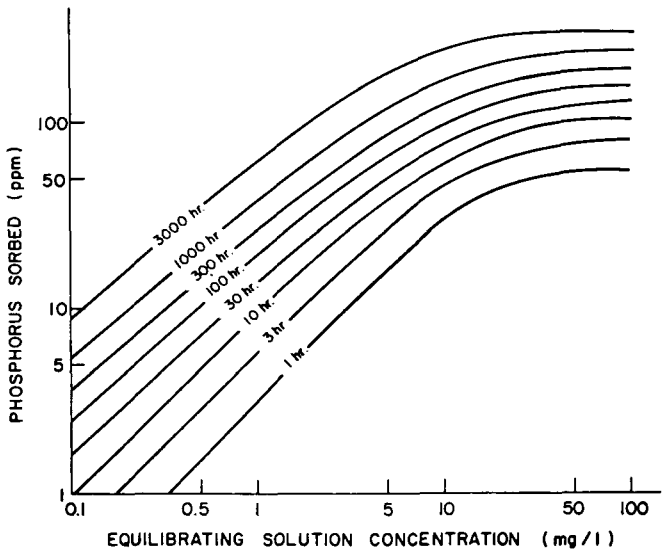

Figure 12. Time dependence of the sorption of phosphorus by the Lakeland soil. This family of curves thus develops a sorption surface.

These sorption surfaces suggest an alternate method of predicting phosphorus transport through soils. By using an approach similar to the equilibrium adsorption isotherm method just presented, but taking into consideration time of application, it is possible to develop breakthrough curves by interpolating times between actual measurements. This is accomplished by selecting an effluent solution concentration; determining the amount of phosphorus which must be supplied at several measurement times, based on flow rate and applied solution concentration; then determining the actual time by linear interpolation. Figure 13 is the breakthrough for the Lakeland soil developed in this manner. Figure 14 is the time dependent sorption surface for the Maumee soil, and Figure 15 is the calculated breakthrough curve. Figure 16 is the time dependent sorption surface for Anway soil, and Figure 17 is the calculated breakthrough curve. In Figure 18 the geometry of the sorption surface for the Chigley soil is quite different from the surfaces for the other soils presented. Here, a radial series of curves were measured with time while, in all the other experimental data, the curves appeared to be more or less parallel. This difference in geometry in the sorption surface is apparent also in both the calculated and measured breakthrough curves presented in Figure 19.

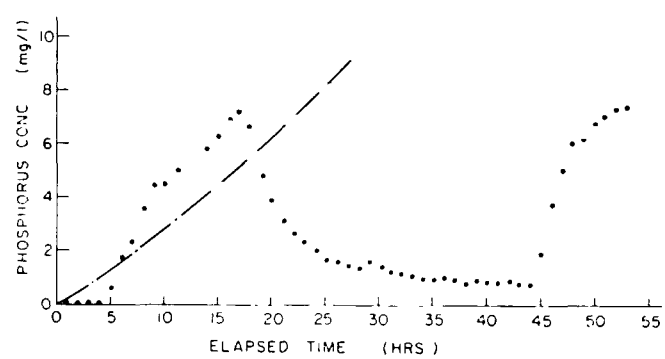

Figure 13. Projected breakthrough curve for the Lakeland soil. This projected curve is based on the sorption surface in Figure 12.

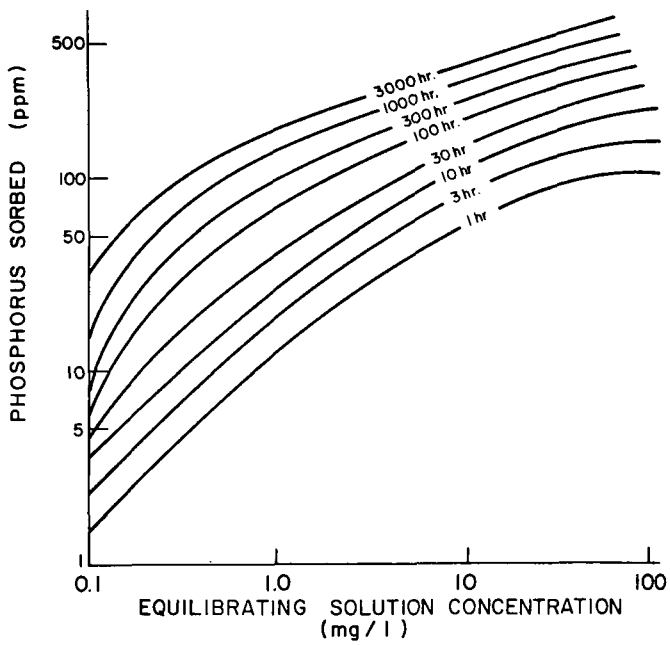

Figure 14. Time dependent sorption of phosphorus by the Maumee soil. The family of curves is used to project the movement of phosphorus through soils.

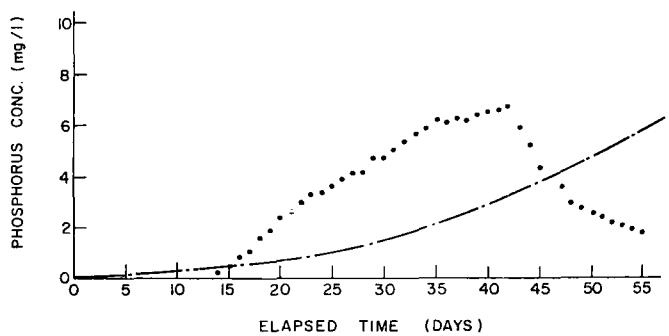

Figure 15. Projected breakthrough curve for the Maumee soil based on the sorption surface in Figure 14.

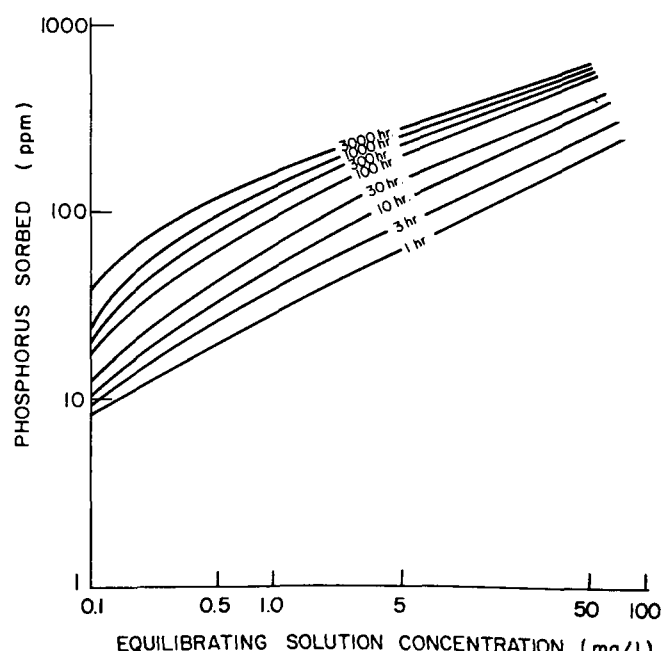

Figure 16. Sorption surface for phosphorus by the Anway soil.

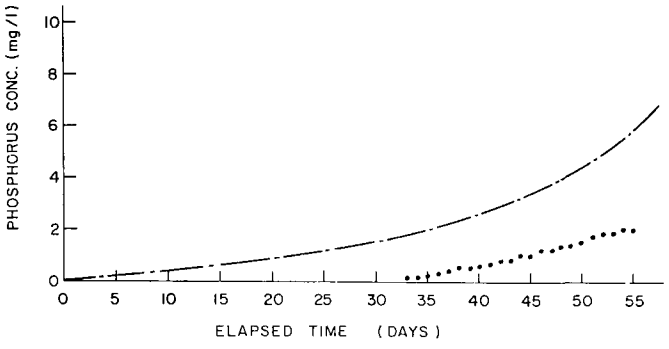

Figure 17. Projected breakthrough curve for the Anway soil based on the sorption surface in Figure 16.

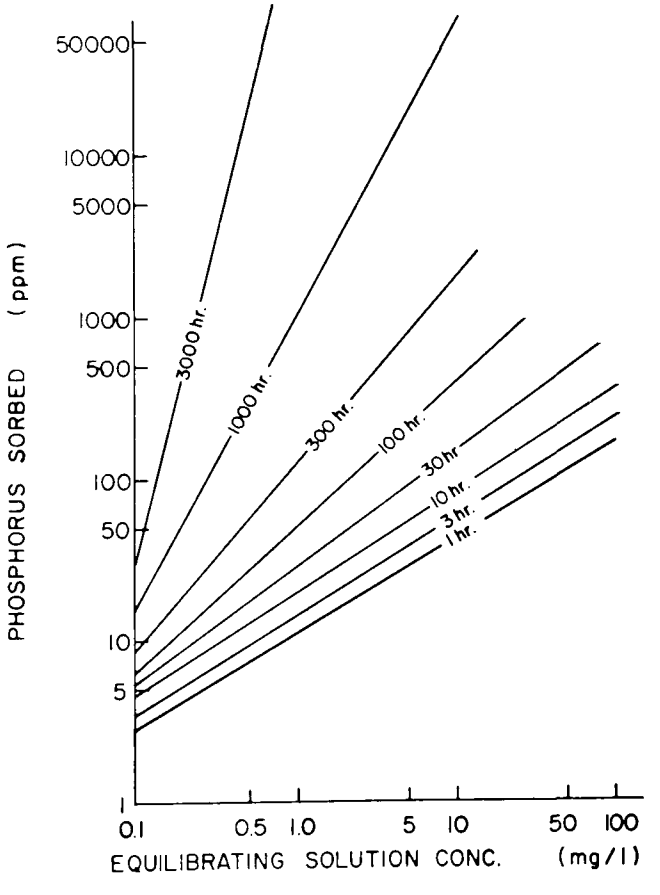

Figure 18. Phosphorus sorption surface by the Chigley soil.

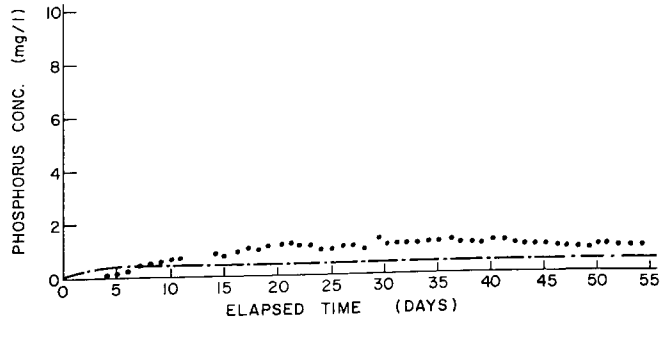

Figure 19. Projected breakthrough curve for the Chigley soil based on the sorption surface in Figure 18.

The two predictive methods thus far presented assume the concentration every place in the profile is the same. This is an obvious limitation of the procedures. Neither approach considers the history of application. The general approach which has been proposed to take these two factors into consideration follows miscible displacement theory. This requires a solution to the differential equation

$$\frac{\partial c}{\partial t} = -\overline{V}\frac{\partial c}{\partial x} - \frac{\rho}{\Theta}\frac{\partial s}{\partial t} \qquad (2)$$

where

c = solution phase concentration of phosphorus (mg/l)

$\overline{V}$ = average pore-water velocity (cm/hr)

x = distance from the beginning of the flow path

ρ = bulk density of the soil (g/cm^3)

Θ = fractional solution-filled-volume in the porous media

s = solid phase concentration of phosphorous ($\mu g/g$)

A miscible displacement approach should accurately predict a breakthrough curve if an accurate sink term ($\partial s/\partial t$) is available. The sink term gives an indication of the rate at which the phosphorus can be sorbed as a function of the equilibrating solution concentration and the amount of phosphorus already sorbed. One sink term which has been proposed is

$$\frac{\partial s}{st} = a\, c^b s^d \qquad (3)$$

where a, b, and d are constants. This is an empirical function which has been shown to conform to many sorption surfaces. Figure 20 is a graphical example of the sink term. Note the similarity between this function and the sorption surfaces presented in Figures 12, 14, and 16. Thus, we could expect this sink term to reasonably predict breakthrough curves for these three soils. Figures 21, 22, and 23 are the predicted breakthrough curves using the above miscible displacement approach. These breakthrough curves were obtained using a finite difference solution to the differential equation. Only part of the elapsed time could be projected using an IBM 1130 computer because of core limitations of the machine.

It appears that a reasonable fit will be obtained for the two soils with "low capacity" but the fit is unsatisfactory for the Anway soil sample. Apparently the sink term $\partial s/\partial t$ does not adequately describe the sorption of phosphorus by this soil. In Figure 24, the projected breakthrough curve for the Chigley soil samples is presented with the experimental data. A reasonable fit is obtained over the projection period even though the shape of the sorption surface is quite different from the one described by the sink term.

CONCLUSIONS

None of the approaches presented are capable of accurately predicting how phosphorus will move through a profile every time. None of these methods are capable of predicting the phosphorus concentration on the desorption side of the breakthrough curve. We can, thus, conclude that additional work is still required to develop more refined predictive methods and

increase our confidence in our ability to understand phosphate transport through soils.

The time dependent sorption surface approach or the miscible displacement approach gives an adequate first approximation to the transport of phosphorus through soils. Using one of these approaches is much better than ignoring the problem altogether and gives a basis for a design philosophy.

Since the models are not capable of predicting the desorption of phosphorus, it is felt a more reliable estimate can be obtained for the entire life of a proposed treatment system by considering the average application rate, thus, taking into consideration the "rest period" and an adjusted applied solution concentration to permit including plant removals and dilution effects of rainwater.

Through use of these design procedures, the confidence limits can be developed and reliability of a given approach determined. It is through application that an approach will be verified. The two above methods are good starting points to develop these design procedures.

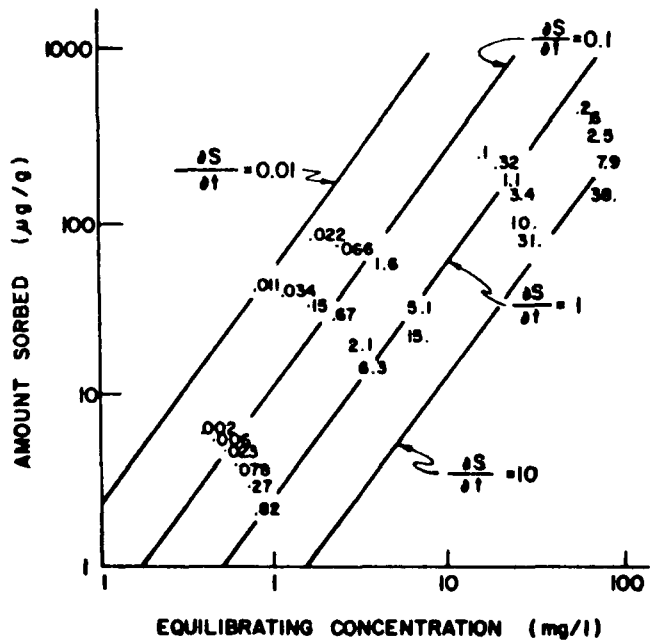

Figure 20. Regression of the empirical rate equation to experimental data of a Maumee soil sample. In the figure, the rate of sorption is presented in parts per million per hour. The experimental data points are plotted numerically with the data point located at the decimal point of the value (a = 7.3; b = 2.28; d = -1.63).

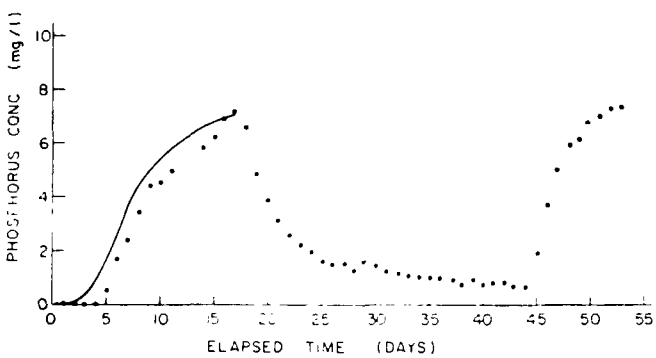

Figure 21. Projected breakthrough curve for the Lakeland soil based on the miscible displacement approach (a = 183; b = 2.40; d = -2.91; ρ = 1.5 g/cc; θ = 0.18; $\overline{V}$ = 1.69 cm/hr).

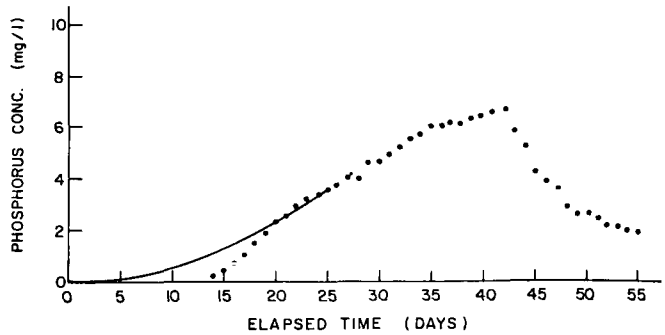

Figure 22. Projected breakthrough curve for the Maumee soil based on the miscible discplacement approach (a = 280; b = 2.08; d = -2.08; ρ = 1.5 g/cc; θ = 0.18; $\overline{V}$ = 1.69 cm/hr).

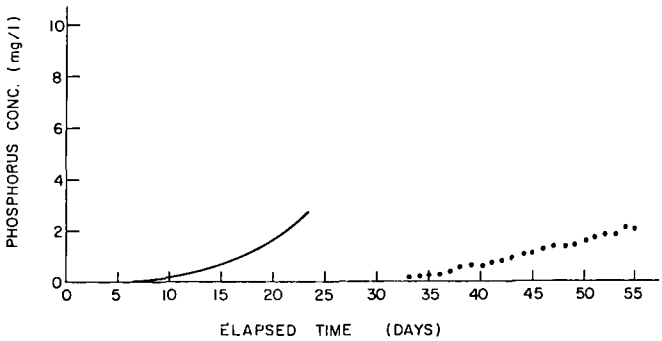

Figure 23. Projected breakthrough curve for the Anway soil based on the miscible displacement approach (a = 612000; b = 2.81; d = -3.87; ρ = 1.5 g/cc; θ = 0.18; $\overline{V}$ = 1.69 cm/hr).

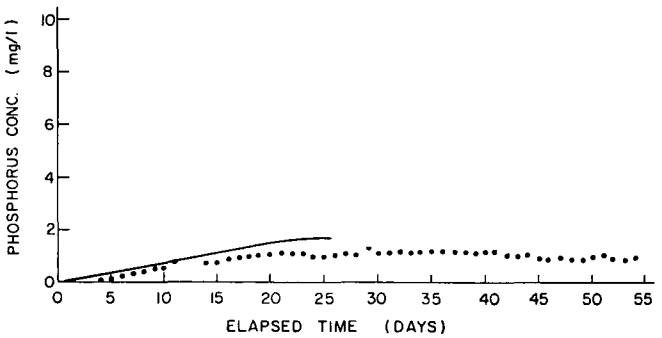

Figure 24. Projected breakthrough curve for the Chigley soil based on the miscible displacement approach (a = 4.88; b = 1.92; d = -1.05; ρ = 1.5 g/cc; θ = 0.18; $\overline{V}$ = 1.69 cm/hr).

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Updating the Nitrogen Cycle

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INTRODUCTION

In a publication discussing disposal of residues on land, it is appropriate that we spend some time reviewing the nitrogen cycle and expanding our concepts about it based on recent research information. Since the fate of the nitrogen (N) applied in waste material often dictates or prescribes what an environmentally acceptable waste management practice would be, it is essential that everyone involved in management decisions concerning the application of wastes on land thoroughly understand the N cycle. Considering this fact, the first part of this paper will deal with a review of where N is found in the biosphere and the N cycle, with emphasis on the physical, chemical and biological processes that affect the transport of N from one pool to another. The remainder of the paper will be devoted to using known principles and research findings to make estimates on how additions of N or changes in soil management can affect the N balance in soils and the amount of N which may be found in various pools or compartments within the biosphere.

Nitrogen in the Biosphere

Nitrogen is found in many chemical and biological forms but most of it resides in the atmosphere, the soil, and the water. Although some N is cycled through man, animals and plants, the amount found in these biological organisms is very small as compared to the amount in the atmosphere, soil and water[9]. The rate of chemical and biological transfers and the rate of hydrologic transport are influenced by man's activities, by climate, and by other environmental factors. As a result, the amount of N in the various compartments or pools will change from time to time. In general, however, our overall goal should be to develop management systems which will result in maximum utilization of available N by plants and minimum loss of N to surface or ground waters.

Soils contain substantial amounts of organic N, generally in a range of 1000 to 3000 kg/ha, but most of this N is resistant to microbial decomposition and mineralizes slowly. Mineralization rates of only 1 to 3% per year are common; at these rates mineral soils would supply only 10 to 90 kg/ha of N annually[11,14]. This means that we usually have to compensate for limited supplies of available soil N by adding fertilizer, manure, sewage sludge or other nitrogeneous waste materials. As the amount of N applied increases, the percent of the applied N recovered by the crop decreases. Some of the nitrogen not used by the crop could become a potential environmental hazard if excess nitrate nitrogen (NO_3-N) enters drinking water supplies. However, it is important to emphasize that the residual NO_3-N constitutes only a potential hazard because it may be converted to atmospheric N by denitrification, immobilized by crop residues, or carried over for use by a succeeding crop. With any of these possibilities the N not recovered by the crop would not be considered an environmental hazard because it would not enter surface or ground water. An exception to this statement would be that nitrous oxide (N_2O), one of the products of denitrification, may cause depletion of the ozone layer in the upper atmosphere[2].

Nitrogen Cycle

Organic-Inorganic Nitrogen Transformations

Nitrogen is transferred between soils, plants, animals, and man so it often does not enter or leave the pools of N in the atmosphere or water. However, the N cycle properly includes all exchanges and transformations noted in Figure 1. A basic understanding of this cycle is necessary in order to predict the fate of all forms of N in the ecosystem.

Ammonification (Reaction 1, Figure 1) is the biological conversion of organic N into ammonium nitrogen (NH_4-N). It occurs over a wide range of soil and climatic conditions, however, the rate of reaction is favored by warm temperatures and good aeration of the soil. Ammonium N is available to plants, but it generally does not leach because the positively charged cation (NH_4^+) is held on the surface of the negatively charged soil particles. On soils with a low cation exchange capacity, especially irrigated sandy soils, some downward movement of NH_4-N may occur.

Nitrification (Reaction 2, Figure 1) is the biological transformation of NH_4-N to NO_3-N. Nitrate is readily available to plants. However, it is a negatively charged anion (NO_3^-) so it remains in solution in the soil and may be leached below the root zone as water percolates through the soil. This fact gives rise to most of the concern being expressed about N in relation to water quality. In warm, well-aerated, and properly-limed soils (pH 5.6–8.0), much of the NH_4-N is changed to NO_3-N within one to three weeks after application. Recent efforts to improve the recovery of NH_4-N fertilizer have been directed toward reducing the solubility of fertilizer, slowing down the rate of nitrification by the use of bacterial inhibitors, or maintaining environmental conditions which are not favorable for the nitrifying bacteria.

Immobilization (Reaction 3, Figure 1) is the process whereby bacteria which decompose carbon-rich crop residues or wastes immobilize or "tie-up" the available N (NH_4-N + NO_3-N). The role immobilization plays in the fate of residual available N must be carefully evaluated because the N not recovered by the crop may be utilized by soil microorganisms as they decompose carbonaceous residues such as straw and corn stover[14]. Even though N immobilized as microbial protein is again mineralized after decomposition takes place, immobilization reduces leaching of NO_3-N during that part of the year when most crops are not assimilating N, i.e., the late fall and early spring.

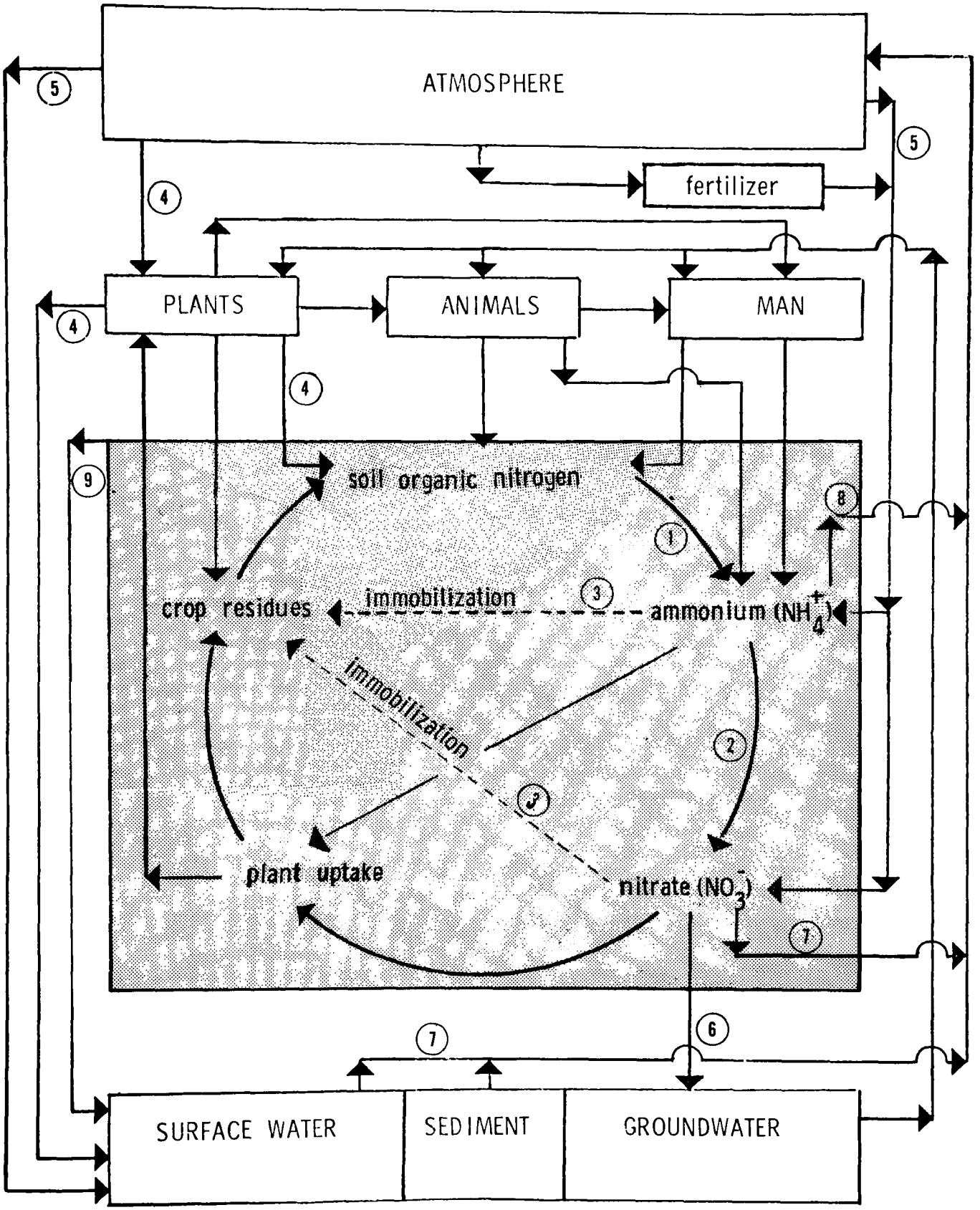

Figure 1: The Nitrogen Cycle and Transfers of Nitrogen Between Various Compartments in the Environment [The Encircled Numbers Refer to Reactions Discussed in the Text [16]].

Additions of Nitrogen to the Soil

Fixation of Atmospheric N (Reaction 4, Figure 1) by bacteria results in the addition of considerable quantities of N each year. In calculating N budgets, perennial legumes contribute a net addition to the soil and should be credited accordingly when determining the N requirement for a succeeding crop. However, annual legumes probably assimilate as much available soil N in the year they are grown as they provide to the succeeding crop. In fact, recent estimates indicate that growing soybeans results in a net removal of N from the soil system, especially when the soil contains residual inorganic N from a preceding crop[6].

As indicated by Reaction 4 in Figure 1, some lower plants, primarily blue-green algae, fix atmospheric N in surface water and may contribute significantly to the N budget in some lakes and streams. For example, 14 percent of the N in Lake Mendota, Madison, Wisconsin is estimated to be fixed by algae[8]

Wastes excreted by animals and man can be returned to the soil as organic N or as some form of available N. Animals produce large quantities of wastes but as much as 80 percent of the N in these wastes probably is lost in the collection handling, and spreading processes and is not returned to cultivated land[15]. Humans excrete significant quantities of N in wastes but only a small portion of these wastes, probably less than 20 percent, are being returned to cropland at the present time. Through better management of animal manure and development of systems to apply more human wastes on land, the amount of N recycled from these wastes could easily be doubled or tripled. More efficient utilization of organic wastes would significantly reduce fertilizer N requirements in some localized areas but nationwide fertilizer needs could be reduced only 10 to 15 percent, even with very efficient waste management systems.

Fertilizer N is added to soils in relatively large amounts, often in the range of 50 to 200 kg N/ha, to replace the N removed by crops or lost by various physical, chemical, and biological processes. As indicated in Figure 1, atmospheric N is converted into NH_4-N or NO_3-N in the manufacture of fertilizer N. However, most of the N fertilizer presently added to the soil is in the form of NH_4-N. Ammonium nitrate contains half of its N as NO_3-N but its usage is declining rapidly because it is more expensive than other forms of N fertilizer. When urea, a soluble organic form of N, is added to the soil, it is quickly converted to NH_4-N by the urease enzyme.

Precipitation (Reaction 5, Figure 1) generally adds 5 to 10 kg/ha acre of available N annually[4]. This is a small addition on a per hectare basis but, since the entire land and surface water area receives precipitation, it is a significant contribution to the total N budget.

Losses of Nitrogen from the Soil

Leaching of nitrate (Reaction 6, Figure 1) can be a serious problem, especially in humid areas on light-textured soils because the water holding capacity of these soils is low and relatively small amounts of rain or irrigation water readily move NO_3-N below the root zone[10]. Loss of NO_3-N by leaching is of environmental concern because it adds to the pool of nitrates in the surface and groundwater. As shown in Figure 1, once the NO_3-N is in the water compartment very little will reenter the N cycle. Only small quantities of water would be consumed by man and animals, or applied to irrigated soils and taken up by plants.

Denitrification, a process by which soil bacteria change NO_3-N into unavailable atmospheric N (Reaction 7, Figure 1), occurs primarily in poorly aerated, waterlogged soils, but some denitrification can take place within the aggregates of well-drained soils, especially when heavy rains occur. Denitrification takes place rapidly. If water stands on the soil more than three or four days during the growing season, much of the NO_3-N will be lost by denitrification. For denitrification to occur, decomposable organic matter must be present as a source of energy. In general, denitrification will not take place deep in the subsoil or in the groundwater because of inadequate sources of energy material to support the growth of denitrifying bacteria. An important exception is that denitrification, and to a lesser extent immobilization, of NO_3-N occurs as groundwater moves through sediments into a lake or stream[8].

Volatilization of ammonia (NH_3) is another way in which N is lost to the atmosphere (Reaction 8, Figure 1). When urea fertilizer, sewage sludge, or fermented manure is surface applied and not incorporated into the soil, relatively large amounts of NH_4-N can be lost as NH_3. Injection or immediate incorporation of these materials eliminates most of the volatilization loss. Some NH_3 volatilization loss also occurs when anhydrous ammonia or low-pressure solutions containing NH_3 are not properly applied. The total losses are thought to be small but in localized situations as much as 50 percent of the NH_4-N, such as from surface applied urea or sewage sludge, may be volatilized and lost as NH_3.

Erosion (Reaction 9, Figure 1) may account for loss of a considerable amount of organic N. Runoff water tends to selectively carry fine soil particles and organic matter from the land. Thus, sediment contains a higher concentration of total N than the soil which remains behind. Runoff water generally contains very low concentrations of NH_4 and NO_3-N, even though fertilizer use and the production of cash grain crops has increased dramatically in recent years.

Crop removal accounts for the transport of much N from the soil to other N pools (Figure 1). Some of the N is returned to the soil in crop residues and manure. Even so, removal of 50 to 150 kg N/ha in the harvested portion of many agronomic and horticultural crops is common.

Nitrogen Balance

In recent years we have been concerned with producing more food and this generally means using more N and following a more intensive crop rotation. Concomitantly, we have been concerned about the addition of excessive amounts of N to natural waters, depletion of soil organic N, erosion losses, and other undesirable side effects which often accompany efforts to increase crop production.

One way of trying to arrive at an answer to these questions, especially the concern about increased leaching of N, is to look at the N budget, i.e., compare N inputs with N removals. Such a comparison has been made on a nationwide basis[15] and is presented in Table I. Even though some of these estimates are speculative, certain trends are apparent. When fertilizer N consumption was low in the 1930's and 1940's, removals of N far exceeded inputs; thus little leaching of fertilizer N could have occurred. Since 1969 most estimates indicate that inputs have equalled or exceeded removals, and some leaching of fertilizer is likely to have taken place in areas of high fertilizer N use.

Even though the balance sheet for 1969 (Table I) shows that inputs and removals were equal, considerably more N was removed from harvested crops than was applied with N fertilizer. This observation has led some to believe that N fertilizer cannot be contributing significantly to the pollution of the natural waters with NO_3-N. However, progressive farmers, especially those producing "cash crops," are often adding more N fertilizer than their crops recover[17].

A more recent estimate for the midwestern states is presented in Table II[16]. It is based on 1975 nutrient removals and inputs and shows that N fertilizer additions exceed removals in several states. When other sources of N, such as manure and legumes are credited, total additions exceed total removals in most of the states surveyed. However, this does not necessarily mean that excess N is being applied. Some N is lost to the atmosphere by

NH_3 volatilization and denitrification. In the case of denitrification, losses will be substantial whenever well fertilized soils become waterlogged.

Table I: Balance Sheet of N in the USA: Estimated Changes from 1930 to 1969 on Harvested Cropland.[15]

Item	Nitrogen--Millions of Tons 1930	1947	1969
Inputs of Nitrogen from:			
1. Fertilizer N	0.3	0.7	6.8
2. N fixed by legumes	1.7	1.7	2.0
3. N fixed (nonsymbiotic)	1.0	1.0	1.0
4. Barnyard manure	1.9	1.3	1.0
5. Roots of unharvested portions of crops	1.1	1.5	2.5
6. Rainfall	0.8	1.0	1.5
Total	6.8	7.2	14.8
Removals of Nitrogen by:			
7. Harvested crops	4.6	6.5	9.5
8. Erosion	5.0	4.0	3.0
9. Leaching of soil N	4.0	3.0	2.0
10. Leaching of fertilizer N[a]	0	0	?
11. Denitrification[2]	?	?	?
Total	13.6	13.5	14.5

[a]Zeros and question marks indicate that little is known about the magnitude of these losses.

Another important concept relating to this question is that some leaching loss of N is inevitable whenever drainage occurs because crops cannot remove all of the NO_3-N from percolating water. Optimum fertilization of deep rooted annual crops such as corn or sudangrass grown on medium- and fine-textured soil, usually results in drainage water containing from 2 to 15 ppm of NO_3-N[1,3]. Other researchers have observed that a concentration of at least 40 ppm NO_3-N may be required in the soil water in the root zone of sudangrass[12] and irrigated potatoes[13] in order to produce maximum yields. It should also be pointed out that some leaching occurs when plants are not growing. In fact, midwestern researchers[18] have found that of the total N leached, about 70% was leached before corn was planted. These observations indicate that some leaching loss of N will occur even under the best management systems.

Nitrogen Model for Wisconsin

If reasonable estimates can be made for all N inputs and losses, and if rates of transfer between the various N pools can be estimated, it ought to be possible to construct a N model which would help predict the effect of many soil, crop and waste management practices on the fate of N in the environment. In some cases, accurate estimates can be made, such as the amount of N fertilizer added or the amount of N exported in crop and animal products, but only crude estimates can be made for other parts of the model such as leaching, denitrification and volatilization losses. Because of these uncertainties, an N model should not be used to try to precisely define the actual amount of N in a pool. However, a model would be effective in predicting general trends, especially when rather large changes in N inputs or outputs are made. A model should find its greatest use as an aid to decision-makers and researchers plan for the future.

Table II: Estimate of Nitrogen Additions and Removals on Cropland in Selected Midwestern States.[16]

State	Approx. Cropland Acreage	N Removal	N Additions Fertilizer	Other Sources	Total	Net Addition (+) or Removal (-)	Ratio of Fertilizer N Applied to N Removed
	x 10^6 acres						
Arkansas	7.7	72241	105870	7867	113737	+41496	1.47
Illinois	22.7	535400	724109	46755	770864	+235464	1.35
Indiana	11.5	371723	345762	54508	400270	+28547	.93
Iowa	23.8	645237	712576	112825	845401	+180164	1.10
Kentucky	4.2	65410	117000	26200	143200	+77790	1.79
Michigan	6.5	155250	120000	36980	156980	+1730	.77
Minnesota	20.9	386300	401000	58500	459520	+73200	1.10
Missouri	12.5	228705	171215	46500	217715	-10990	.75
Tennessee	4.6	73273	115808	51800	172283	+99010	1.58
Wisconsin	9.5	210625	125000	85000	210000	-625	.59
					weighted regional aver. =		1.10

Agricultural N Balance

An N model was recently developed for the state of Wisconsin[7] and will be used as an example of how an N model can be developed and employed as an aid in decision-making.

Data for 1974 were used in constructing this model[19]. The flow of N in Wisconsin agriculture is depicted in Figure 2. Nitrogen inputs to agricultural land included fertilizer (127 x 10^6 kg N), precipitation (46 x 10^6 kg N), symbiotic fixation (310 x 10^6 kg N), nonsymbiotic fixation (39 x 10^6 kg N), and imports of animal feed (60 x 10^6 kg N), with a total input of 582 x 10^6 kg N. (Particulate N in precipitation is assumed to be mainly soil derived so its net contribution is zero). Nitrogen losses from agricultural land were estimated to be as follows: leaching, 84 x 10^6 kg N; denitrification and volatilization of available soil N, 130 x 10^6 kg N; direct NH_3 volatilization from fertilizer, 5 x 10^6 kg N; direct NH_3 volatilization from manure and other wastes, 130 x 10^6 kg N; erosion of organic N into surface water, 18 x 10^6 kg N; human waste not returned to land, 27 x 10^6 kg N; exports of crop and animal products out of the state, 86 x 10^6 kg N; and unaccounted losses in the handling and utilization of crop and animal products, 62 x 10^6 kg N. Losses total to 542 x 10^6 kg N which is slightly less than the estimated inputs but this is reasonably good agreement considering the lack of good data for many of the estimates.

Some of the estimates used in determining the inputs and outputs listed previously are as follows. The soil organic N pool was calculated assuming 0.15% N (4000 kg N/ha 20 cm; bulk density, 1.33 g/cm^3) and net mineralization was estimated at 1% year. Inputs to the dynamic available soil N pool total to 393 x 10^6 kg N/yr (70 kg N/ha avg.). Outputs due to crop uptake are estimated by the difference between total crop removal and residual and symbiotic N_2 fixation. Leaching lesses were estimated at 10 mg/liter of NO_3-N in 15 cm of drainage (15 kg N/ha/yr). The gaseous loss of N (denitrification plus volatilization) of 130 x 10^6 kg N or 23 kg N/ha/yr was probably largely due to denitrification. An additional 130 x 10^6 kg N is estimated volatilized from animal wastes, and 5 x 10^6 kg N is estimated to be volatilized directly from urea, NH_3 and N solution fertilizers.

Most of the crop N is transferred to the animal, with the majority of this N transferred on to wastes. Human consumption and exports account for 113 x 10^6 kg N (27% of the harvested plant N). Consumed N is approximately equal to fertilizer N.

Input into the soil organic pool is 263 x 10^6 kg N/yr, or 1.2% of the total. This is slightly more than the estimated annual mineralization rate. Erosion output to streams are estimated at 3 kg N/ha/yr. On balance, the model predicts that Wisconsin agricultural soils are not being depleted in organic N. More detailed information on how each of the estimates for inputs and outputs were arrived at cannot be provided here but they are included in the original report[7].

Response of Wisconsin Agriculture to N Fertilizer Inputs

The Wisconsin agricultural N balance is less sensitive to fertilizer N changes than might be expected with a strictly cash

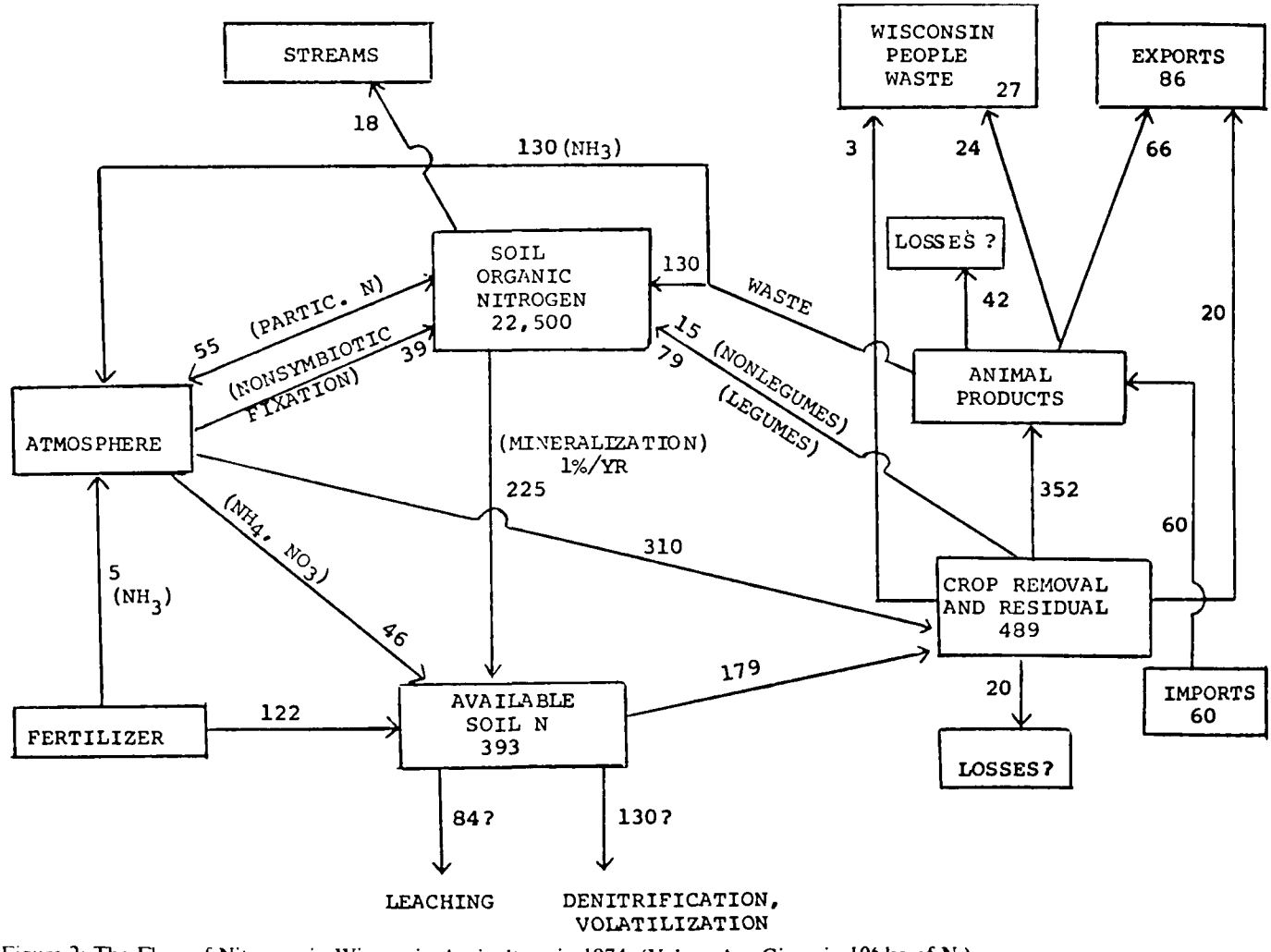

Figure 2: The Flow of Nitrogen in Wisconsin Agriculture in 1974. (Values Are Given in 10^6 kg of N.)

grain system, since a relatively large input from soil organic N mineralization exists. The area in corn silage has remained relatively constant at about 400,000 ha. However, area devoted to corn for grain has increased 59% in a decade while average fertilizer rates have more than doubled. The state-wide average corn yields reflect weather more than they do N fertilizer rates. In 1974 (the year chosen for the N balance in Figure 2) N removal by corn was considerably below average, due to a late spring and an early frost.

The model in Figure 2 can be tested by extreme pertubations on the N fertilizer input, holding corn acreage constant (i.e., changing only the average rate of fertilizer N on corn). If fertilizer N inputs were reduced 50% it would constitute 17% rather than 31% of the available soil N pool. Using N response data for Wisconsin,[5] average corn grain yields would decline by 18% (1,070 kg/ha or 17 bushels/A). At present prices, this decline would result in a loss of $115 million in crop value or a net loss of $100 million due to $15 million less investment in fertilizer. Leaching and denitrification would decrease by about 23%.

On the other hand, a doubling of N fertilizer use would increase this input to 48% of the total available soil N pool, and increase leaching and denitrification by 58%. Crop uptake would increase by 20 x 10^6 kg N (11%). A yield increase of 10% would be expected, increasing gross returns by about $61 million but costing $30 million in extra fertilizer N for a net return of $31 million. This analysis, however, is highly dependent on the balance between corn and fertilizer prices.

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Fate of Nitrogen From Fertilizer Practices

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The fate of fertilizer nitrogen in the soil-plant system has concerned agriculturalists for many years. Lack of nitrogen limits crop production on United States soils more than any other essential plant nutrient. Methods to most economically correct nitrogen deficiencies have received intensive investigation by researchers throughout the nation. The use of inorganic nitrogen fertilizers has emerged as the most economical and most widely used corrective measure.

The use of nitrogen fertilizers by US farmers to satisfy their crop's nitrogen needs increased dramatically in the last 45 years (Table I) and has contributed more than any other single factor to the concomitant increases in grain and forage yields. Corn receives more nitrogen than any other crop (Table II).

Table I. Nitrogen fertilizer use (Statistical Reporting Service, USDA)

Year	US	Minnesota
	-1000 Metric Tons-	
1930	343	-
1950	912	-
1960	2484	50
1968	6157	228
1973	7565	385

Table II: Nitrogen fertilizer use by crop (USDA Statistics) (1973 - US Total)

Crop	Hectares (Millions)	Rate (Kg N/HA)	Total (Million KG)
Corn	25.1	119	2990
Wheat	21.9	34	745
Soybeans	22.7	3	68
Cotton	4.9	61	299

The availability and continued use of nitrogen fertilizers is essential if food production is to keep abreast of population increases. But unnecessary and excessive use of nitrogen fertilizers can waste scarce energy sources and contaminate surface and subsurface water supplies. Determining the most economical and least environmentally damaging methods to use nitrogen fertilizers is the goal of all those involved with agriculture.

Forms of Fertilizer Nitrogen

The production of fertilizer nitrogen begins with the fixation of atmospheric nitrogen gas (N_2) into anhydrous ammonia which can be transformed by further chemical processes into other nitrogen fertilizers such as ammonium nitrate and urea. Because anhydrous ammonia (NH_3, 82% N) is produced in the first step of the chemical synthesis, it is the least expensive form of nitrogen available. Being a compressed gas, it is more difficult to use than dry fertilizers and can be dangerous if improperly handled. Its application requires special equipment that can inject it at least four inches below the soil surface to prevent escape of ammonia. Nevertheless, its low cost generally overrides these disadvantages and its extensive use verifies its acceptance by farmers to satisfy their crop's nitrogen needs (Table III).

Table III: Nitrogen use by material (Crop Reporting Board, USDA)

Material	1970	1974
	Million Metric Tons of N	
Anhydrous Ammonia	3.1	3.8
Nitrogen Solutions	2.9	3.7
Ammonium Nitrate	2.6	2.9
Urea	0.5	0.9

Ammonium nitrate (NH_4NO_3, 33% N) has traditionally been the main source of dry fertilizer nitrogen in this country. Its popularity has waned in the last few years, however, because its manufacture involves an additional step for the oxidation of ammonium to the nitrate form which requires more energy and greater cost. One of its advantages is the ease with which it mixes with other dry fertilizers which is important when applying a mixed blend of nitrogen-phosphorus-potassium fertilizer.

Urea (NH_2CONH_2, 45% N) is another popular nitrogen fertilizer that is manufactured from anhydrous ammonia. The process of converting anhydrous ammonia to urea involves less energy than ammonium nitrate production making urea available at a lower cost than ammonium nitrate. Because of its lower

cost, urea is being used in larger quantities and prospects for an increasing share of the fertilizer market are good because the newer nitrogen fertilizer plants produce urea only. In the future, urea is also likely to compete well with anhydrous ammonia due to its ease of handling and its ability to mix with other solid fertilizers.

Solutions of urea-ammonium nitrate mixtures (28 to 32% N) are an important part of the fertilizer market. Non-pressure liquids are easier to handle than solids, can be more accurately applied, and allow the addition of trace nutrients. The slightly higher prices of liquids have not slowed their increasing popularity.

Nitrogen fertilizers which have more limited use include calcium nitrate and sodium nitrate. Various nitrogen-phosphorus-potassium blends are also produced in both solid and liquid forms.

Application Techniques

The method of application of nitrogen fertilizers depends on the physical form of the material. Solid, granular fertilizers can be broadcast by various types of spreader machines which is usually done prior to planting which allows the application of fertilizer in close proximity to the seed which can increase the efficiency of the fertilizer compared to the broadcast technique.

Fertilizer solutions which contain no anhydrous ammonia are called nonpressure solutions and can be applied to the soil surface without significant volatilization loss of nitrogen. This allows the broadcast application of solutions by spreader trucks prior to the time of seeding or they can be applied by planter attachments.

Anhydrous ammonia and pressure nitrogen solutions which contain ammonia must be injected beneath the soil surface to prevent gaseous loss of ammonia. The various types of applicators designed for this injection generally include a shank which penetrates the soil at least four inches with a tube near the bottom of the shank in which the solution is discharged into, and immediately covered by, the soil.

Foliar applications of nitrogen to an established crop can be an effective method of satisfying the nitrogen requirement, but its use is limited because only small quantities of nitrogen can be applied per application to prevent salt burning of the leaves. Another method of applying nitrogen solutions is the metering of the solution into irrigation water and allowing the fertilizer to be distributed across the field through the irrigation system.

Soil Pathways of Fertilizer Nitrogen

The nitrogen cycle has been examined in detail by other papers in this conference and the specifics will not be dealt with here. The key to understanding what happens to nitrogen after soil application is a solid grasp of the relationships between ammonium and nitrate-nitrogen forms and how they are biologically and chemically related.

The ammonium ion is a cation (positively charged) and is attracted to the negatively-charged clay particles that are present in all soils. This attraction is a very effective barrier against movement of the ammonium ions through the soil. In other words, the ammonium ion will stay where it is placed until it is changed to other nitrogen forms or removed by plant roots.

Nitrification is a biological process which converts ammonium to nitrate. If soil conditions exist which promote active biological activity (warm, moist soils), the conversion occurs rapidly within a few days or weeks. In the form of nitrate, the nitrogen is more available for plant uptake—desirable for good plant nutrition. This nitrate; however, is subject to other less beneficial losses.

Nitrate is an anion (negatively charged) and is repulsed by negatively-charged clay particles in the soil. Thus it remains in the soil solution and is susceptible to leaching losses. How much is lost due to leaching depends on several factors such as the amount of moisture received and the permeability of the soil. Generally, sandy soils are more prone to leaching losses than are clay soils.

Nitrogen may also be lost from the nitrate form by volatilization of nitrogen gases through denitrification. This biological process converts nitrate into nitrogen gases, primarily N_2 and N_2O, which are lost into the atmosphere. Soil conditions which encourage denitrification are water logging, the presence of easily oxidizable organic matter, warm soil temperatures and the presence of nitrate ions. An example of when significant denitrification losses could occur is after heavy and continuous rains on a warm, poorly-drained soil in the late spring or summer.

Losses of nitrogen due to denitrification are hard to measure precisely because the main end product, N_2, is so abundant in the atmosphere. It has been shown in carefully controlled laboratory experiments, and indirectly shown by nitrogen balance calculations in field experiments, that denitrification can account for significant losses of nitrogen and contributes detrimentally to the efficiency of plant use of fertilizer nitrogen.

Ammonia volatilization is another source of potential loss of nitrogen. The most extreme ammonia volatilization losses occur when ammonium containing fertilizers are applied on the soil surface and allowed to remain without incorporation for several days. Hot, windy, drying conditions and soils of high pH encourage ammonia volatilization losses. Urea is particularly susceptible to this loss because it is readily hydrolyzed by the urease enzyme to give off ammonia gas.

Fertilizer Nitrogen Losses in Surface Runoff

Movement of fertilizer nitrogen with surface runoff has received attention by researchers because of the high water-solubility of most nitrogen fertilizer materials and concern that nitrogen on or close to the soil surface would tend to dissolve or diffuse into surface water. There are several factors that could affect nitrogen loss in runoff water: intensity of rainfall; slope of the land; total amount of runoff; soil texture and infiltration rate; vegetative cover; antecedent soil moisture levels; and depth of fertilizer incorporation.

Moe et al[7,8] found that nitrogen loss in rainfall runoff was greatest when ammonium nitrate applied without incorporation to wet silt loam soils or to fallow soils with a surface seal. The maximum nitrogen loss was 15% of the 224 kg N/ha applied. When runoff losses from soil treated with urea and ammonium nitrate were compared, it was shown that less ammonium was lost from the urea plots, probably because urea was leached deeper in the soil before hydrolysis than the more highly ionized ammonium nitrate, thus making the ammonium (formed after hydrolysis of the urea) less susceptible to dissolution into surface waters.

When the nitrate content of runoff from cultivated soils in South Dakota was compared to the nitrate in the runoff from a virgin prairie, White and Williamson[14] found no differences. The quality of the runoff was influenced by how long the precipitation remains on the surface and the amount of precipitation, but not by agricultural practice. Similar results were recorded by Thomas and Crutchfield[12] in Kentucky. They reported that the nitrate content of streams draining agricultural watersheds was correlated to local geology and not land use.

After working with an irrigated soil in Nebraska, Edwards et al[2] reported that once nitrate moves below the soil surface it usually will not enter surface water unless it moves with erosion or with plant residues. If the soil is initially saturated, however, nitrate will not move downward as rapidly as the water.

Knight[5] found very little nitrate in tailwater off fertilized, permeable soils in Kansas. After the first one and one-half hours of irrigation there were no differences between the nitrate in tailwaters off the control and fertilized plots.

Nitrate runoff losses from a simulated 12.7 cm rainfall reported by White et al[13] were only 0.15 percent of the 224 kg N/ha applied as ammonium nitrate to plots in sod on a sandy loam soil in Georgia. On fallow plots the loss was still a low 2.3 percent. It was suggested that the first few minutes of rainfall leached the fertilizer into the soil and made it less available to runoff loss.

Research has shown that fertilizer nitrogen will not be lost in surface runoff except during the most severe runoff events in which soil erosion occurs. Adequate soil incorporation of the fertilizer, a vegetative cover and dry antecedent soil conditions will tend to reduce nitrogen losses in surface runoff.

Leaching of Fertilizer Nitrogen Into Groundwater

Most of the inorganic nitrogen in soils is in the form of nitrate—an anion with no electrostatic attraction to the negatively charged soil colloidal particles and susceptible to movement with water. Factors which could affect movement of nitrate into groundwater are several: amount of nitrate present in the soil; soil conditions which are conducive to denitrification; the leaching volume which is determined by precipitation and the hydraulic properties of the soil; plant uptake; and microbial immobilization.

Gentzsch[4] found less nitrate in poorly-drained Illinois soils with impermeable horizons. The levels of nitrate in soils without impermeable horizons were related to the amount of fertilizer used or to animal activity. Impermeable horizons could enhance conditions conducive to denitrification and lower losses of fertilizer nitrogen.

Layers which restrict drainage were also found by Pratt[10] to lower the leaching of nitrate in soils of California. Concentrations of nitrate of up to 123 and 70 ppm were found in the water in the unsaturated zone beneath row crops and citrus, respectively. There were three main factors influencing these nitrate levels: the difference between nitrogen input and crop removal; drainage volume; and soil profile characteristics (restricted drainage) that apparently control denitrification. In soils without restricted drainage the nitrate levels could be predicted by the difference between nitrogen input and crop removal of nitrogen.

In a deep coring study in the South Platte River Valley in Colorado, Stewart et al[11] found increased total nitrate in the top 6.1 m of irrigated and dryland-cultivated fields compared to native grassland. Alfalfa fields had somewhat less nitrate than native grassland fields. They estimated that 28 to 34 kg N/ha were lost annually to the groundwater beneath irrigated fields. Significant amounts of nitrate were found beneath the root zone in dryland-cultivated fields even though the average rainfall is only 38 cm/yr. It was noted that much of this nitrate could have come from mineralization of native organic nitrogen.

Bower and Wilcox[1] reported that even though nitrogen fertilization increased greatly over a 30-year period on irrigated land adjacent to the Upper Rio Grande River, the average nitrate content of the river did not increase. Denitrification in saturated soil close to the water table was suggested as an explanation for the apparent lack of nitrate movement to the river. Willardson and Meek[15] were able to show that nitrate reduction can indeed occur at the water table.

Linville and Smith[6] studied the fate of fertilizer nitrogen as affected by rate of application and soil texture on continuous corn plots in Missouri. Large accumulations of nitrate were found in the soil at rates of 168 kg N/ha and higher, while rates of 112 and 134 kg N/ha caused no movement of nitrate below 244 cm. Generally, the coarser textured soils had deeper movement of nitrate than the finer textured soils. It was concluded that nitrogen applications greatly in excess of crop requirements increase the potential for nitrate leaching.

Gast et al[3] measured nitrogen loss through tile lines in plots that had received up to 448 kg N/ha on a Minnesota soil. Total nitrogen loss through the tile lines under the plots which received 112 kg N/ha (the recommended rate) was only slightly greater than under the plots that received no nitrogen. The 224 and 448 kg N/ha rates significantly increased the total loss of nitrogen in one year, but the increased loss was much less than the additional fertilizer applied over the recommended rate.

In an investigation of factors influencing the nitrogen content of waters of Nebraska, Muir et al[9] found little correlation between nitrogen content of waters and the use of fertilizers. Only where there was irrigation on sandy soils with shallow water tables was there contamination of groundwater by fertilizer nitrogen.

Research has shown that applications of fertilizer nitrogen in great excess of the nitrogen removed by the crop will result in nitrate accumulations in the soil and with sufficient leaching volumes movement to the groundwater. There are factors that can lower nitrate accumulations, such as layers of restrictive drainage in the soil which encourage denitrification. Most research showing leaching loss of fertilizer nitrogen has involved the extreme cases of high application rates. These high rates are rarely used by farmers, who recognize the diminishing returns in yields and profits from the higher rates. As nitrogen fertilizer prices continue to increase, farmers will become even more conscious of the inefficiency of applying nitrogen in great excess of that removed by the crop.

Farming Practices That Reduce Nitrogen Losses

Numerous researchers have shown that there is very little nitrogen loss from soils that have received the application rate recommended by state extension agencies. These rates are determined by field trials which compare different ratesof nitrogen and are correlated to soil test results. The optimum rate is the one which gives the maximum yield from the least amount of nitrogen applied. Even though most recommended rates are higher than that removed by the crop, the balance is made up by biological immobilization in the soil and gaseous losses through denitrification.

Nitrogen losses can be reduced by proper timing of the fertilizer application. The most efficient timing would be to add nitrogen only as the plant needs it or feeding the plant periodically throughout the growing season. On a field-scale basis this is impractical, however, because of the high cost of the energy required to spread the fertilizer and because of the crop damage when the plants are large. The most common practice now is to apply all of the projected crop fertilizer needs prior to planting. This leaves the nitrogen in the soil, where it is susceptible to leaching and denitrification losses, for several weeks before the plants are large enough to take up significant quantities of the nitrogen. Applying the fertilizer as close to planting time as possible reduces chances for nitrogen loss. Some corn producers are now optimizing yields and nitrogen use efficiencies by applying side-dress applications of nitrogen after the corn plants are well established. Split applications of nitrogen have also been a common practice on pastures for many years because several small applications throughout the growing season are more efficient and produce higher yields than a single large application early in the season.

In an effort to reduce the spring workload, many farmers apply their fertilizers in the fall. If applied late enough in the fall and if the weather cooperates, no significant losses of nitrogen will occur. If there is a late warm fall or an early warm spring, however, in which the nitrogen is exposed to soil conditions conducive to nitrification, there can be losses of nitrogen prior to the growing season. This makes fall application of nitrogen fertilizers generally less efficient than spring applications. When fall applications are made, it is best to apply ammonium-based fertilizers such as urea or anhydrous ammonia which are less sus-

ceptible to loss. If ammonium fertilizers are applied late enough in the fall when the soil temperatures are cool enough to prevent biological nitrification of the ammonium into nitrate, there will be little or no movement of the nitrogen until the following spring.

Slow-release nitrogen fertilizers are available which have lower water solubilities due to surface coatings on the fertilizer prill or to combination with materials which lowers the water solubility. Sulfur-coated urea is one type of slow-release fertilizer. The sulfur coating restricts water penetration and subsequent release of the nitrogen into the soil solution, thereby extending the nitrogen availability over longer periods. This material has shown to be an effective method to increase nitrogen efficiency on soils that are subjected to high leaching losses such as highly permeable irrigated sands. The higher cost of this material restricts its use to soils which have high leaching losses or when more frequent applications of nitrogen are not practical.

Preventing the conversion of ammonium to nitrate by nitrification can lower leaching and denitrification losses. Chemical additives to ammonia-based fertilizers are available which temporarily lower the activity of the soil organisms that carry out nitrification. These chemicals, called nitrification inhibitors, can be mixed prior to application with anhydrous ammonia and urea. Upon application, they stop the nitrification process in the zone immediately around the fertilizers, thus keeping the nitrogen in the ammonium form longer.

Good soil conservation practices that prevent soil erosion can lower significantly the nitrogen lost into surface waters. If erosion is controlled, nitrogen loss in runoff is negligible.

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Fate of Nitrogen From Manure Disposal*

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INTRODUCTION

Nitrogen from animal manure has polluted our water level several times during the past ten to fifteen year years and caused eutrophication of our lakes and streams. Some livestock deaths and even infant deaths have been attributed to excessive nitrate concentrations in drinking water. Such nitrogen pollution has warranted the U.S. Public Health Service to set concentration limits of 10 parts per million (ppm) nitrate-nitrogen for drinking water. To abide by these limits, we must control the fate of the nitrogen in the animal manure we add to the soil.

Controlling the fate of nitrogen involves understanding the process by which nitrogen from decaying manure is released to the soil; how it can be returned to the atmosphere; how it can accumulate in the soil; or, how it can be leached from the soil to the ground water below. Most of all, we need to know the amount and form of nitrogen being added to the soil.

Knowing the form of nitrogen is necessary because nitrogen in the form of nitrate (NO_3^-) is highly soluble and moves easily with the water in the soil; however, nitrogen in the ammonium form (NH_4^+) is attracted to the negative soil articles and doesn't move easily with the soil water.

The following are the objectives of this presentation: (1) Discuss the nitrogen concentration in animal manure, (2) discuss the factors affecting the pathways nitrogen will follow in the nitrogen cycle and (3) review publications on management practices to control the fate of nitrogen in animal manure.

We will discuss first the nitrogen concentration in manure because this probably has the greatest influence on its fate.

Concentration and Forms of Nitrogen in Manure

The chemical and physical properties of manure vary widely across the United States. Important factors affecting the properties of manure are the physiology, ration, and environment of the animals. Most nitrogen consumed by the animal is in the form of plant protein. These proteins vary in digestibility, and most plant nitrogen excreted by the animal in the solid form is that which resists digestion. Except for those used to build flesh in the animal, the digested proteins are absorbed, cycled from one protein to another, and are later excreted.[22] Table I shows the percentage of nitrogen recovered in manure from various types of animals.

Table 1: Percent of Fed Nitrogen Recovered in Animal Manure[a]

Type of Animal	Nitrogen Recovered (Percent)
Dairy Cattle	74
Beef Cattle	75 - 89
Sheep	68
Swine	72

[a]Adapted from Table 4 of Azevedo and Stout (2).

Because nearly all nitrogen excreted is protein, the decay process and the factors affecting the rate of decay are paramount when considering the availability of nitrogen in animal manures. The rate and process of decay are dynamic and highly dependent upon the nitrogen content of the manure. This decomposition which converts the nitrogen in the organic form to the inorganic form such as nitrate (NO_3^-) is called mineralization. (Many of the terms we will use here are found in the Resource Conservation Glossary published by the Soil Conservation Society of America.[5]) It is this rate of nitrogen mineralization that determines the availability of the nitrogen and its potential to pollute.

At the present time, the best method to express the rate of nitrogen mineralization is one using a decay series. As described by Pratt et al.,[18] the decay series concept is based on mineralization of organic nitrogen into inorganic or available nitrogen. The rate of mineralization will be most rapid in the first year after application and will decrease in subsequent years. For example, 40% of the applied nitrogen might become available in the first year, 25% of the residual nitrogen in the second, 6% of the residual nitrogen in the third year, 3% of the residual nitrogen in the fourth, and 3% all subsequent years. That decay series would be expressed as 0.40, 0.25, 0.06, and 0.03. The percentages after the first year refer to the organic nitrogen remaining in the soil and not the original amounts of nitrogen applied. Manure higher in nitrogen content will decay faster. For example, a manure with 3.5% nitrogen may have a decay series of 0.75, 0.15, 0.10, 0.05; a manure with 1.0% nitrogen may have a decay series of 0.20, 0.10, 0.05.

The effect of the nitrogen on the decay series demonstrates the

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need to know the nitrogen concentration of the manure. However, upon examining Table II, we see that the nitrogen concent of manure from a given species and handling system can range from a relatively low to a high value.

Table II: Maximum and Minimum Values for Total Nitrogen Content of Animal Manures[a]

Species and Type of Manure	Minimum Value (percent)	Maximum Value (percent)
Beef		
Solid	0.6	4.9
Runoff	0.0011	0.86
Slurry(D)[b]	11.00	11.0
Slurry(U)[b]	1.9	9.0
Dairy		
Solid	1.5	3.9
Runoff	4.8	4.8
Slurry(D)	-	-
Slurry(U)	1.8	5.1
Swine		
Solid	2.0	7.5
Runoff	0.4	4.8
Slurry(D)	8.8	12.0
Slurry(U)	3.4	19.0
Poultry		
Solid	1.1	11.0
Runoff	-	-
Slurry(D)	2.2	7.8
Slurry(U)	7.4	7.4

[a]Beef runoff data is on wet weight basis, all other is on a dry weight basis. Single values indicate only one value found. Table adapted from Table 1 of Powers et. al. (16).

[b]D refers to digested and U refers to undigested.

The variability of the nitrogen content of manure is due to factors such as climate, species, ration, and manure handling. Figure 1 is a schematic diagram of factors affecting the nitrogen concentration of the manure.

Climate can affect the nitrogen composition in many ways. If the manure is stored where it is exposed to rainfall, the natural precipitation can dilute the manure when it is in the liquid form or it can remove soluble nitrogen compounds by leaching them from the solid manure. This process will proceed at greater rates in regions of higher rainfall. In climatic regions characterized by hot drying conditions, manure can lose large quantities of nitrogen by ammonia volatilization. It has been estimated that under conditions similar to those of Southern California, about 50% of the nitrogen in dairy manure is lost to the air by ammonia volatilization and denitrification between the time of excretion and the time manure is incorporated into the soil.[1]

The species and animal size also contribute to the variable nitrogen content of the manure. Poultry and swine are considered to produce manure highest in nitrogen.

Modern rations used in today's feedlots can be altered, thereby increasing the variability of the nitrogen content of the manures. Rations used today range from 70 to 80% in digestibility.[2] This means that the materials excreted by the animals are less resistant to decomposition and thus speed decaying to release the nitrogen.

The nitrogen content, more than any other constituent, is sensitive to management. The method of manure handling and storage between the time of excretion and application can have a major effect on the quantity of nitrogen contained in the manure. Nitrogen can be lost by ammonia volatilization, leaching of soluble nitrogen compounds, dilution, and microbial utilization. Several researchers have shown that up to 50% of the nitrogen excreted by cattle can be lost through ammonia volatilization.[7,8,19] Leaching of solid waste can remove much of the water soluble nitrogen, which can comprise as much as 50% to 60% of the total nitrogen in steer manure.[19] Up to 80% of the nitrogen in swine manure can be removed by treatment in an oxidation ditch.[20]

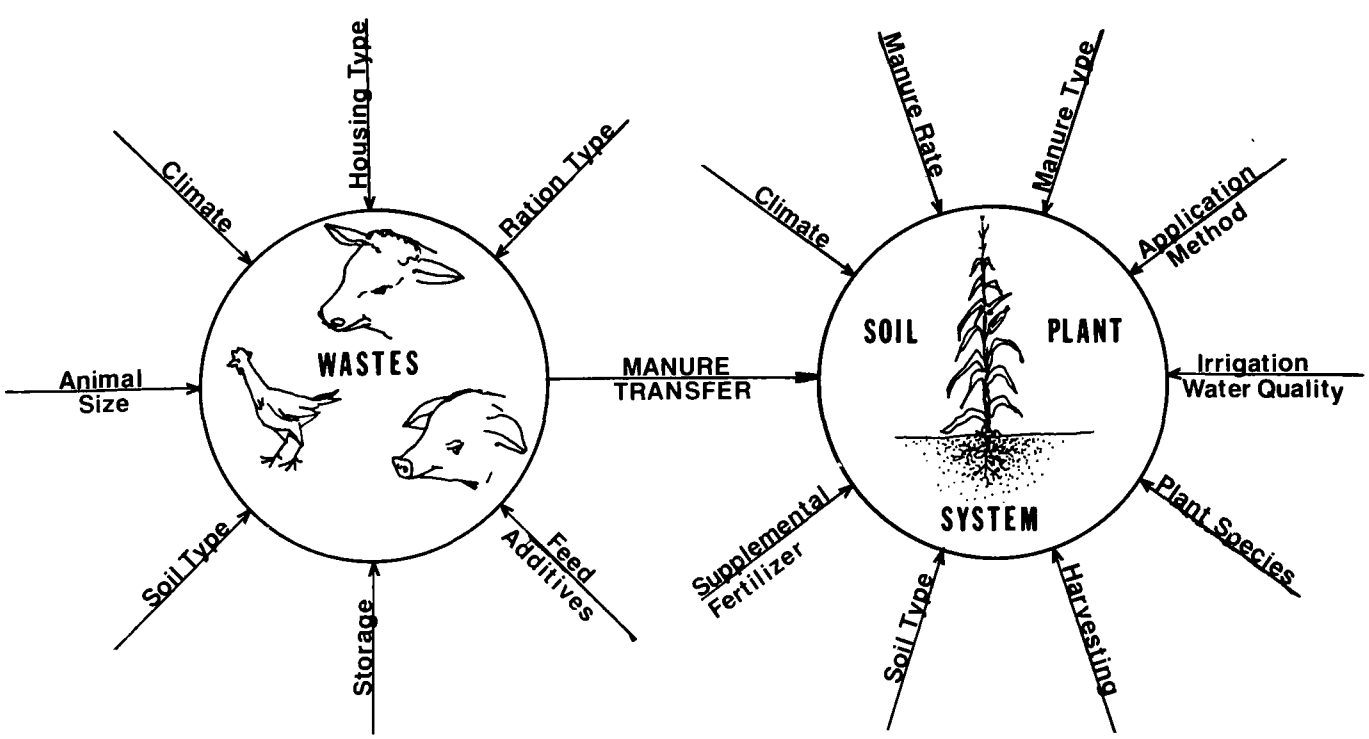

Figure 1. Schematic summary of factors affecting waste composition and influencing the efficiency of its use on cropland.

Pathways for Nitrogen Movement in the Nitrogen Cycle

To control water pollution from nitrogen, we need to understand the various pathways the nitrogen will follow after the manure is spread on the soil. Earlier in this conference we discussed the nitrogen cycle. Here we will review some of the pathways in this cycle. Once the factors which determine the pathway the nitrogen will follow are known, we can control the nitrogen movement to surface and ground water.

The variability in the nitrogen content of manure causes difficulty in establishing application guidelines for all areas of the United States. The above factors indicate that sampling to determine nitrogen content should be done as close as possible to the time of application so that the sample will represent the nitrogen content of the manure as it is applied to the soil.

In the next section we will see how the nitrogen content and its availability affects the pathway the nitrogen takes in the nitrogen cycle.

Figure 2 is a schematic diagram of the various pathways the nitrogen can follow once it has been added to the soil. From this figure we see that when the manure is first added to the soil, some of the nitrogen might be volatilized as ammonia (NH_3) and returned to the atmosphere. Warm, dry and alkaline conditions favor the volatilization of ammonia gas.[2] The nitrogen movement in the runoff can be of any chemical form and usually occurs on sloping land in connection with heavy precipitation, snow melt on frozen ground, or overirrigation.

Once the manure is incorporated into the soil and starts to decay, the nitrogen can follow several different pathways depending upon the soil aeration, texture, water content, and temperature. When the soil is well drained and aerated, the decomposition is aerobic. The first step in aerobic decomposition is the hydrolysis of the nitrogen-containing proteins in the manure to yield polypeptides, amino acids, and some ammonia.[2] This step is referred to as amination and makes available the amine compounds which may be synthesized by microorganisms into their own protoplasm. Amine groups not used by microbes or releasetions of the microbes die are converted to ammonia (NH_3). This process is termed ammonification. Ammonia, if not lost by volatilization, is rapidly converted to the ammonium ion (NH_4^+). As the nitrogen appears in the ammonium form, it may be absorbed by plants or microorganisms or it may be held by the negatively charged soil particles. The ammonium ion is usually converted rather rapidly to the nitrate (NO_3^-) form. This is called nitrification. Nitrate is the end product of aerobic decay. All compounds of nitrates are water soluble, and the negative nitrate ion is not attracted to the negatively charged soil particle. Thus, it moves easily with the soil water to be leached to the groundwater. The nitrate form is also the most easily taken up by the plant and so nitrogen in this form can be recycled through cropping.

When the soil is cool and poorly drained, the decomposition is usually aerobic and the end products are often gaseous compounds of nitrogen such as nitrogen (N_2) and oxides of nitrogen. The nitrate from aerobic digestion can also be converted to gaseous compounds if anerobic conditions develop. This process is called denitrification. However, denitrification is not likely to occur below the root zone of the crop because this process needs a source of oxidizable carbon not generally found at such depths in the soil. Therefore, once nitrate gets below the root zone, it moves to the ground water in that form.

If precipitation or irrigation water is insufficient, nitrogen compounds can accumulate in the soil profile. The accumulated nitrogen can be found in the form of organic compounds such as proteins of plants or bacteria or in the inorganic forms such as the nitrates. Figure 3 shows some research results where nitrogen has been concentrated in the soil profile.

Explaining the decay process has been simplified for the presentation here because it would take too long to cover in detail. Many research papers have been written on each of the many

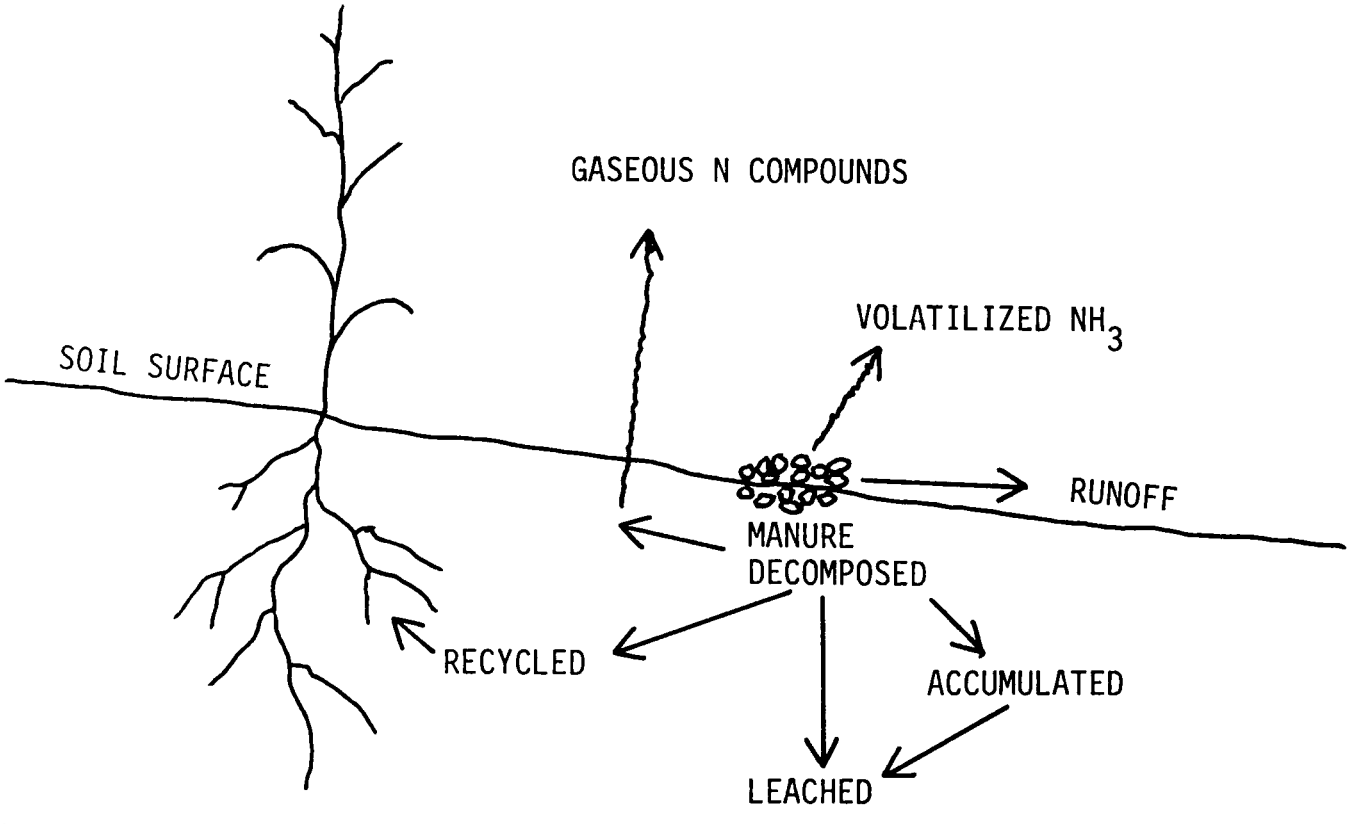

Figure 2. Pathways for nitrogen movement from decaying manure applied to cropland.

pathways of the nitrogen cycle and their accompanying chemical reactions. However, our version should provide sufficient background to understand some management practices to control water pollution from nitrogen in manure.

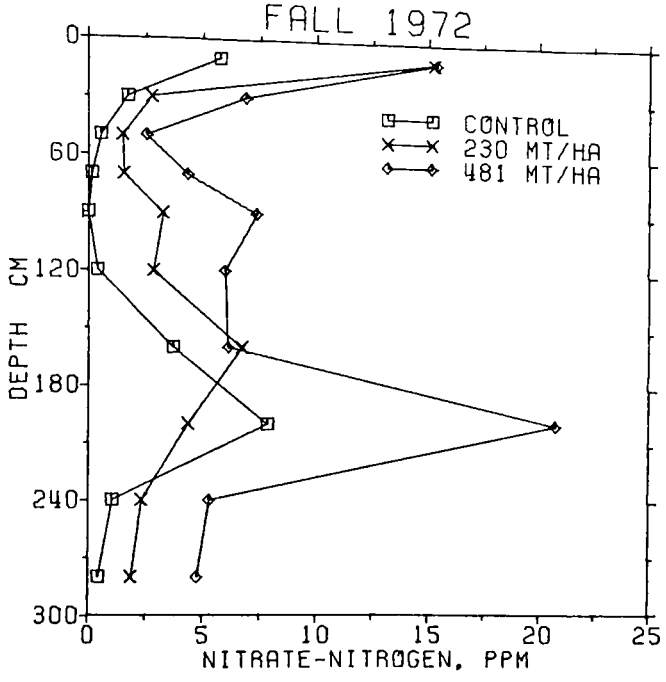

Figure 3. Nitrate nitrogen in soil profile after a single application of beef feedlot manure in the fall of 1969, Wallingford (25).

Management Practices to Control Nitrogen Pollution

Nitrogen pollution can best be controlled by sending it down the least polluting pathway of the nitrogen cycle. If we return to Figure 2, we can see several pathways we do not want the nitrogen to follow. Obviously we do not want it to flow into surface streams in runoff nor do we want it to leach into our ground water. It could accumulate in the soil if it didn't become toxic to plant and animal life, and if it didn't later leach downward to the ground water. It appears difficult to control nitrogen accumulation so this may not be a good pathway either.

We could leave the manure on the soil surface to volatilize as ammonia, but then the manure would be subject to movement to streams in runoff. Also, Azevedo and Stout[2] feel that volatilized ammonia could be transported to other areas and reabsorbed by plants or surface water downwind from the application site.

Of the remaining pathways of denitrification and plant intake, the latter is most preferred because we have a wealth of information on nitrogen use by various crops. We also have information about denitrification and anerobic decay process although it is not so easily controlled as the uptake by plants. However, if we have enough experience with anerobic decomposition and denitrification to know how much nitrogen can be returned to the atmosphere as a gas, then we could count on this process to remove some nitrogen added to the soil.

What this all boils down to is the question of what management practices we can use to move the nitrogen down the pathway to plant uptake, or possibly, denitrification and anerobic decomposition. These management practices are timely incorporation of manure into the soil to reduce runoff and volatilization and application of manure in amounts which allow all of the nitrogen applied to be recycled by the soil-plant system so no nitrogen would accumulate in the soil profile or leach to the ground water.

Now we have to determine the proper application rate of manure. If we know the nitrogen content of the manure and the rate at which it decays to release the nitrogen, i.e., the decay series, we can calculate the application rate. This sounds simple enough except that we saw earlier how much the nitrogen content of the manure varies. Why not use an average nitrogen content? Would you buy yourself a pair of shoes the size of the average foot in the United States? Of course you wouldn't. You must match the pair of shoes to your foot just as we must match the manure to our soil and climate.

Large errors can be made if average nitrogen concentrations are used to calculate application rates. For example, assume that the average nitrogen content of solid poultry manure is 5%. If we applied the poultry manure of Table II with the maximum value of 11% nitrogen, based on the 5% average, the application rate would be 2.2 times larger than what it should be. If the actual nitrogen content were 1.1% (the lowest value in Table II) then the application rate based on the 5% average value would be less than one quarter of what could be recycled by the system. This illustrates the importance of knowing the nitrogen content of the manure applied to your soil and that you must know your soil and crop at the application site.

The application rate affects substantially the pathway the nitrogen will follow in the nitrogen cycle. As seen in Figures 4 and 5 of, [24] overapplication of manure can reduce the ability of the crop and soil system to recycle nitrogen. Not only is the potential for nitrogen pollution increased by the additional manure added, but the system's ability to recycle nitrogen has been impaired. Some operators like to apply heavy amounts of manure every three or four years and let the system recover between applications. It has been shown that such a practice may temporarily overload the system's ability to recycle the nitrogen and thus increase the potential for groundwater pollution (see Figure 3 and Ref. 17).

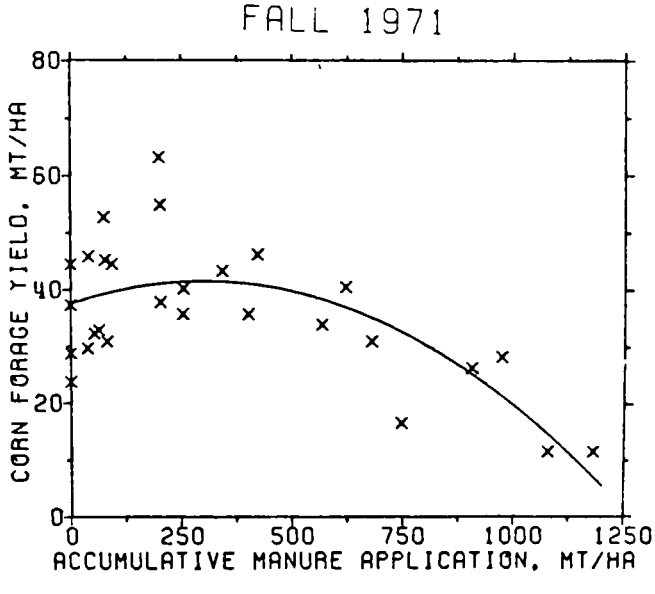

Figure 4. Corn forage yields as affected by application of beef feedlot manure that began in the fall of 1969, Wallingford (24).

We have discussed considerably the variability of the nitrogen content of manure and the factors affecting the pathways the nitrogen will take in the nitrogen cycle. We also have decided to send the nitrogen down the less polluting pathway. We have not

discussed specific management practices for given areas of the United States because of the limited time and space. However, we should now have enough background to look at some of the recent guidelines and manuals on the application of manure to land.

Several publications on animal waste disposal have appeared the past few years. Most are based on the concept of trying to recycle the nitrogen and secondly, of trying to avoid a buildup of toxic substances such as ammonium, inorganic salts, and heavy metals. Good guidelines must consider the area climate, soil type, crop and nitrogen release of the manure. Several states, some of which are Indiana,[3] North Carolina,[9,10,11,12] Maine[23] and Kansas[13,14] have developed guidelines on animal waste applications. Formulas have been developed for applying manure to land based on the decay series for a given manure and region.[15,16] Two publications give the general concept of manure application to land.[2,16] There are also regional guidelines which may help you.[4,7,21]

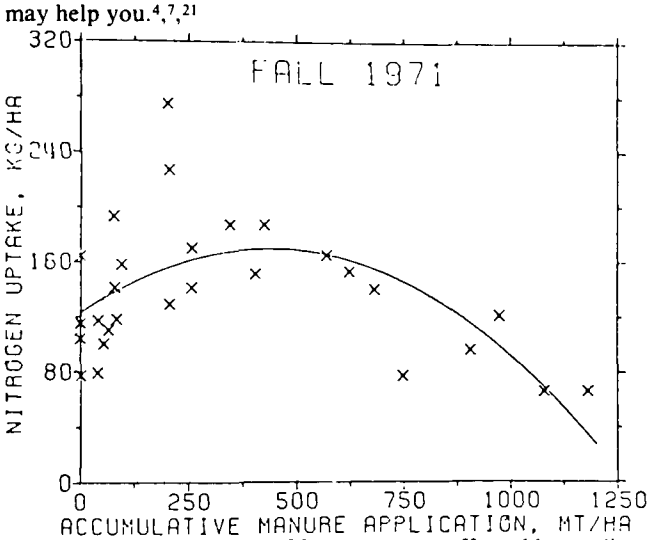

Figure 5. Nitrogen uptake of forage corn as affected by applications of beef feedlot manure that began in the fall of 1969, Wallingford (24).

SUMMARY

We have discussed the variability of nitrogen concentration in manure and its effect on the pathway the nitrogen will take in the nitrogen cycle. We have also found that the soil, climate, and application rate influence this pathway. The best management system apparently is one which recycles the nitrogen in the manure either through plant uptake or denitrification and anerobic decomposition. Further, we found no universal management system to control nitrogen pollution, but because of the variable nitrogen content, each application of manure must be considered an individual case. Several publications are now available or in process to provide guidelines for sound management decisions.

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Fate of Nitrogen from Municipal Sludges

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INTRODUCTION

The increasing interest in land application of sewage sludge in the past ten years has led to a considerable amount of research on the effects of agricultural use of sludge. Although the heavy metal content of sludge will determine the total quantity that can safely be applied over the lifetime of a site, it is generally agreed that the nitrogen content will dictate the annual rate of sludge application. Consequently, it is important to know the nitrogen content of sludge, the forms of nitrogen present, the nitrogen transformations that occur when sludge is applied to soil, and the pathways the nitrogen follows after application.

Nitrogen Content

One of the first steps taken in determining a suitable application rate for a particular sewage sludge is the analysis of a sample for total nitrogen content. However, an important characteristic of sludge is the fact that the nitrogen content can vary considerably among treatment plants and with time at the same treatment plant. An example of variation with time is shown in Figure 1. The data depicted are the total nitrogen content of liquid digested sludge from Chatham, Ontario (unpublished data). During the six month period nitrogen content fluctuated by a factor of three. During a one week period in October there was a factor of two fluctuation.

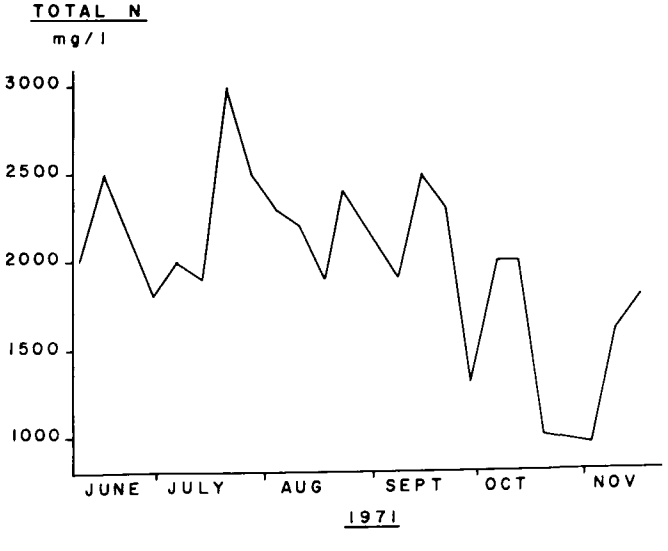

Figure 1: Variation of total nitrogen content of liquid sewage sludge from Chatham, Ontario (unpublished data).

In an effort to obtain sludge with a constant nitrogen content for field experiments, sludge was withdrawn over a two day period from the same depth in a digester at the wastewater treatment plant in Guelph, Ontario.[2] The nitrogen content of the sludge ranged from 2900 to 3580 mg/l or 23% of the lower value. Since it is important to apply sludge nitrogen at a reasonably precise rate to preserve environmental quality and to assure acceptable crop production, it is evident that management steps must be taken to produce a more homogeneous sludge at treatment plants where land application is practiced.

Nitrogen Forms

Since sludge undergoes perhaps 30 days of anaerobic digestion, nitrogen mineralization stops at the ammonium step because oxygen is required to proceed from ammonia to nitrate. Consequently, liquid sludge from the digester contains ammonium nitrogen and a host of protein, amino acid, etc. nitrogen forms which we lump together and call organic nitrogen. Table I shows values of total nitrogen and soluble ammonium nitrogen gathered from various references. The organic material in sludge has undergone decomposition in the digester and has developed some of the same properties of soil organic matter. One of these properties is cation exchange capacity. Since ammonium nitrogen exists as a cation (NH_4^+) we find that in addition to the ammonium nitrogen in solution there is also some held on the cation exchange complex of the sludge. The organic nitrogen content can be determined by subtracting the soluble and exchangeable ammonium nitrogen from the total nitrogen.

The data in Table I point out the variation in nitrogen among treatment plants. Also of interest is the variation in ammonium nitrogen expressed as a percentage of total nitrogen. This variation is probably a function of such factors as digestion time, type of inputs to the sewer system, and type of secondary treatment (e.g. activated sludge *vs* trickle filter sludge).

Transformations and Subsequent Pathways

Ammonia

Under alkaline conditions, ammonium ions (NH_4^+) give up a hydrogen ion (H^+) and become ammonia (NH_3). Ammonia volatilizes readily and thus can be lost as a gas. This is commonly what happens to a portion of the ammonium nitrogen in sludge because sludges are generally slightly alkaline.

Ryan and Keeney[17] found that when containers of liquid sludge were allowed to air dry in the laboratory approximately 90% of the ammonium nitrogen was lost via volatilization. Since the ammonium ion is positively charged it can be adsorbed onto the cation exchange complex in the soil. Consequently, ammonia loss from soil-applied sludge is less than that from sludge

dried in the absence of soil. Ryan and Keeney[17] reported lower ammonia losses with soil-applied sludge than with container-dried sludge. The losses were inversely proportional to the clay content of the soil—an indirect measure of cation exchange capacity:

Soil	*% NH_4-N loss*
Sand	29
Sandy loam	18
Clay loam	13

Other laboratory studies[11, 15] have shown ammonia losses ranging from 4 to 36% of the applied ammonium nitrogen. Through periodic soil sampling, Stewart *et al.*[19] estimated a 30% loss of applied ammonium nitrogen from liquid sludge applied for corn production.

The more intimately sludge is mixed with soil after application the lower the loss of ammonia. Thus, ammonia is lost most readily from surface applications and less so when sludge is applied and then plowed or disked into the soil. Subsurface injection behind some type of tillage implement essentially eliminates ammonia loss.

Generally, the volatilization occurs rather rapidly after the sludge is applied. Figure 2 shows that most of the loss from a surface application occurred during the first week after application.

The ammonium nitrogen that is not lost via volatilization can move through several pathways:

1. Direct uptake by crops.
2. "Fixed" within the crystal structure of certain clays thus, rendering it unavailable for crop uptake or further biological action.[14]
3. Temporarily adsorbed onto the cation exchange sites in the soil.

Table I. Nitrogen content of anaerobically digested liquid sewage sludge.

Total N	Soluble NH_4-N		Exchangeable NH_4-N	Reference
	mg/l	% of total N		
mg/l			mg/l	
2250	520	23	-	7
2180	340	16	-	7
2710	550	20	-	10
3250	490	15	-	11
2620	690	26		12
2090	1020	49	-	15
1620	950	59	-	17
2240	650	29	-	17
2350	950	40	-	18
3160	840	27	110	19
2300	700	30	60	L. D. King (unpublished data)
Range				
1620-3250	340-1020	15-59		
Mean				
2430	700	29	85	

4. Converted by nitrifying bacteria to nitrate which may then be taken up by plants, leached out of the soil, or converted to nitrogen gas via denitrification.

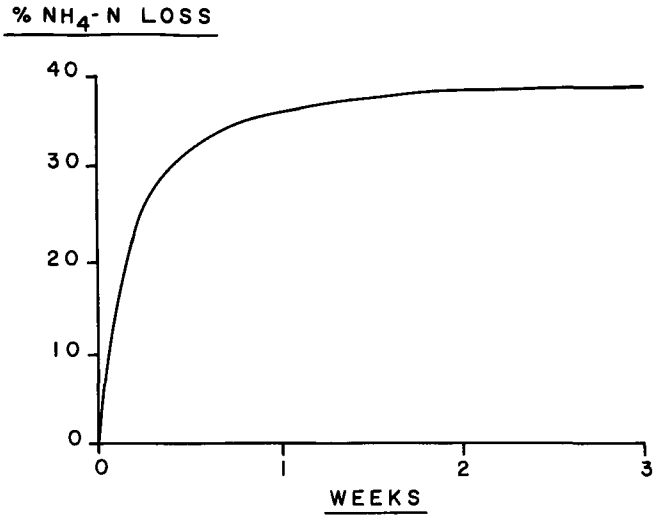

Figure 2: Ammonium nitrogen loss from surface-applied sewage sludge.[11]

It should be pointed out that nitrification is an acidifying process:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$$

the application of sludge will therefore increase soil acidity[8] unless the sludge contains sufficient cations (Ca, Mg, etc.) to offset the acidifying effect of nitrification. Consequently, an adequate liming program is essential in managing a land application site.

Denitrification occurs when nitrate moves into an environment that is devoid of oxygen but contains sufficient available carbon for anaerobic bacteria to use as an energy source to convert the nitrate to nitrogen gas. The application of sludge to soils can bring about these conditions. We don't usually think of nitrification (an aerobic process) occurring simultaneously with denitrification (an anaerobic process). However, it has been found that in a normally aerobic soil there can be small areas or microsites which are anaerobic. The addition of organic material such as sludge can produce anaerobic zones within the soil due to oxygen depletion caused by decomposition of the organic material. Thus, sludge additions supply nitrogen to be nitrified in aerobic sites and organic material which can deplete oxygen and provide available carbon in other sites. As a result, some of the sludge-applied nitrogen can be lost by denitrification.

Ryan *et al.*[18] found that where high rates of sludge were incubated with soil from 24 to 38% of the applied nitrogen was lost via denitrification. In an incubation study[10] and a greenhouse leaching study[11] I found denitrification losses ranging from 15 to 27% of the applied nitrogen.

Organic Nitrogen

The anaerobic digestion process used at wastewater treatment plants converts most of the readily available organic nitrogen in the sludge to ammonium nitrogen. The remaining organic nitrogen is relatively inert and resistant to further mineralization. Premi and Cornfield[15, 16] reported that only about 3% of the organic nitrogen was mineralized during laboratory incubation studies with sludge. Ryan *et al.*[18] reported 4 to 48% mineralization of organic nitrogen during a 16-week incubation study. They found that as the sludge application rate increased, the percent mineralization decreased. Larson *et al.*[13] used relative plant response to estimate an annual mineralization rate of organic nitrogen of 5%. Stewart *et al.*[20] found very little mineralization of organic nitrogen in solids separated from liquid sludge or in solids collected from plots which had received liquid sludge 6 months earlier.

In a laboratory incubation study, I found that about 40% of the organic nitrogen in sludge was mineralized during an 18 week period.[10] In a field study[9] samples of sludge crust that had accumulated from surface sludge applications the previous two summers were collected. From these samples it was determined that 33% of the applied organic nitrogen had been mineralized.

It should be remembered that the availability of organic nitrogen in sludge will depend on how well the sludge has been stabilized in the digestor. Poor stabilization will result in lower ammonium/organic nitrogen ratios and consequently organic nitrogen which is more available for mineralization.

From the above data, I think we can draw the general conclusion that the nitrogen in liquid sludge exists in two distinct phases: (I) The ammonium form which can be readily taken up by plants, volatilized, nitrified, etc., (II) The organic form which mineralizes slowly. Once the organic nitrogen is mineralized it follows the same pathways mentioned earlier for ammonium nitrogen.

The low availability of organic nitrogen in sludges leads one to question the practice of dewatering the sludge prior to land application. This practice greatly reduces the amount of nitrogen available for crop production. It also imposes an increased nitrogen load on the treatment plant since the high nitrogen supernatent (or filtrate) must be recycled back through the plant. Removal of the liquid fraction also reduces the nitrogen/heavy metal ratio and makes the sludge less suitable for crop production.

Application of Research Results

One of the purposes of the research efforts that have been cited (plus a vast number that have not been cited) is to aid regulatory agencies in setting up guidelines for use of sludge on land. Hopefully, these regulations will not only protect environmental quality but will also allow maximum utilization of the resources in the sludge.

Various agencies have or are developing guidelines for sludge application. I have used the nitrogen guidelines from several sources to construct Table II. It should be stressed that all but the Wisconsin guidelines are provisional and could be revised. Also the guidelines have special restrictions based on heavy metal levels. These restrictions could limit sludge application to lower rates than might be calculated from Table II. However, the data are presented for comparison purposes with the assumption that heavy metals are not a limiting factor.

All the guidelines except those from Ontario take into consideration ammonia volatilization in determining ammonium nitrogen availability. However, there is considerable variation among agencies. In addition to the effect of soil incorporation the Illinois guidelines also consider the effect of cation exchange capacity as evidenced by the soil texture variable.

Organic nitrogen availability is described as a decreasing series over a period of 4 to 5 years. The total availability over a five year period is the same for EPA and Wisconsin but Illinois suggests a much higher availability.

The Wisconsin and Illinois guidelines state that sludge will be applied at a rate such that the available ammonium and available organic nitrogen will supply nitrogen equal to the recommended fertilizer nitrogen requirement for the specific crop. The EPA guidelines suggest twice the nitrogen requirement of the crop. This would be approximately the recommended fertilizer nitrogen requirement. Ontario limits sludge application to the

amount that would apply 120 lb/acre of ammonium nitrogen. This could be applied once every four or five years depending on the crop, or it could be split into a series of smaller applications not to exceed a total of 120 lb/acre over the specified time period. This low application rate is an effort to distribute the sludge over a larger land area to better utilize the sludge phosphorus and to limit heavy metal accumulation. This more conservative approach negates the need to be concerned about availability of the organic nitrogen.

Using the data in Table II calculations were made to determine the volume of liquid sludge and the resulting amounts of sludge-applied total nitrogen and ammonium nitrogen that could be applied to a corn crop (nitrogen requirement: 120 lb nitrogen/acre/year) over a five year period. The results are shown in Table III. Although EPA, Wisconsin, and Illinois allow the same available nitrogen application rate, the more rapid mineralization rate suggested by Illinois limits the sludge application rate to 63% of that permitted by EPA and Wisconsin. At first glance one might expect the application rate permitted by Ontario to be 1/5 of that permitted by the other agencies. Since Ontario does not consider mineralization of organic nitrogen it turns out that the Ontario rate is actually 55% of that permitted by Illinois.

Table III. Total volume of sludge and pounds of nitrogen that could be applied over a five year period using the regulations for nitrogen application shown in Table II.

	Sludge Volume	Sludge-applied N	
		Total N	NH_4-N
	gal/acre	lb/acre	lb/acre
US EPA	120,000	1565	345
Wisconsin	61,200	1590	350
Illinois	38,400	1000	220
Ontario	20,700	540	120

Assumptions: Sludge 2430 mg/l total nitrogen
700 mg/l ammonium nitrogen
1730 mg/l organic nitrogen
Soil texture loam
Crop corn with 120 lb/acre N requirement

Table II: Guidelines for use of sewage sludge on agricultural land.

Agency	Ammonium Nitrogen (NH_4-N) Availability	Organic nitrogen (ON) availability — Year after application					5 year Total	Recommended nitrogen application rate
		1	2	3	4	5		
	------%------	----------%----------						
US Environmental Protection Agency (4)*	Surface -50 Incorp. -100	15-20	3	3	3		25	Available (NH_4-N+ON) + N mineralized from soil not to exceed twice the soil requirement
Wisconsin, Department of Natural Resources (5)	Surface 50 Incorp. 100	15	6	4	2		25	Available (NH_4-N +ON) not to exceed the fertilizer N requirement
Illinois Environmental Protection Agency (5)*	Surface 0 Shallow incorp. sandy soil-50 non-sandy -30 Subsurface application sandy soil-50 non-sandy -100	40	20	10	5	2.5	58	Available (NH_4-N+ON) not to exceed the fertilizer N requirement
Ontario Ministries: Agriculture and food Environment (1)*	100	Not considered						Corn and Hay: 120 lb/A NH_4-N once every 5 years or equivalent. Commercial sod: 120lb/A NH_4-N once every 4 years or equivalent.

*Guidelines are provisional.

SUMMARY

Sludges applied to land have usually undergone an extended period of anaerobic digestion. This process results in two basic nitrogen forms: (1) ammonium nitrogen which is readily available to plants; (2) organic nitrogen which mineralizes slowly and is thus less available. The concentration of these forms can vary greatly among treatment plants and with time at the same treatment plant.

Much of the ammonium nitrogen can be lost via volatilization if the sludge is not incorporated with the soil or subsurface applied. The remaining ammonium nitrogen and mineralization of organic nitrogen provide nitrogen for crop uptake or loss by leaching if excessive sludge is applied. A sizeable fraction of the applied nitrogen may also be lost via denitrification.

Guidelines being developed by various regulatory agencies generally base the sludge application rate on the amount of available nitrogen the sludge will supply. The available nitrogen is defined as a fraction of the ammonium nitrogen (a function of volatilization) plus a fraction of the organic nitrogen (a function of the rate of mineralization).

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Disposal of Industrial Nitrate Effluents by Means of Forest Spray Irrigation*

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INTRODUCTION

Trends in water pollution control practices recognize, in addition to technological solutions to effluent processing, that ecological criteria to maintain environmental quality are necessary.[15] The ecological approach relies on maintenance of the physical, chemical, and biological integrities of the landscape, whereas the technological solution involves removal of materials to some maximum permissible discharge level based on water quality criteria. Applicable legislation, which imposes a timetable for compliance,[1] also requires changes in pollution treatment practices to meet new water quality standards. Broadly categorized, these new treatment procedures involve: (1) total elimination of waste discharge following development of industrial recycle techniques; (2) imposition of land-use controls for nonpoint pollution sources; and (3) recycling of materials by land disposal.[15] Because of low initial and annual maintenance costs,[2] land disposal of wastes is receiving widespread attention as a means to meet higher water quality standards. Where land is available and engineering criteria can be met, land disposal is justifiably a logical choice.

Land disposal utilizes the terrestrial ecosystems as a "living filter" to renovate waste water by incorporating effluent material into natural biogeochemical cycles. Land disposal requires careful management because the introduction of materials into the terrestrial environment must take into account the biologically determined capacity of the ecosystem to assimilate effluent material, particularly when the effluent material occurs in the environment in small quantities such as in the case of nitrate. Environmental degradation resulting from improperly managed land disposal has consequences similar to those presently experienced in direct effluent discharge to aquatic ecosystems because both procedures are limited by a discrete assimilative capacity of the system for introduced materials. Numerous examples of land disposal of domestic sewage have been reported; disposal efficiency of nitrate (efficiency being determined as the proportion of effluent material incorporated in the biological system compared to the total added) ranges up to 85%.[13] Factors affecting disposal efficiency are not well documented. Limited information is available on the success of land disposal of highly concentrated industrial nitrate wastes.

Nitrate-nitrogen accounts for a small amount of the total nitrogen in a terrestrial ecosystem. Nitrates are readily leached by percolating soil water, as well as immobilized by vegetation and microorganisms. Once introduced to the soil ecosystem either through decomposition of *in situ* organic nitrogen or as nitrate salts, nitrate can be: (1) rapidly leached to groundwater, (2) absorbed by plants (0.1% annual of the total pool of soil nitrogen), (3) immobilized through assimilation and conversion to organic forms by soil microbes, and (4) denitrified to gaseous form, N_2, by anaerobic soil microbes with diffusion to the atmosphere. Under predominately aerobic soil conditions, dissimilatory denitrification accounts for no more than 10–15% of annual nitrogen losses.[2] Therefore, land disposal of nitrates relies on conversion of inorganic nitrogen to an organic form which is subsequently mineralized (transformed from organic to inorganic form), recycled, and lost from the system at a slow rate. However, a finite capacity for assimilatory denitrification can be expected; the consequences of exceeding this capacity can be severe.

Addition of nitrogen, an essential element for microbes as well as plant growth, improves the nutritional quality of the growth substrate (dead plant parts and plant residues comprising forest litter) for microbes. Decay of organic residues (humic compounds), [which are the principal "disposal sinks" for nitrogen], by microbial activity is accelerated. Transformation of organic nitrogen contained in humic compounds to NO_3 exceeds the rate of utilization by other ecosystem components and loss of environmental quality occurs when groundwater is contaminated by NO_3-rich soil water. Degradation of the chemical and structural integrity of the disposal system could also occur as the result of accelerated decay of both dead plant parts and humic compounds.

This paper summarizes field experiments initiated in June 1972 to evaluate the feasibility of land disposal of high nitrate salvage solutions. Pollution abatement procedures for Energy Research and Development Administration operations at Oak Ridge, Tennessee, currently are being updated in accordance

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[1] The amendments to the 1970-71 legislation (S. 2270 and H.R. 11896) require elimination of point source discharge by 1981, implementation of "best practicable" technology by 1976 and "best available" technology by 1981. "Practicable" refers to the average of best available technologies and "best available" refers to the best performer.

[2] Based on data from a Corps of Engineers study of the Chicago metropolitan area, initial costs of land disposal are from 50-80% less than physical-chemical and advanced biological treatment of domestic sewage and urban runoff. Maintenance costs of land disposal were estimated to be less than 50% those of other systems (Sopper and Kardos 1973).

with federal legislative directives for higher water quality standards. Among the local waste practices examined was the disposal of acidic effluents resulting from the operations of the Oak Ridge Y-12 plant. As a consequence of many processing operations, large quantities of waste solutions with high nitrate content require disposal. These wastes were being transported to disposal ponds (Figure 1). Seepage from the storage ponds and entry into headwaters of Bear Creek constituted an immediate problem to be solved while longer term concerns involved: (1) reduction in total volume of acidic effluent by means of inplant recycling, and (2) elimination of any point source discharge by means of alternative disposal practices.

Land disposal was suggested as both: (1) a backup system to inplant recycling procedures, and (2) a permanent system to dispose of wastes receiving inplant treatment to reduce total effluent volume and nitrate concentration. The purpose of these experiments was to determine:

1. the overall annual efficiency of landscape disposal at several application rates;
2. major biotic and abiotic accumulators of effluent NO_3-N;
3. rates of nitrogen loss; and
4. the optimum rate of nitrate application without loss of water quality or degradation of the terrestrial ecosystem.

Experimental Procedures

A series of 16 circular plots (each 0.088 acre, ~0.04 ha) was established in a mixed deciduous forest along the 1010-ft contour north of Bear Creek (Figure 1). In order to evaluate the capacity of the forest to incorporate nitrate, nitrogen concentration values were determined for the terrestrial ecosystem components (represented by boxes) in Figure 2. The nitrogen budget for the forest ecosystem, which is calculated from these data, serves as the basis for determining the assimilative capacity of the forest ecosystem for additional nitrogen. Periodic sampling of ecosystem components was used to determine seasonal and annual rates of nitrogen transfer (represented by arrows in Figure 2) about the system. The existence of many extant data from previous and ongoing Environmental Science Division (ESD) research projects on terrestrial element cycling minimized the amount and frequency of additional sampling needed.[10] Direct measurements of litter organic matter pools and nitrogen concentrations of both litter and soil were required, since these components are known to have large spatial variability.

Forest biomass was estimated from allometric relationships of tree diameter and weight of tree components (e.g., bole, branch, foliage, stump). Estimates of atmospheric input of nitrogen (~7.8 kg/ha annually) were obtained from the ongoing

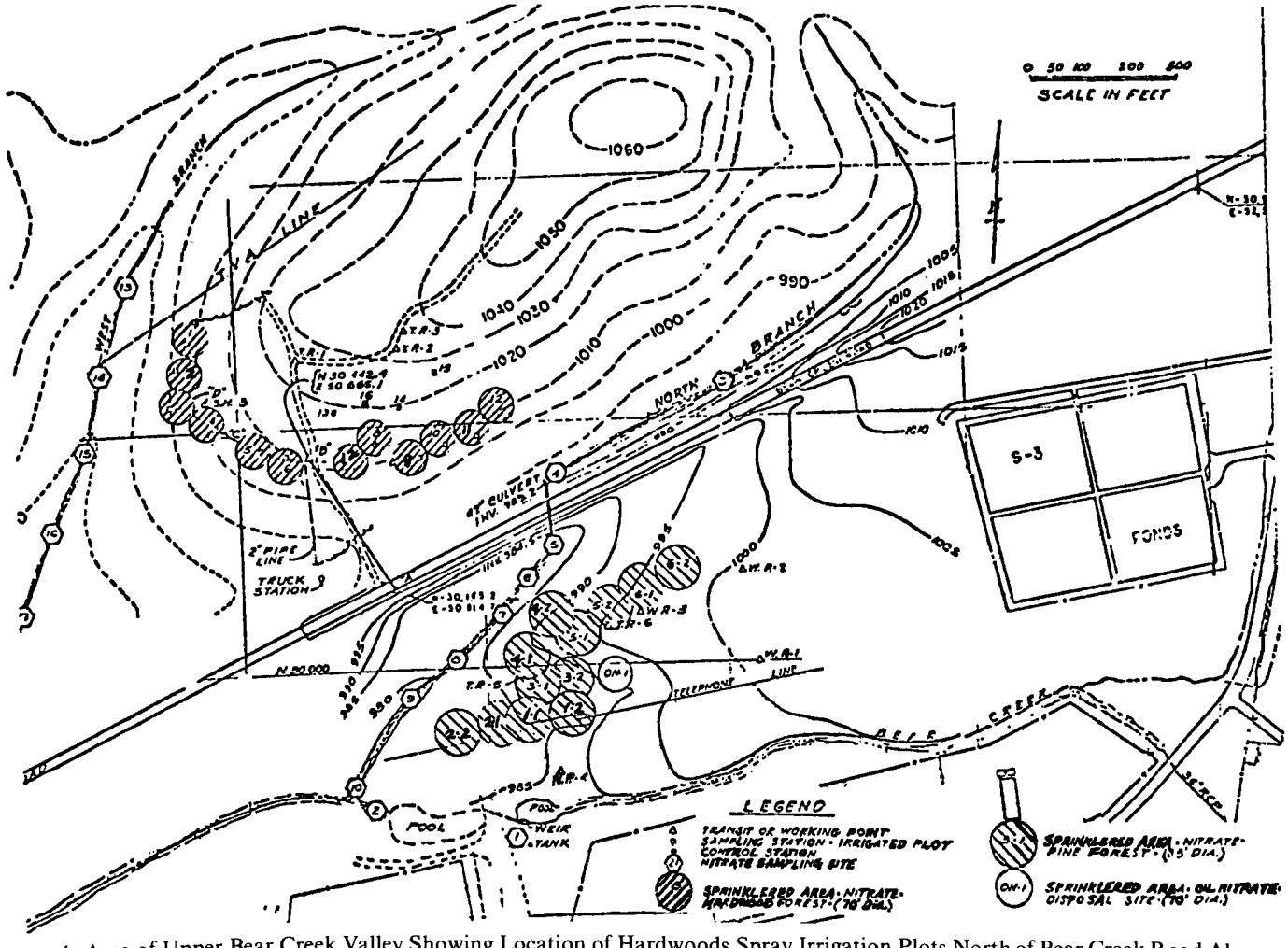


Figure 1: Area of Upper Bear Creek Valley Showing Location of Hardwoods Spray Irrigation Plots North of Bear Creek Road Along the 1010-foot Contour

Walker Branch Watershed Project located about one-half mile southwest of the irrigation site.[1] Nitrate, ammonia, and total-N (NH_4 and organic N) losses from each plot at Bear Creek were measured by extracting samples of percolating soil water at 75-cm depth with ceramic cup lysimeters. The porous ceramic cups have an entry value of 1 bar and, therefore, sample the gravitational soil water leaving the zone of major biological activity. Nitrate flux in soil water could be estimated from simulation models of water movement in the plant soil system as influenced by climatic variables, precipitation, temperature and solar radiation[14] or from known values of subsurface drainage in similar forested environments. Measured drainage from Walker Branch Watershed, a long-term environmental watershed study, was used in the present analysis. The experimental design provided for four replications of a control and three treatments (50, 125, and 200 kg NO_3-N per ha). The maximum application was that required for disposal of current salvage solution discharge on 1000 acres (404 ha), while the minimum rate represented the amount annually accumulated in vegetation. The intermediate rate was included to evaluate the nature of the forest responses to NO_3-N amendments.

Irrigation involved neutralization of salvage solution (containing 12,500 ppm nitrate) with lime hydrate to precipitate aluminum and other elements. The resultant supernatant of calcium nitrate was transported by truck to the irrigation site (effluent composition is summarized in Table I). Three applications (spray irrigation) of similar proportion were required to achieve the desired total N-amendment. Operations began on June 27, 1972, and the final application was delivered on August 24, 1972. Similar irrigation regimes were followed in 1973. Applications coincided with periods of depleted soil moisture to minimize rapid leaching of the highly soluble nitrate. By increasing the residence time of nitrate amendments in the upper soil zone, an increased amount of assimilatory denitrification (microbial immobilization) could be attained.

Table I: Summary of Effluent Composition and Application Utilized in the Bear Creek Irrigation Experiment.

	pH	Treatment (lb NO_3 per acre)[a]		
		200	500	800
June 27	10.2	27	161	292
July 27	10.8	89	177	265
August 14[b]	3.6	84	168	250

b. effluent composition chemical analysis[c] (ppm)

Element	ppm
Al	59.0
Ca	5000.0
Cr^{+6}	0.1
K	40.0
Li	10.0
Mg	0.3
Na	148.0
Cl	21.0
CO_3	546.0
F	0.5
NO_3	11514.0
SO_4	<15.0
PO_4	< 0.1

[a] One pound NO_3 per acre = 0.25 kg NO_3-N per ha.

[b] Lower pH is the result of addition of nitric acid neutralized salvage solution.

[c] Transport tanker water sample 7/27/72.

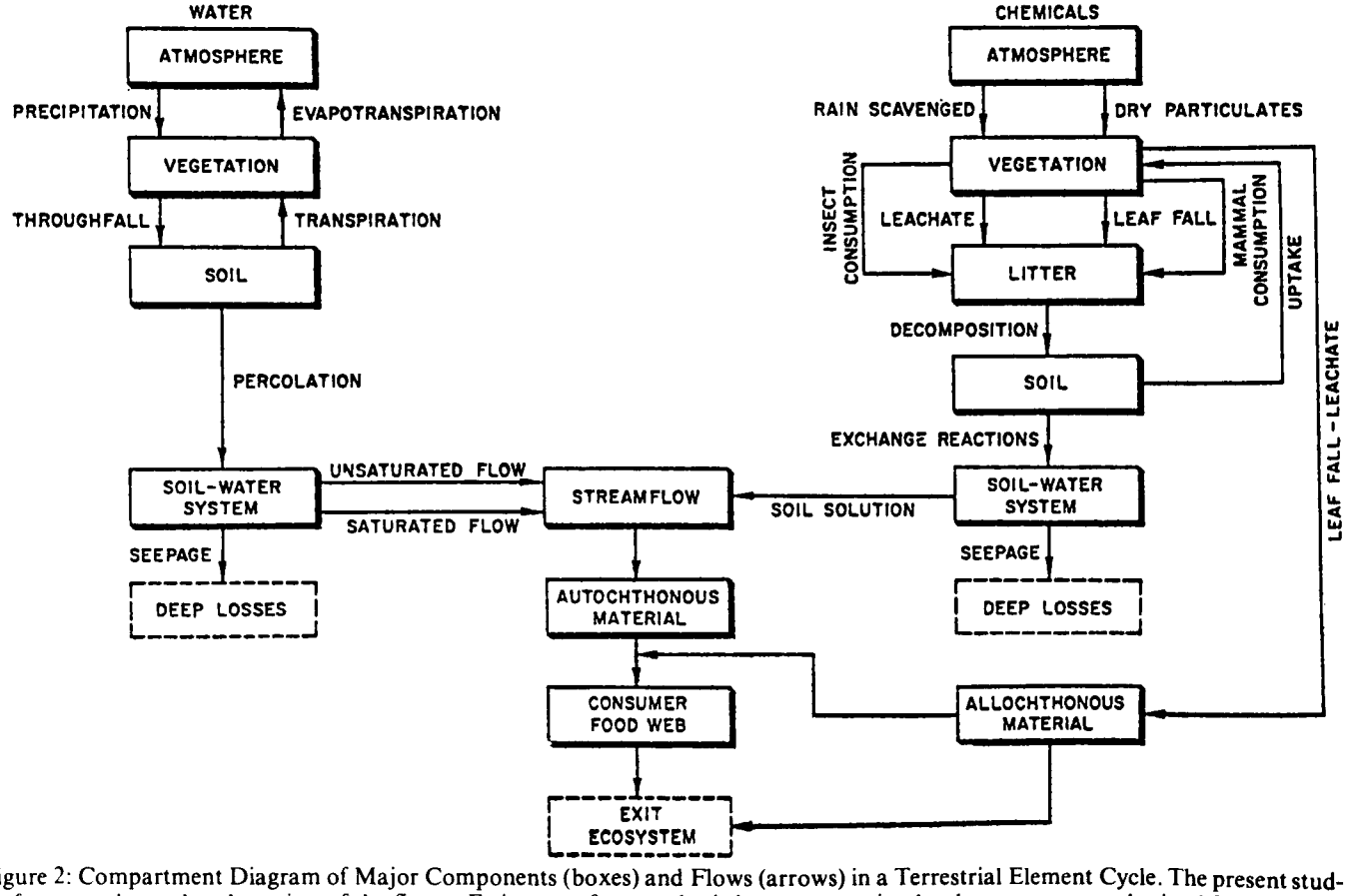


Figure 2: Compartment Diagram of Major Components (boxes) and Flows (arrows) in a Terrestrial Element Cycle. The present studies focus on the enclosed portion of the figure. Estimates of atmospheric input, vegetation leachate, etc., were obtained from Walker Branch Watershed studies. The exit point from the irrigated ecosystem is soil water percolating beyond the limits of the rooting zone (approximately 60 cm).

Results and Discussion

Forest Nitrogen Cycle - Pretreatment

Apportionment of nitrogen in the forest ecosystem depends on both biomass and nitrogen concentration in ecosystem components. The mean biomass of living vegetation (1.8×10^5 kg/ha) is of similar magnitude as other intensively studied local forests and is summarized in Table II. Estimates of root biomass pool size, mean annual net production, and turnover through annual root death were based on general forest growth patterns determined in other ongoing ESD research programs. Values of N-concentration were determined for the Bear Creek disposal site following standard procedures or based on local values reported.[10] Limited additional sampling of foliage and litter for N-concentration at the Bear Creek site was necessary to accurately establish baseline conditions since some enhancement of nitrogen uptake by plants was anticipated, which subsequently will be reflected in litter input and accumulation of N in woody material. Estimates of forest litter weight are averages (N = 16) for the irrigation area; no significant differences existed among plots.

Table II: Summary of Forest Organic Matter Pools; Net, Annual Accumulation, and Nitrogen Content (% Dry Weight)

Forest component	Standing pool (kg/ha)	N content (%)	Net annual biomass accumulation (kg/ha)
Foliage	5,500[a]	1.26	
Branch	32,450	0.42	3,536[b]
Bole-stump	122,800	0.17	
Lateral root			
<0.5 cm	10,050[c]	0.84	5,970[d]
>0.5 cm	10,050	0.42	(1,450)[e]
Litterfall			
Leaf	4,090[f]	0.60	
Branch	400[g]	0.42	
			% carbon
Litter			(Reichle et al. 1972)
O_1	6,875	1.42	46.5
O_2	11,900	2.43	38.7
Wood	3,250	0.54	47.0

[a]Estimates of forest biomass density were calculated from the diameters on irrigation plots.

[b]Net annual aboveground biomass accumulation based on average for similar forests on Walker Branch Watershed.

[c]Based on analyses on Walker Branch Watershed, lateral root biomass density is equal to stump biomass density (20,100 kg/ha).

[d]Total root biomass accumulation equals annual root death of roots <0.5 cm (~40% of standing pool <0.5 cm) plus 0.16 of net aboveground production (including foliage); proportions are based on extensive data collected in conjunction with Walker Branch Watershed.

[e]Represents net biomass accumulation (0.16 of total aboveground production).

[f]Litterfall is ~74% of peak leaf biomass density due to translocation of material from the leaf prior to abscission.

[g]An average value for similar forests on Chestnut Ridge.

Forest biomass represented only 8.7% of the total terrestrial nitrogen; dead organic matter in forest litter accounted for another 6.5%. The nitrogen associated with mineral soil comprised the bulk of the terrestrial nitrogen (Table III). Of the 6290 kg/ha of total nitrogen, nitrate-nitrogen accounts for 2.4% and is almost exclusively associated with soil. Nitrate-nitrogen amendments during effluent irrigation therefore were 0.32, 0.80, and 1.28 times as large as the mean pool of NO_3-N.

While N-pool sizes are based on biomass parameters specific to the Bear Creek site, atmospheric input, rate coefficients for vegetative uptake, root decay, and total system losses are based on forest responses determined during the course of other related research on forest ecosystems (Table III). Calculation of forest budgets is based on conservation of mass; the sum of inputs and initial compartment size equals the sum of final compartment value and all losses from that compartment. For example, estimates of litter decay assume that the size of litter compartments and annual decay fluxes change very slowly from year to year. Other assumptions involved in budget calculations are:

1. all vegetative N-uptake is from the soil compartment;
2. dissimilatory denitrification loss equals 15% of total system losses and is equal to microbial N-fixation. Both processes proceed slowly in the forest ecosystem;[3] and
3. the rate coefficient for measured system losses in soil water is assumed to be proportional to soil nitrogen; this implies that the mineralization of soil-N is substrate dependent and mineralization reactions follow the Law of Chemical Equilibrium.

Analysis of annual N-transfers among ecosystem components indicates that the largest fluxes of nitrogen are associated with decay of forest litter and root organic matter (129 kg N per ha per yr), and uptake by vegetation (120 kg N per ha per yr). Decay and vegetation uptake account for 93% of total annual nitrogen transferred within the system (Table IV). The forest ecosystem represents a close coupling of chemical and biological processes such that the overall ecosystem behavior is extremely conservative with respect to nitrogen; only 2.5 kg N per ha per yr of a total transfer among compartments of 266 kg N per ha per yr is lost from the system. The natural forest ecosystem conserves 99% of this annual N-flux (Table IV). Land disposal of nitrate requires manipulation of this efficient set of processes. Total inputs to litter annually amount to 38 kg N per ha per yr; NO_3-N amendments in current experiments elevate this input to 88, 163, and 238 kg N per ha per yr—up to a 619% increase over natural input rates.

Soil Water Quality

The efficiency of forest nitrogen cycling following effluent application was determined from analysis of nitrogen content of water exiting the rooting zone as gravitational soil water. No sustained significant elevation in NO_3-N concentration following effluent applications up to 200 kg NO_3-N per ha per yr was observed; Figure 3 summarizes average irrigation plot NO_3-N concentrations of soil water and control data from Bear Creek control plots and similar forest plots on Walker Branch Watershed. Elevation of NO_3-N concentration was coincident with each date of effluent application; concentrations did not exceed 0.5 ppm and occurred during a period of depletion of free soil water due by seasonally high evapotranspiration. Each application was closely followed by significant rainfall (Figure 3). The effect of summer rainfall, while adding insignificantly to the amount of free soil water, would readily leach nitrate into the soil profile. Elevation of NO_3-N in soil water from control areas also occurred (June 23) following rainfall totaling about 1.10 in (2.8 cm). The periodicity of elevated NO_3-N content closely follows control plot responses. The responses observed following effluent irrigation was confounded with typical responses following significant amounts of summer rainfall which followed irrigation operations.

[3] Broadbent and Clark (1965) have summarized results from lysimeter studies where unaccounted nitrogen averaged 15%. Since measured losses in deep seepage from the forest ecosystem are small in comparison to other N-fluxes and Todd (1972) reports similarly small N-amendments in forest soils due to fixation of atmospheric nitrogen, these two flux pathways are assumed to be small, equal, and therefore offsetting.

Table III: Forest Nitrogen Cycle. Compartment listing summarizes the average values for total-N (forest-litter components) and NO_3-N and NH_4-N for soil. Total organic soil nitrogen equals total-N less NH_4-N. Matrix to right summarizes estimated annual N-fluxes among components

	Pool – 6/72 (kg ha^{-1})			Source Compartment	Destination Compartment									
	Total-N	NO_3-N	NH_4-N		1	2	3	4	5	6	7	8	9	10
Atmosphere														
1. Wetfall N-fixation				1.	–	–	–	–	–	7.8	0.33[b]			–
Vegetation														
2. Foliage[a]	69.6	–	–	2.	–	–		40.6[c]		24.6	–	–	–	–
3. Branch	136.3	–	–	3.	–	–	–	–	–	–	4.4[d]	1.68[e]	–	–
4. Bole-Sump	206.3	–	–	4.	–	–	–	–	–	–	–	–	–	–
5. Lateral Roots	126.6	–	–	5.	–	–	–	–	–	–	–	–	41.0[f]	–
Subtotal	538.8													
Litter														
6. O_1	97.6	–	–	6.	–	–	–	–	–	–	21.5	–	–	–
7. O_2	289.2	–	–	7.	–	–	–	–	–	–	–	–	62.59	–
8. Twig Branch	17.6	–	–	8.	–	–	–	–	–	–	2.16	–	2.16	–
Subtotal	404.4													
Soil														
9. 0–6	2164	76.0	248	9.	0.33[g]			69.6[h]	50.15		–	–	–	2.25[i]
6–12	1174	33.8	100											
12–18	1020	27.1	81											
18–24	837	19.6	52											
Total Soil	5195	156.5	481											
10. Losses	2.25			10.	–	–	–	–	–	–	–	–	–	–
Total	6294.7													

[a] Litterfall amounts to 4090 kg/ha.

[b] Nitrogen fixation by soil-litter microbes assumed to be equal to dissimilatory denitrification.

[c] Net N-accumulation is equal to foliage uptake less amounts leached in throughfall and returned to annual litterfall. This calculation assumes no net change in N-concentration of woody components from year-to-year.

[d] Throughfall estimates from Walker Branch Watershed (Henderson and Harris 1975).

[e] Twig-branch litterfall estimate is for similar forests on Walker Branch Watershed (Henderson and Harris 1975).

[f] Root death/production estimates from other research (Harris et al., unpublished ms.).

[g] Denitrification losses estimated to be 15% of annual amount leached.

[h] All nitrogen uptake assumed to come from soil; seasonal (within year) distribution within tree not differentiated.

[i] Leachate losses are the mean of 1969-70 losses in streamflow from Walker Branch Watershed.

Table IV: Summary of nitrogen transfers in undisturbed forest ecosystem. Numerical code refers to source-destination legend in Table III.

Compartment input (kg ha^{-1} yr^{-1})		Compartment	Compartment loss (kg ha^{-1} yr^{-1})	
9 → 1	0.325	Atmosphere	7.80	1 → 6
9 → 2	69.60	Vegetation	4.40	2–5 → 7
	50.15		24.60	2 → 6
			1.68	3 → 8
			41.00	5 → 9
1 → 6	7.80	Litter	69.59	7 → 9
2 → 6	24.60		2.16	8 → 9
2–5 → 6	4.40			
3 → 8	1.68			
5 → 9	41.00	Soil	2.25	9 → 10
7 → 9	62.59		69.59	9 → 2
8 → 9	2.16		50.15	9 → 5
9 → 10	2.25	Groundwater	?	
Total	266.55		266.55	Total

Note: Efficiency of terrestrial nitrogen cycling

$$100 \times \frac{\text{total system efflux}}{\text{total annual N-transfers}} \quad \frac{(2.25)}{(266.55)} = 99+\%$$

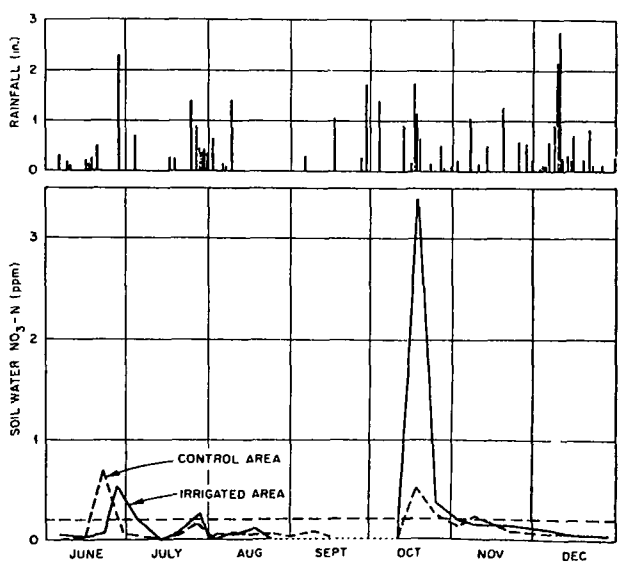


Figure 3: Summary of average NO_3-N concentrations for treated plots. There was no free soil water at the Bear Creek site from August 25-October 10, 1972; control plot data are for Walker Branch (when available). From October 18 on, control plot data are from Bear Creek. Effluent applications occurred on June 27, July 27 and August 14

As soil moisture recharge occurred beginning in late September, elevated NO_3-N concentration probably was due to small amounts of nitrate produced during mineralization of organic-N (augmented by salts introduced in effluent) and accumulating in the soil profile. Due to dry soil conditions which eliminate movement through the soil and sharply reduce biological activity, this material is retained until sufficient water is available for transport or immobilization by stimulated microbial activity. The period of elevated NO_3-N concentration was short. Average NO_3-N concentration the following week was 0.3 ppm. Irrigation plot responses indicate that nitrate losses following irrigation of up to 200 kg NO_3-N per ha per yr can be expected to increase NO_3-N concentration in soil water by small amounts during the year following summer irrigation.

A similar pattern of NO_3-N concentration was observed through 1974 (the termination of the monitoring program): temporarily elevated NO_3-N in free soil water coincident with irrigation returning quickly to less than 0.2 ppm. Averaging some 15 sampling dates from January 1973 to April 1974, NO_3-N concentrations (ppm) for 0, 50, 125, and 200 kg ha per hr applications were: 0.007, 0.069, 0.066 and 0.160, respectively. While these values are well below any regulatory limit or known damage threshold, such an increase could forebode another class of problem—non-point pollution inputs. Assuming drainage flux characteristics remain the same, this irrigation practice could increase the N export (and potential input to streams) by as much as a factor of 20. This increase in itself is not a problem but emphasizes the need to plan such operations recognizing other land-use impacts, watershed size and need for long-term monitoring.

Organic Matter Losses

The carbon-to-nitrogen ratio (C/N) of an organic substrate (e.g., litter) is a main determinant of microorganism activity. At a C/N ratio above 20 to 25, microorganisms are nitrogen limited; as the C/N ratio is lowered below 20 to 25 (e.g., addition of nitrate salts), microbial activity is accelerated since nitrogen no longer limits metabolic processes. As the C/N ratio approaches 15, other factors (probably the amount or chemical form of substrate carbon and/or phosphorus) become limiting to further increases of microbial activity. Thus, a land disposal system may be limited by the amount of organic substrate available to support assimilation of nitrogen into the natural biogeochemical cycle. Adding wastes beyond the assimilation capacity which is limited in part by the carbon-nitrogen balance could produce deleterious effects on the disposal system attributed to the removal of litter organic matter.

The layer of forest litter organic matter appeared to undergo accelerated decay with the initiation of irrigation operations. In order to evaluate the effect of NO_3 irrigation on litter decay, litter compartment sizes were compared with initial values (Table V).

Table V: Percent of initial (6/72) litter organic matter following irrigation with NO_3-N at rates of 0, 50, 125 and 200 kg ha yr. Irrigation applications were made in three equal treatments between June 27 and August 14, 1972.

Irrigation rate (kg/ha/yr)	Date		
	September 1972	February 1973	May 1973
0	89	90	85
50	84	96	87
125	82	85	79
200	66	73	68

Treatment levels up to 125 kg NO_3-N ha^{-1} yr^{-1} had little effect on litter compartment size compared to the control. Only at an application rate of 200 kg NO_3-N ha^{-1} yr^{-1} was litter appreciably decreased (Table V). Much of the observed decrease was the result of accelerated disappearance of woody litter. Woody litter nitrogen content at this treatment level also exhibited a nearly twofold increase from pre-irrigation levels (0.5% pre-irrigation to 0.97% in September following completion of irrigation). This increase in woody litter N content combined with the accelerated disappearance of this substrate type suggests that one impact of high nitrogen wastes could be on the C/N ratio or organic substrates essential to microbial immobilization.

Longevity of Land Disposal System—Simulation Models

Experimental data indicated some reduction in litter organic matter at the highest rate of application. However, any addition of nitrogen gradually changes the initial conditions. Annual N-amendments could gradually lower C/N ratios of litter components and thus promote accelerated decay. Within a few years the nitrogen balance within the forest ecosystem could change such that any subsequent addition of NO_3-N could result in deleterious effects on the litter and soil nitrogen balances.

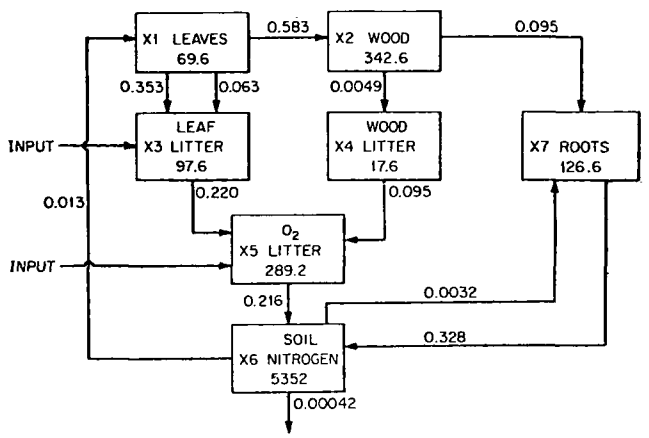
In order to evaluate the long-term response of land disposal system without further experimentation, which was not feasible in this case, linear compartmental simulation models were constructed for both nitrogen (control and minimum treatment of 50 kg NO_3-N per ha per yr) and carbon (revised after).[12] The results of model simulation are not a substitute for a monitoring program, but they do facilitate selection of ecosystem parameters essential to an effective monitoring program. Model simulation also assists in cost analysis since capital cost outlay for relocation of the irrigation area can be projected from a minimal program of further ecosystem analysis. Model simulation can further assist in cost analysis by allowing for *a priori* study of disposal system longevity and efficiency for alternative types of ecosystems.

The basis for calculation of rate coefficients for N cycling was the budget and annual flux summary (Tables III and IV). A diagrammatic summary of the nitrogen model and the equations used in calculations are shown in Figure 4. Simulation of NO_3-N irrigation involved changing the input constant to leaf litter from 7.85 to 57.85 kg NO_3-N per ha per yr. The simulation further assumed that a 50 kg NO_3-N amendment would increase foliage N-content by 67%.[11] Data on effects of nitrogen fertilization on hardwood forest production are inconclusive; therefore, a constant amount of forest production was assumed in the simulation on the basis of current growth rates (leaves = 2000, wood 1750, and roots = 3750 kg C per ha per yr, Figure 5). Other transfers were calculated from extant data on forest carbon cycling.[12] The criterion used to estimate the maximum disposal period was depression of total litter C/N to the value of the C/N ratio (pre-irrigation) of the fragmented layer (O_2) of litter organic matter.

The results of simulation suggest that the hardwood forest could withstand a 3-4 yr chronic input (summer) of 50 kg NO_3-N per ha per yr (200 lb NO_3 per acre). In the simulation, nitrogen accumulation in litter results in depression of the C/N ratio to a level generally observed to accompany accelerated organic matter decay (Figure 6). The time required for recovery of the carbon-nitrogen balance of litter in the hardwood forest was not determined in this case. Where effluent disposal does affect the ecosystem, recovery time should be determined in order to establish a rotation cycle for disposal.

Since the amount of organic matter and its carbon-nitrogen balance appear to be the factors largely determining the capacity of the forest ecosystem to assimilate nitrate-nitrogen, we summarized nitrogen and carbon budgets for pine forests. Pine typically has a lower nitrogen content and therefore a higher C/N ratio. These characteristics result in greater accumulation of organic matter in the litter (Table VI). A typical pine forest has a

total litter C/N ratio of >31. Based on the compartment designs in Figures 5 and 6, but with transfer coefficients specific for pine forests (Table VI), nitrogen cycling of this forest ecosystem was simulated using a chronic additional nitrogen input of 50 kg NO_3-N per ha per yr by utilizing a forest system with a large litter C/N ratio, disposal on the same forest area could continue for 6 yr before nitrogen accumulation would depress the litter C/N ratio to a level accompanying accelerated decay of litter organic matter.



$\dot{X}1 = 0.013\,(X6) - 0.583\,(X1) - 0.353\,(X1) - 0.063\,(X1)$
$\dot{X}2 = 0.583\,(X1) - 0.0049\,(X2) - 0.095\,(X2)$
$\dot{X}3 = \text{INPUT} + 0.353\,(X1) + 0.063\,(X1) - 0.220\,(X3)$
$\dot{X}4 = 0.0049\,(X2) - 0.095\,(X4)$
$\dot{X}5 = 0.220\,(X3) + 0.095\,(X4) - 0.216\,(X5) + \text{INPUT}$
$\dot{X}6 = 0.216\,(X5) + 0.328\,(X7) - 0.0032\,(X6) - 0.013\,(X6) - 0.00042\,(X6)$
$\dot{X}7 = 0.0032\,(X6) - 0.328\,(X7) + 0.095\,(X2)$

Figure 4. Summary of linear compartment model of annual nitrogen cycling. Initial conditions for each compartment are based on compartment values listed in Table III. Rate constants are the quotient of annual N-flux (kg N ha^{-1} yr^{-1}) and compartment size (kg N yr^{-1}). The leaf compartment (Xl) includes a transfer associated with litterface (0.353) and foliar leaching by rainfall (0.063)

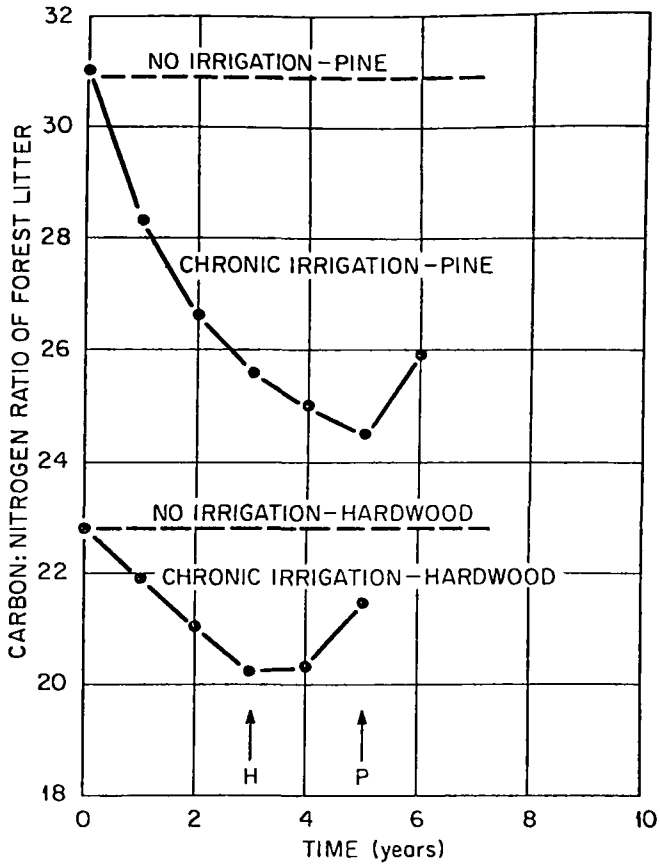
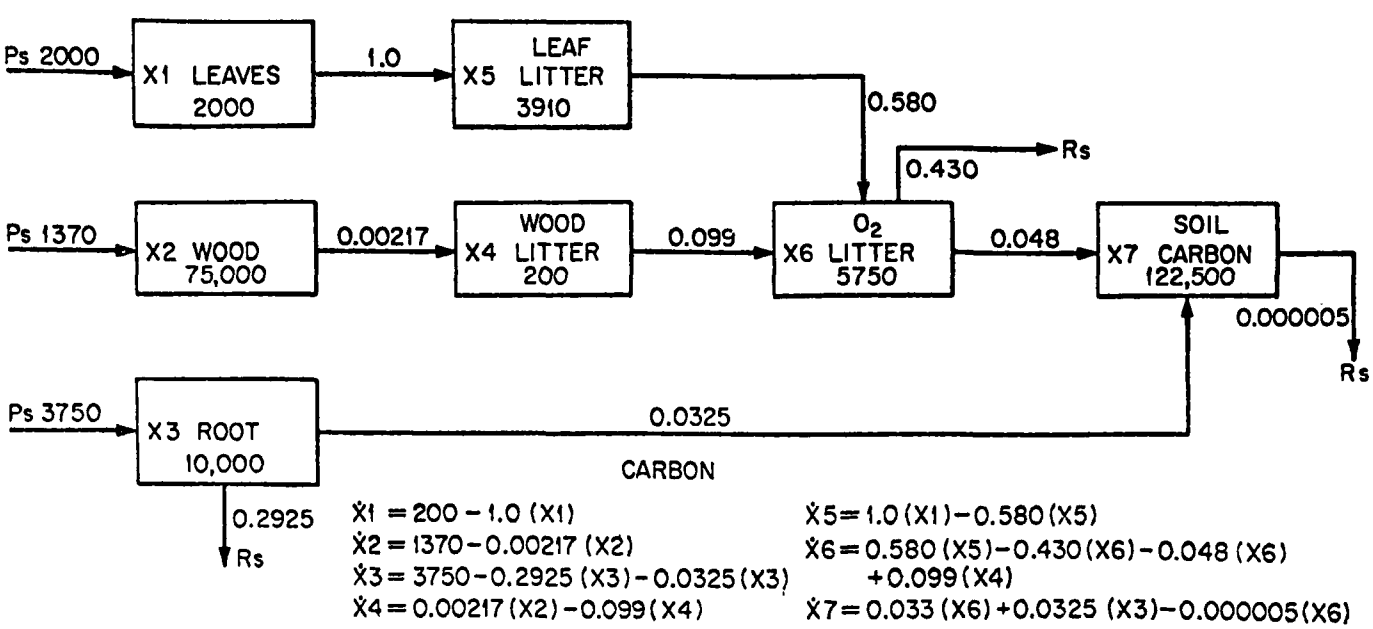


Figure 6: Effects of annual NO_3-N irrigation on forest litter carbon-nitrogen ratios. Results of model simulation indicate that pine forests have twice the longevity as disposal areas compared to hardwood forests for an annual application of 50 kg NO_3-N ha^{-1}



$\dot{X}1 = 200 - 1.0\,(X1)$
$\dot{X}2 = 1370 - 0.00217\,(X2)$
$\dot{X}3 = 3750 - 0.2925\,(X3) - 0.0325\,(X3)$
$\dot{X}4 = 0.00217\,(X2) - 0.099\,(X4)$
$\dot{X}5 = 1.0\,(X1) - 0.580\,(X5)$
$\dot{X}6 = 0.580\,(X5) - 0.430\,(X6) - 0.048\,(X6) + 0.099\,(X4)$
$\dot{X}7 = 0.033\,(X6) + 0.0325\,(X3) - 0.000005\,(X6)$

Figure 5: Summary of linear compartment model of carbon accumulation in the forest ecosystem. Compartment values are for the Bear Creek site based on 50% carbon content. Rate constants were determined from data summarized by Reichle *et al.* (1972). Carbon pool sizes are expressed as kg C ha^{-1}. Allocations of net photosynthate (Ps) to tree components were assumed to be constants. Heterotrophic respiration of decay organisms (Rs) is included where compartment carbon losses are largely as CO_2

Table VI: Summary of Carbon and Nitrogen Pools Used in Pine Forest Simulation

Compartment	Carbon (kg/ha)[a]	Nitrogen (kg/ha)[b]
Living vegetation		
Wood	2,000	36
Roots	75,000	201
Forest litter		
O_1	6,050	159
O_1-wood	2,000	9
O_2	5,550	237
Soil	122,500	5,350

[a] 1.12 kg/ha = 1 lb/acre.

[b] 1 kg NO_3–N per ha = 4 lb NO_3 per acre.

SUMMARY AND RECOMMENDATIONS

Land disposal of high nitrate-bearing wastes was evaluated using a limited experimental program and extant data on forest ecosystems With effluent applications limited to dry summer periods, NO_3-N content of soil water exiting the root zone was increased on the average but content remained low relative to the content of effluent input. Even small changes in water quality such as those observed in the present study need to be evaluated relative to existing water quality, other land-use practices or options and potential long-term impact.

First year responses of the litter compartment of the treated ecosystems suggested that over repeated applications litter decay could be appreciably accelerated. Altered balance of carbon-nitrogen appeared to be the controlling factor. Simple linear compartment models of the forest carbon and nitrogen cycles were used to conservatively project the dynamics of the litter C/N ratio. Assuming constancy of biomass production and decay rates, hardwood and pine forests were estimated to have a longevity of from 3 to 6 years respectively before significant narrowing of the C/N ratio occurred. This may be an underestimate of longevity since the only nitrogen content appreciably increased was woody litter—a small fraction of the total litter.

A mass balance of the disposal system could not be determined because nitrogen increments added in effluent were a small fraction of the total nitrogen in the ecosystem, particularly of the soil compartment. Determination of mass balance is essential to determine the actual disposal efficiency, fate and potential for deleterious effects of the disposal, but represents a cost and time allocation well beyond the interest and resources of most clients. In the present case, land disposal and *in vitro* denitrification (packed column and stirred reactor types) were simultaneously evaluated as possible means of disposal. Considering the prompt effects on forest litter, the relatively short longevity of particular disposal sites, the large land area required and the very successful trials with denitrification processes, land disposal was not selected as a primary means of disposal.

ACKNOWLEDGMENTS.

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Transport and Reaction of Contaminants in Ground-Water Systems

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INTRODUCTION

Problems of mineral-resources utilization and waste-product disposal include assessment of the environmental impact of waste-product incorporation into the subsurface layers of the earth. Assessment of this kind concerns itself primarily with the possible pollution of useable ground-water resources. Among other things, it must consider the possibility of moderating or eliminating such dangers by using the natural dispersive, pollutant-fixing, and pollutant-degrading capabilities of the subsurface. Accurate assessment of such problems requires the capability to predict quantitatively the transport of solutes and the resulting concentrations of pollutants in the subsurface environment, including saturated and unsaturated zones. It is the purpose of this paper to discuss briefly the present status of techniques for making such predictions in the saturated zone.

Theory

The most often used and probably the most promising of the currently available tools for predicting solute transport in the subsurface environment are mathematical models that utilize digital computers. Of these, the ones that now are being developed extensively are based on adaptations, generalizations, and extensions of an approach (the analytical solutions of the defining differential equations) that has been used for some time in connection with certain chemical applications, such as chemical engineering and chromatography (Bird[2] Helfferich[9]). These generalizations, extensions, and modifications are needed because the systems dealt with in connection with environmental problems are often more complex than those in the chemical-processing applications. For instance, environmental models that cannot handle layered or other types of nonuniform systems would have little general utility. On the other hand, most operational chemical-engineering models assume uniformity of the porous media analyzed.

The models of solute transport in subsurface layers ordinarily consist of two parts. One part, the waterflow submodel, computes water seepage velocities in the subsurface region investigated. The second part, the solute-transport submodel, uses these velocities (as well as other parameters) to compute the concentrations of the solutes of interest.

The seepage velocity necessary to the solution of the solute-transport equation is computed using Darcy's law and can be written as

$$V_i = \frac{-K_{ij}}{\epsilon} \frac{\partial h}{\partial x_j} \qquad (2)$$

where V_i is the seepage velocity in the x_i direction, LT^{-1}. The solute-transport submodel is usually considerably more complex than the waterflow submodel. The waterflow submodel describes a single, purely physical process involving a single, mobile, system component (water). On the other hand, the solute-transport submodel may be concerned with many processes, each one of which may involve many, usually miscible, system components.

Solute transport includes at least two processes that are physical in nature: convection (solute transfer by and with flowing water) and hydrodynamic dispersion (the mixing between the incoming solutes and those originally present in the pore water). In addition, the submodel under consideration very often must takeinto account chemical and biological processes. Reddell and Sunada[17] and Bredehoeft and Pinder[4] present the following equation to prepresent solute transport with reactions through porous media. The present authors have generalized and added into such an equation the chemical reactions of the solute species both within the void space and on the solid surface.

$$\epsilon \frac{\partial c}{\partial t} + \frac{\partial}{\partial x_i}(\epsilon c V_i) - \frac{\partial}{\partial x_i}\left(\epsilon D_{ij} \frac{\partial c}{\partial x_j}\right) + C'W^* = CHEM \qquad (3)$$

where CHEM equals

$-\rho_b \frac{\partial \bar{c}}{\partial t}$ for equilibrium-controlled ion-exchange reactions

$\sum_{k=1}^{s} R_k$ for s chemical rate controlled reactions

$-\lambda(\epsilon c + \rho_b \bar{c})$ for radioactive decay

where

- c is the concentration of the solute (mass of solute/volume of liquid), ML^{-3};
- D_{ij} is the coefficient of hydrodynamic dispersion, L^2T^{-1};
- C' is the concentration of the solute in the source or sink fluid, ML^{-3};
- ρ_b is the bulk density of the solid (mass of solid/volume of sediment), ML^{-3};

$\bar{c}$ is the concentration of the species adsorbed on the solid (mass of solute/mass of sediment), ML^{-3};

R_k is the rate of production of the solute in reaction k of s different reactions, $ML^{-3}\ T^{-1}$;

λ is the radioactive-decay constant (equal to 1n 2/half life), T^{-1}.

The solute-transport equation contains several flux and sink/source terms that merit further consideration and definition.

Physical Processes

The second and third terms on the left-hand side of Equation 3 define solute transport due to dispersive and convective fluxes, respectively. The dispersive flux is proportional to D_{ij}, the coefficient of hydrodynamic dispersion, and the concentration gradient, and accounts for the mixing process that occurs within pores between the native and contaminant fluid. The dispersion coefficient is assumed to be a function of the seepage-velocity vector V_i and the characteristic lengths, $_L$ for the longitudinal direction and $_T$ for the transverse direction. Bear[1] gives in detail the formula for calculating the various components of the dispersion tensor if the velocity and characteristic lengths are given. Bear[1] also indicates that D_{ij} includes both diffusion and mechanical dispersion, and is equal to the latter when diffusion is negligible.

Chemical Processes

Two types of chemical reactions often occur in contamination problems and are given as examples; these are ion-exchange reactions that may be considered equilibrium controlled and irreversible rate reactions. Because several field contamination problems have been modeled, a discussion of the chemistry that affects the analysis of these processes follows:

Equilibrium-controlled ion exchange

A typical reaction might be written as follows (Bolt, 1967; Helfferich, 1962)

$$b\,\bar{c}_1 + a\,c_2 \rightleftharpoons a\,\bar{c}_2 + b\,c_1 \tag{4}$$

where 1 and 2 are chemical exchanging species with a and b valences respectively.

The adsorbed species are given as $\bar{c}_i$ and the dissolved species as c_i, i = 1,2. The use of a selectivity coefficient may be used to relate the concentration of products and and reactants at equilibrium:

$$K_s = \frac{(\bar{c}_2)^a\,(c_1)^b}{(\bar{c}_1)^b\,(c_2)^a} \tag{5}$$

where K_s is the ion-exchange selectivity coefficient.

Equation 5, when incorporated into the solute-transport equation, results in nonlinear terms. Rubin and James[21] treat this case, as well as cases involving two or more exchanging species. A simplified equation results from the common situation that occurs when the exchanging ion is very low in concentration relative to the other ions. Then the exchange process will not materially affect the concentration of the other exchanging ions, either in solution or adsorbed on the matrix. The adsorbed phase of the major ion is then nearly equal to the cation-exchange capacity (CEC), and the solution phase of the major ion is equal to the total concentration (C_o), which remains constant. Equation 5 can then be rewritten as,

$$K_s = \frac{(\bar{c}_2)^a\,(C_0)^b}{(CEC)^b\,(c_2)^a} \tag{6}$$

or

$$K_d = \frac{\bar{c}_2}{c_2} = \left[\frac{K_s\,(CEC)^b}{(C_o)^b}\right]^{1/a} \tag{7}$$

where K_d = ion-exchange distribution coefficient.

Equation 7 postulates a linear relationship between the adsorbed species and the solute species where the slope of the equilibrium ion-exchange isotherm is the distribution coefficient. Equation 7 thus provides the relationship between the adsorbed species and dissolved species necessary to solve the solute-transport equation.

Rate-controlled chemical reactions

The R_k term in Equation 3 denotes all possible rate-controlled chemcial reactions occurring within the pore space, including both homogeneous (liquid-liquid) and heterogeneous (liquid-solid) reactions. Homogeneous reactions could include ion-complex dissociation and formation, and heterogeneous reactions, precipitation-dissolution, and ion exchange.

Radioactive decay

The subsurface disposal of radioactive products presents an example where a first-order irreversible rate reaction occurs. This reaction is the radioactive decay of the adsorbed or dissolved species. The rate constant can be derived in the following manner. The disappearance of a species by a first-order, irreversible reaction is given by the equation

$$\frac{dc}{dt} = -\lambda c \tag{8}$$

when λ is the rate constant, T^{-1}. This equation can be integrated with integration limits chosen as the time necessary for the initial concentration to decrease by half

$$\int_{c_0}^{c_0/2} \frac{dc}{c} = -\lambda \int_0^{t_{1/2}} dt \tag{9}$$

where

c_o = initial concentration, ML^{-3}; and

t = half life of species, T.

The equation is integrated and solved for λ to obtain

$$\lambda = \frac{0.693}{t_{1/2}} \tag{10}$$

These reaction terms can be incorporated into the solute-transport equation in the following manner: Assume that during its transport a radioactive chemical species is disappearing by a

first-order irreversible rate reaction and is being exchanged reversibly by an equilibrium-controlled process in which the exchange isotherm is linear.

Equations 7 and 8 give the relationships between c and $\bar{c}$. The term $\bar{c}$ is $K_d c$; and $\partial\bar{c}/\partial t$ is $K_d\,(\partial c/\partial t)$.

Substitution of these terms into Equation 3 gives

$$\epsilon \frac{\partial c}{\partial t}\left(1+\frac{K_d\rho_b}{\epsilon}\right) = \frac{\partial}{\partial x_i}\left(\epsilon D_{ij}\frac{\partial c}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(\epsilon c V_i) - c'W^* - \epsilon\lambda c\left(1+\frac{K_d\rho_b}{\epsilon}\right). \quad (11)$$

A retardation factor, R_f, which appears in equilibrium-controlled trace-exchange reactions, is defined as

$$R_f = 1 + K_d\rho_b/\epsilon. \quad (12)$$

Equation 11 is divided by this retardation factor to obtain

$$\frac{\partial c}{\partial t} = \frac{1}{R_f}\frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial c}{\partial x_j}\right) - \frac{1}{R_f}\frac{\partial}{\partial x_i}(cV_i) - \frac{1}{R_f}\frac{c'W^*}{\epsilon} - \lambda_c. \quad (13)$$

The retardation factor thus retards the flux of the solute species with respect to the fluid flow. This reduced velocity of ions effectively provides a safety factor that prevents excessive movement of harmful pollutants.

Numerical Techniques and Field Studies

The equations discussed in the preceding section describe how changes in concentration, resulting from various processes, are related to each other. These partial differential equations may be solved for concentrations provided that certin necessary data about the system in question are available to describe the system properties, sources and sinks, and initial and boundary conditions. Several ways of solving the equations are available—analytical techniques, analog computers, and numerical techniques. Under conditions usually met in environmental problems, it seems that only the combined use of numerical techniques and digital computers can provide sufficient generality for routine performance of the task under consideration.

Many numerical methods are known (Remson[18] von Rosenberg,[23]). In all of these the basic transport equations must be approximated by other questions (usually algebraic) that subsequently are used to write the computer program. This transformation reduces the original mathematical problem to the solution of large systems of simultaneous algebraic equations. Also, note that in all numerical methods concentrations are computed only for certain discrete points in space. This is done for successive time values, the intervals between these values usually being relatively small. The points in space and time for which computations are made are called grid points, and the intervals between them are called grid intervals. Numercial methods yield concentration values that are approximate. However, by decreasing the size of the grid intervals, it is possible to increase the accuracy of numerical results as much as one wishes (within the limitations of the conceptual model used and the data available). The numerical accuracy of the solution usually exceeds the measurement accuracy of the system parameters. Use of smaller grid intervals requires more time-consuming (and hence more expensive) computer calculations. Therefore, the grid intervals may be too small to be practical. Various numerical methods differ in the degree of accuracy they may yield for any particular problem with a given set of grid intervals. They also may differ in computer size and speed requirements, in the degree of mathematical sophistication needed to use them, and in other features. Because of such differences and because of the variety of needs the models must satisfy, it is usually better to select the most efficient numerical method for a given type of a problem than to try to develop one general method applicable to all the expected problems.

The numerical methods used earliest in solute-transport models were the finite-difference methods. Although the finite-difference methods performed very satisfactorily in connection with the waterflow submodel, their use in the solute-transport submodel produced considerable difficulties whenever the effects of convection were large in comparison with those of dispersion. These difficulties are caused by numerical dispersions—artifacts that distort the model's predictions and that result from the nature of approximation made by the difference methods. They express themselves by the smearing of sharp fronts or by oscillations.

These difficulties can be rectified by using either large artificial dispersion coefficients or small space increments. However these techniques produce either inaccurate results or involve excessive computer storage and time requirements.

Peaceman and Rachford[13] presented a finite-difference scheme to solve the two-dimensional transport equation. They illustrated the oscillation problem, caused by small dispersion coefficients, for the one-dimensional case and presented a "transfer of overshoot or undershoot" correction technique. Shamir and Harleman[22] studied a steady-state water-flow situation and solved the solute-transport equation in terms of streamlines and velocity potentials. Because velocity is parallel to a streamline, one-dimensional flow along a streamline could be assumed and cross-produce terms of the dispersion tensor omitted. Unfortunately, both of these approaches have restrictions. The method of Peaceman and Rachford[13] is not rigorous and the use of streamlines assumes steady-state flow conditions and unrealistic one-dimensional flow.

In an effort to avoid difficulties associated with finite-difference methods a numerical technique was developed by appropriately modifying the method of characteristics (MOC). Garder and others[6] were among the first to use the MOC to solve the solute-transport equation. Their modification of the method included a point-tracking technique in which particles were assigned initial concentrations and allowed to move with the velocity of water to new locations during successive time increments. Concentrations were averaged over the various grid domains and the dispersion changes calculated by an explicit finite-difference method. Reddell and Sunada[17] and Bredehoeft and Pinder[4] expanded the one-dimensional case of Garder and others[6] to two-dimensions. Pinder and Cooper[15] as well as Reddell and Sunada[17] utilized the MOC to include density dependence and solved a salt-water encroachment problem.

The method and the computer program developed by Bredehoeft and Pinder[4] have been extensively used within the U.S. Geological Survey to solve field problems involving contamination. Bredehoeft and Pinder investigated a contamination problem in Georgia, where saline water upwelled into a fresh-water aquifer, and computed the effects of discharge or barrier wells to limit the migration of the contaminant. Hughes and Robson[10] investigated contamination from sewage lagoons and industrial cleaning areas, and predicted the results of various ground-water-quality containment practices. Konikow and Bredehoeft[11] investigated the effects of irrigation and return flow on water quality in the ground-water system and in the adjacent river. Robertson and Barraclough,[19] at the National Reactor

Testing Station (now the Idaho National Engineering Laboratory), Idaho, modeled the movement of injected pollutants into a basaltic aquifer and predicted the concentration profile for a period of 20 years. Robertson[20] modified the solute-transport equations to include the chemical-reaction terms that accounted for ion exchange and radioactive decay.

The Galerkin finite-element method has been utilized recently to solve transport equations of all types. It can be a highly accurate and efficient method, but is difficult to program. In the foreseeable future this method probably will be used with increasing frequency whenever the hydrodynamic-dispersion effects are small in comparison with the convection effects.

Price and others[16] first showed the superiority of the Galerkin, finite-element method over the standard, finite-difference method to solve the one-dimensional mass-transport equation. Guymon and others[8] solved the multidimensional convection-diffusion equations using finite-element methods.

Pinder[14] used a Galerkin finite-element technique with isoparametric quadrilateral elements to solve a ground-water contamination problem on Long Island, New York. In this case, elements could take on a variety of configurations and be reduced to rectangles by a mapping procedure. The resulting set of linear equations was solved by a direct-matrix technique. This application was conservative in that chemical reactions involving the solute were not considered.

Grove[7] used the Galerkin finite-element technique to solve the field problem of Robertson[20] that included the chemical-reaction effects of ion exchange and radioactive decay. Since 1952 chemical and low-level radioactive wastes were disposed of into the ground-water system at the Idaho National Engineering Laboratory in southeastern Idaho. These wastes migrate down the hydraulic gradient and, unless removed from the aquifer by physical or chemical means, discharge into the Snake River. Figures 1 and 2 present typical modeling results matching the numerical and field data for groundwater contamination by tritium and strontium-90. The model closely approximates the movement of these two ions. The tritium decays radioactively but moves with the velocity of the ground water, while the strontium-90 is greatly retarded by ion exchange as well as being influenced by radioactive decay.

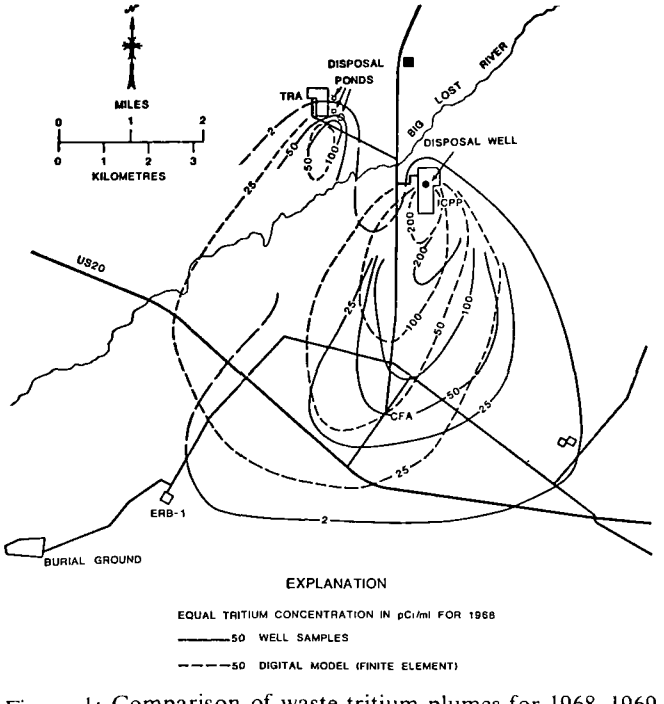

Figure 1: Comparison of waste tritium plumes for 1968–1969 based on well sample data and computer model

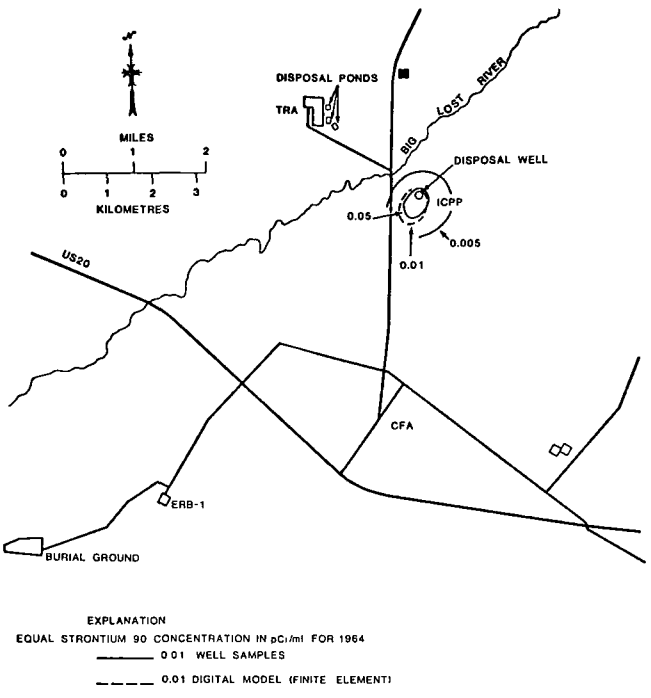

Figure 2: Comparison of waste strontium-90 plumes for 1964 based on well sample data and computer model

Some Unsolved Problems

The lack of data concerning chemical parameters that control solute concentrations during movement through porous media is a weak link in the modeling process. The independent determination of chemical-reaction parameters that are applicable to field situations is indeed a most difficult task. The concentration of moving solute may be influenced by concentrations and reactions of other adsorbed and dissolved chemical species. The capability to model multiple reactions may be limited by computer size and economics. Another matter that must be considered is the development of methods to use field geochemical data available at point locations to generalize the chemical characteristics of the aquifer matrix through which reacting solute species pass.

The determination and understanding of the dispersion coefficient is another research need. Although the dispersion process is idealized by analogy with Fick's law of diffusion it most likely results through permeability variations in the aquifer. A more complete understanding of dispersion through field studies that involve fracture flow and anisotropic systems would be of value.

The unsaturated zone as a source to the ground-water aquifer must be more fully defined concerning solute transport. Dispersion phenomena, chemical reactions, and possible biological reactions need additional attention. Proper verification of models with independently determined chemical and physical parameters and carefully selected field locations are the ultimate test.

SUMMARY

There are currently available mathematical formulations and numerical techniques that can be used to predict the transport and reaction of solutes in the saturated ground-water environment. These techniques use a water-flow submodel with a concentration computing submodel. The numerical techniques have been verified with analytical solutions and in a number of cases the models as a whole have been verified with field tests. In the latter verification predictions of solute transport involving irreversible rate reactions and equilibrium-controlled ion-exchange reactions were successfully made.

Future research needs include chemical-parameter identification and more insight into the physical process of dispersion. Unsaturated zone research that provides information concerning the sources to the saturated ground-water system should receive increased emphasis.

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Field Verification of Hazardous Waste Migration from Land Disposal Sites

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INTRODUCTION

In Illinois, 62 land disposal sites are permitted by the State Environmental Protection Agency to receive hazardous chemical wastes. In addition, more than 2000 active or abandoned landfill sites and private industrial disposal sites have received large but unknown quantities of all types of wastes, which may have included toxic chemicals. Some of these are adjacent to or directly underlain by shallow aquifer systems vulnerable to pollution from surficial sources.

The amount and areal extent of hazardous material migration from these disposal sites is not known. Few sites are monitored for possible pollution of contiguous aquifers, and most that are monitored appear to be ineffectively instrumented. Traditionally, monitoring wells are installed and water samples collected and analyzed periodically. However, these wells generally cannot monitor very large vertical segments of an aquifer, and the water samples are not always analyzed for the many different organic or inorganic chemical compounds that may originate from the disposal sites.

Existing air and surface-water pollution regulations are forcing an ever increasing volume of hazardous chemical waste to the land for ultimate disposal. This is true particularly in the heavily populated and industrialized regions of the United States where most of these wastes are generated, used, and eventually discarded. In the humid parts of the country, shallow groundwater reservoirs are recharged by precipitation infiltrating through the land surface. As a result, some shallow aquifers may be in danger of serious water quality degradation if soils are not effective in keeping hazardous wastes from migrating downward to the aquifers.

Purpose of Study

The primary purpose of this study is to develop effective investigative and monitoring techniques for detecting and evaluating quantitatively the extent of groundwater pollution from surface toxic waste disposal sites. The study also is designed to verify in the field the effectiveness of glaciated region soils and associated surface deposits in retaining specific hazardous chemicals.

The findings of this study should provide an invaluable tool for predicting possible long-term effects of hazardous chemical disposal on land. Also, the methodologies used should be immediately applicable in evaluating the extent of hazardous chemicals migration from disposal sites situated in similar geohydrologic environments throughout Illinois and other humid-region states in the country.

Site Selection

Four sites were selected for study on the basis of geology, the types and quantities of hazardous wastes generated, and the manner of waste disposal. Sites were selected where the unconsolidated materials range from about 15 to 75 feet thick. Three consist predominantly of low-permeability silt and clay soils, and the fourth, selected later, is sandy. Pennsylvanian-age shales or sandstones also lie beneath the glacial deposits at all four sites. Thus, from the geology, at least three of the sites would theoretically be desirable disposal areas with little resulting groundwater pollution.

Three sites (A, B, and D) are secondary zinc smelting plants located in central Illinois. A large quantity of waste from these plants has been disposed of in solid form on the plant property over many years of operation. Site C is a chlorinated hydrocarbon processing plant. Approximately half of the liquid waste from this plant is stored and pretreated in lagoons or pits on the plant property and then injected into a deep disposal well. The possible effects of the surface lagooning and storage pits are the principal concern in this study. This discussion will be limited to work accomplished at site A.

Site A:

Site A is a secondary zinc smelter located in southcentral Illinois. The plant, which started operations between 1885 and 1890, initially processed zinc ore. It was converted to a secondary zinc smelting facility about 1915. Wastes from the smelting operations during the first 85 years were principally heavy metals-rich cinders and ashes. During the early years large quantities of cinders were used as road fill or surfacing for secondary roads and farm lanes in the plant area. The remainder was used as fill material around the plant buildings and as surfacing over the property. As a result of these disposal practices, there now is a 1- to 10-foot thick layer of metals-rich cinders covering about 12 acres of the plant property.

In compliance with air pollution control regulations, a scrubber was installed on the plant stack in 1970. Prior to that time, wind-blown ash, rich in zinc and other heavy metals, was deposited on the plant site and on approximately 100 acres of surrounding farmland. This source of pollution has now been minimized, but wastewater from the scrubber (about 14,500 gallons per day) is deposited in a seepage pit constructed on the cinder materials that form the land surface at the site. Several hundred tons of high zinc content sludge have accumulated from the frequent cleaning of this pit and are now being reprocessed for zinc and lead recovery. Most of the water from the pit infiltrates into the ground underlying the plant property.

Prior to the study, limited data suggested that groundwater pollution might be occurring from three possible sources: (1) the large volume of solid waste materials (cinders and stored junk to be processed) at the plant site; (2) highly mineralized liquid wastes from the stack scrubbers, and (3) wind-blown ash from the smelter furnaces prior to installation of the scrubbers.

Because of the long period of operation at this facility and the various sources and forms of pollution likely to be present, this site appeared to be most desirable to study in detail. The decision was made to devote maximum time, effort, and money at this site to develop the study methodology and optimize its application to other sites.

Method of Investigation

An extensive drilling program to obtain unconsolidated sediment cores and groundwater samples has been undertaken at each site. Chemical analyses of the core and groundwater samples are being used to define: (1) the vertical and horizontal migration patterns of chemical pollutants through the shallow glacial deposits and aquifer profiles, (2) the seasonal variation of toxic chemical levels in groundwater near these sites, and (3) the residual toxic chemical buildup in the unconsolidated materials in the vicinity of the sites.

Coring:

Continuous vertical core samples for geologic study and chemical analyses have been obtained with conventional Shelby tube and split spoon sampling methods through hollow stem augers. These dry drilling techniques were used to minimize chemical alteration of samples from drilling fluids or external water during excavation.

Coring has been done with a truck-mounted Central Mining Equipment (CME) 55 and a CME 750 rig mounted on an all-terrain vehicle. The drilling crew consisted of an equipment operator and helper, assisted if necessary by the principal investigators. For the first few test holes drilled at each site, a geologist from the State Geological Survey assisted in collecting samples and made preliminary soil identifications for use in subsequent testing.

Shelby tube and split spoon samples were extruded in the field as collected, cut into 6-inch lengths, placed in wide-mouth glass jars, and delivered to the State Geological Survey and Environmental Analytical Research Laboratory at the University of Illinois for processing and analyses. One 6-inch length of core from each 5-foot segment and/or change in formation was taken by the drilling contractor for moisture content determinations before being sent for geological and chemical analyses.

Core Analysis:

Core samples for heavy metals determinations are being analyzed at the Environmental Analytical Research Laboratory with zinc as a target element. Previous experience in determining heavy metal contaminants in soil showed that digestion of a dried soil sample in 3*N* HCl at slightly elevated temperatures effectively releases the heavy metals without destructing the silicate lattice of the soil. The heavy metals so released are determined by atomic absorption spectroscopy, the principal methodology used to date.

For a limited number of soil samples, the multi-element capability of optical emission spectroscopy has been used to determine the Cd, Cu, Pb, and Zn concentrations. Semi-automated multi-element analysis for a larger number of elements has shown these four elements to be the main metal present.

Preliminary tests using atomic absorption measurement of small spot samples indicate that the 6-inch long samples are too heterogeneous to permit reproducible analysis. Reproducible results have been attained by homogenizing the samples and subdividing them to sample weight levels of 1 gram for atomic absorption and 50 milligrams for emission spectroscopy. Pelletized samples of approximately 2 grams have been prepared for X-ray emission spectroscopy.

Well Construction:

Analyses of water samples from observation wells has been the traditional method for monitoring groundwater pollution. To demonstrate the effectiveness of such an approach and the relative cost of using wells as compared to coring, a number of small-diameter (2-inch) observation wells were constructed. At site A, where heavy metal contaminants were expected, plastic casing, screen, and pumping equipment were used.

Observation wells at site A were constructed in the following manner. A 7-inch diameter hole was constructed, and a 2-inch diameter PVC pipe (bottom 2 feet slotted with a hacksaw) was placed in the hole. Gravel was placed from the bottom of the hole to a level about 1 foot above the slotted portion of the pipe followed by about 6 inches of sand. The remainder of the annulus was filled with bentonite slurry to land surface (see Figure 1). A shallow well (10 to 15 feet deep) was constructed at each location (see Figure 2), and deeper wells just above the bedrock were added at nine locations.

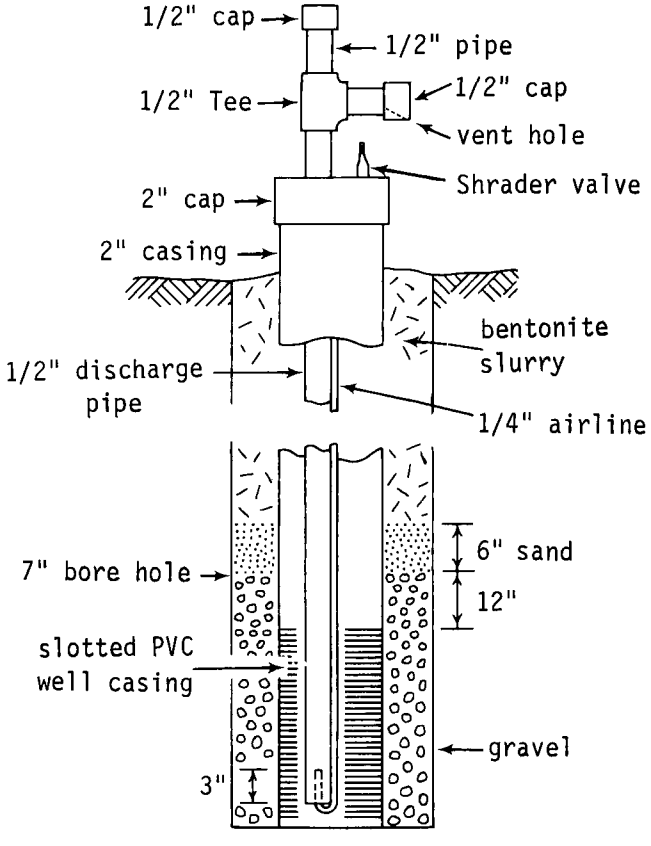

Figure 1. Typical Well and Pumping Mechanism.

Observation wells are equipped with individual pumping devices to minimize possible contamination of well samples from other wells. The pumping device consists of a ½-inch diameter PVC discharge pipe that extends from above the 2-inch well cashing to the bottom of the well. A tee fitted with short nipples and removable caps is placed at the top of this pipe (Figure 1). The cap on the vertical segment can be removed to allow for water level measurements within the ½-inch pipe. The cap on the horizontal segment (water discharge outlet) is vented to permit stabilization of the water level within this pipe.

A ¼-inch plastic air line also is installed in each well. The air line is attached to a Shrader valve at the top of the well casing and extends the entire depth of the well. . The lower end of the air line is bent up into the bottom of the ½-inch discharge pipe for a distance of about 3 inches.

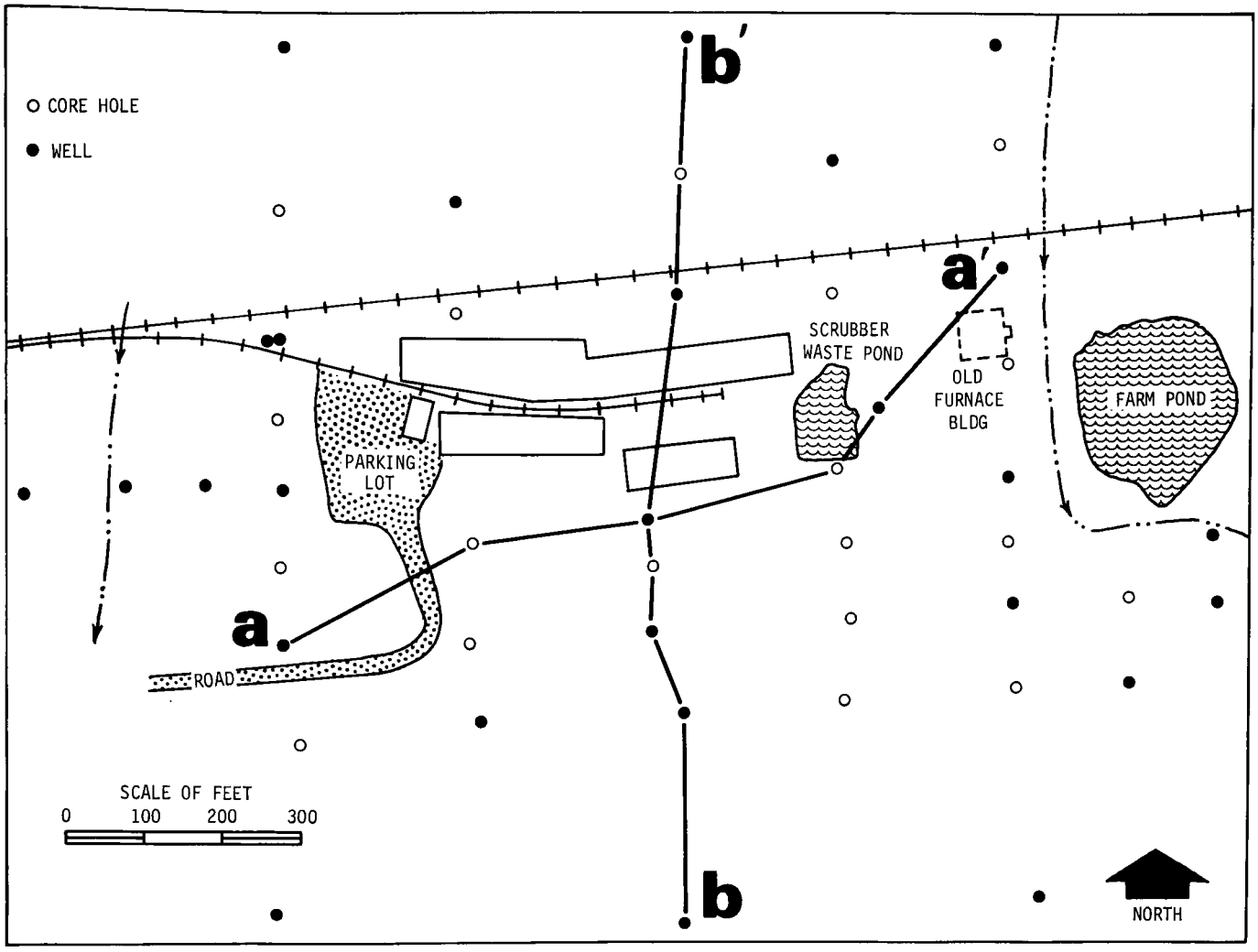

Figure 2. Location Map, Site A.

Water is pumped from the wells by removing the cap from the horizontal portion of the ½-inch pipe and applying air to the system through the Shrader valve. Pumping from depths as great as 70 feet is possible with only a bicycle-type hand pump. A gasoline powered 4-cylinder air-compresser capable of delivering about 5 cubic feet per minute at pressures up to 60 psi is being used. An activated charcoal filter has been placed in the discharge line from the compressor to insure that air from the compressor is not introducing airborne contaminants.

Water Sample Analysis:

Water level measurements are made and water samples collected from each well once a month. Samples are collected in 6-ounce plastic containers and placed on ice until they can be refrigerated in the laboratory. Each well is pumped for a period adequate to insure that all stored water in the well casing has been removed. The wells are allowed to recover and a sample is then collected from the water that has just entered the well. This procedure insures that the water sample collected is representative of the water flowing through the aquifer at the time of collection.

Heavy metals are determined by atomic absorption spectroscopy with appropriate correction for blank and background absorption. Concentrations of Zn, Pb, Cd, or Cu below the detection limit of atomic absorption spectroscopy are determined by anodic stripping voltammetry.

Secondary Methods:

A number of qualitative methods of groundwater pollution detection and mapping have been used with varying degrees of success. In an effort to evaluate the relative effectiveness of a few of these methods, electrical earth resistivity surveys, soil temperature surveys, soil and vegetation mapping, and color-thermal infrared and normal color photography have been employed at site A.

Results

To date, 47 wells at 34 locations have been completed at site A. Cores were taken at each well and at 19 additional sites (Figure 2). Total well and core sampling footages are about 1300 and 1275 feet respectively.

The glacial materials at this site are about 60 to 75 feet thick. The stratigraphic units recognized are essentially uniform in character and thickness and generally flat. The elevation of the surface of the Pennsylvanian bedrock dips from 447 feet above sea level on the east to about 432 feet on the west. A brief description of the units, from top down, follows:

(A) Peoria Loess (4 to 6′)—Brownish gray clayey silt, noncalcareous, with iron stains

(B) Roxanna Silt (3 to 4′)—Dark brown clayey silt with up to 34% sand (av. 20%), noncalcareous Glassford Formation

(C) Berry Clay Member (3 to 4′)—Dark gray sandy silty clay with trace gravel, up to 40% sand, noncalcareous (an accretion gley)

(D,E) Vandalia Till Member (2 to 8′)—Yellowish brown, oxidized in upper portion, little yellowish gray at base,

(F) Smithboro Till Member (25 to 31')—Dark gray sandy silt
(G) Lierle Clay Member (1 to 2')—Dark olive brown sandy silty clay, with little gravel, noncalcareous, soft. Banner Formation
(H) Unnamed Till Member (1 to 2')—Gray clayey silty till, sandy, with some gravel, mottled yellowish brown, brown and gray in upper part, strongly calcareous, hard, dry, a few scattered silt and sand lenses, predominantly dry Bond

Formation (Pennsylvanian bedrock)—Greenish gray shale with abundant mica; hard, dry

The stratigraphic units and the textural mineralogical data are shown in Table I. The expandable clay minerals, generally referred to as montmorillonite (M), make up more than 80% of the clay minerals within the Peoria Loess, Roxana Silt, and Berry Clay Member, thereby suggesting a high base exchange potential in the upper 13 feet of the materials encountered. The thin, continuous silty sand zone at the top of the Vandalia Till would appear to be the only "permeable" unit to allow groundwater to travel laterally at any moderate rate away from the site. Although there is probably some downward movement of groundwater through the remainder of the Glasford Formation, it would be expected to be extremely low.

Water level measurements taken in the shallow wells were used to construct monthly water table contour maps for the site. These wells are from 10 to 15 feet below land surface and are all finished in the sandy unit (D) at the top of the Vandalia Till Member. Data collected to date show no significant change in the shallow water levels at this site. The principal groundwater flow paths from the plant site are illustrated in Figure 3. Water from the eastern half of the plant, including the liquid disposal pond, appears to be moving east southeast; water from the western half of the plant site seems to be moving west southwest. Therefore, any pollutants in the shallow groundwater system should be moving in the same general directions.

Table I: Textural and Mineralogical Data.

Units	Thickness (ft)	% Sd	% St	% Cl	% M in Cl	Total % M
(A) Peoria Loess	4-6	3	58	39	86	33
(B) Roxana Silt	3-4	20	49	31	91	28
(C) Berry Clay	3-4	28	28	44	87	38
(D) Vandalia Till	.5-1.5	51	31	18	38	7
(E)	2-8	34	35	31	28	9
(F) Smithboro Till	25-31	29	42	29	53	15
(G) Lierle Clay	1-2	21	40	39	71	28
(H) Banner	1-2	28	41	31	56	17

Sd = sand, St = silt, Cl = clay,
M = montmorillonite

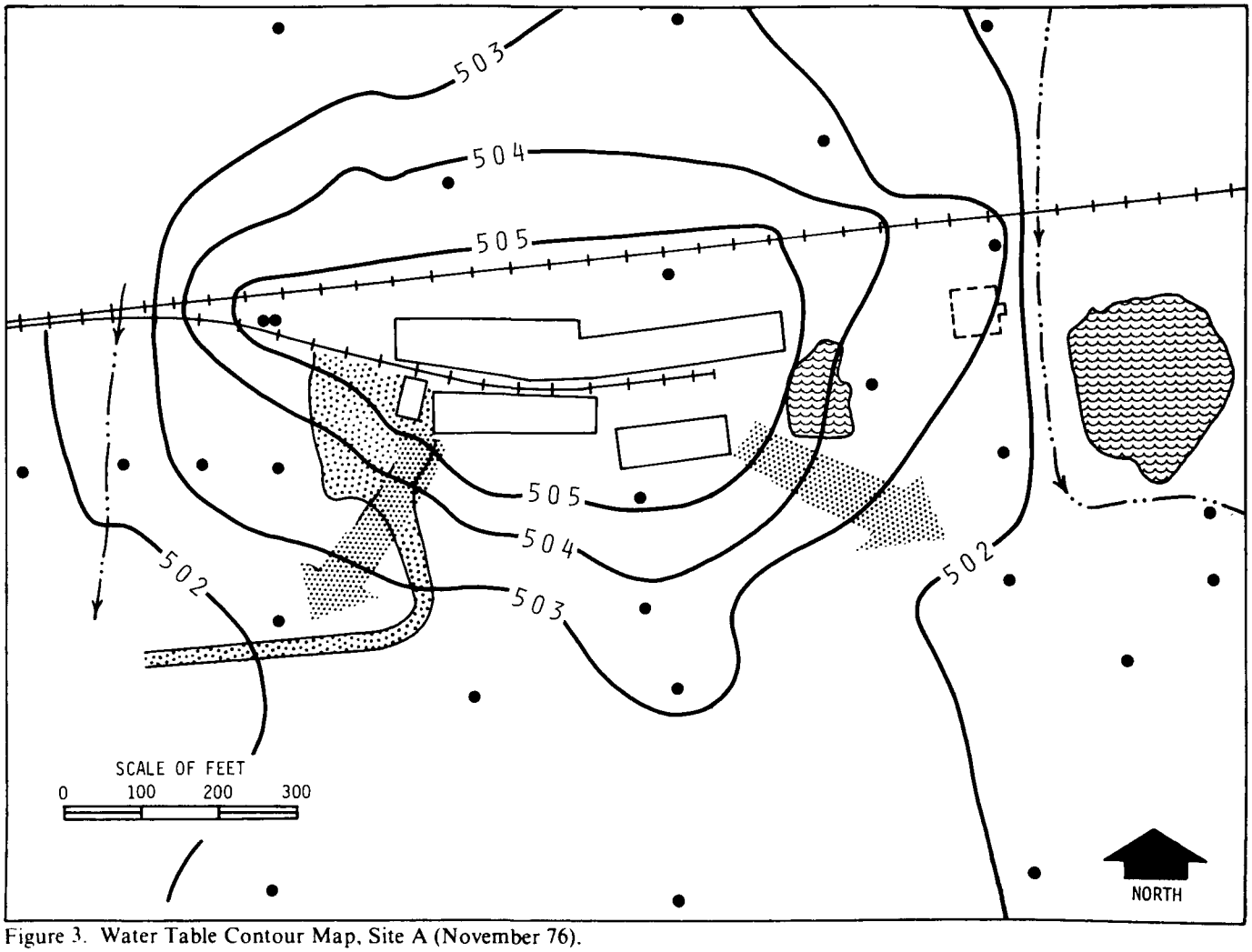

Figure 3. Water Table Contour Map, Site A (November 76).

No piezometric surface maps have been prepared for the deeper units at this site. Measurements in the wells indicate that water levels have not stabilized even after 5 to 6 months of nonpumping (Figure 4). This is due to the low permeability of the unit (Banner Formation) in which these wells are finished.

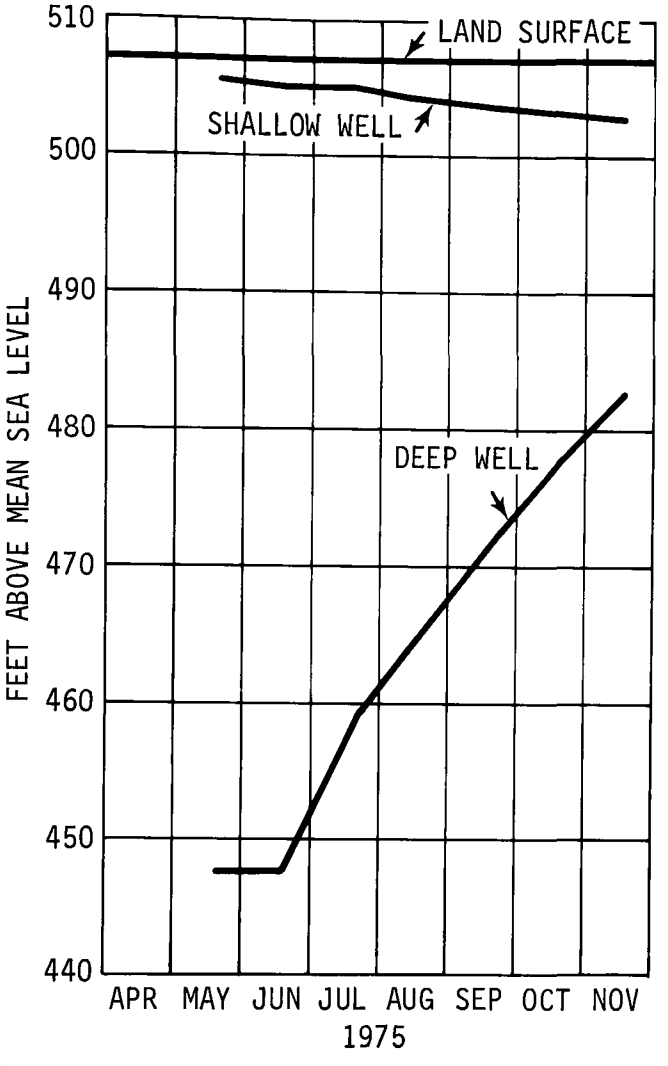

Figure 4. Water Level Elevations.

Single element analyses for zinc have been completed on samples from most of the core holes at this site. Figure 5 illustrates zinc concentrations in the soil along two vertical cross sections through the study area. An explanation of the physical and chemical phenomena controlling the movement of zinc into the soil cannot be made until multi-element chemical analyses and textural and mineralogical data are available for all soil samples.

From general observations, it is noted that the higher zinc concentrations in soil are limited to the area directly beneath the cinder fill covering the plant property. The deepest vertical penetrations also seem to lie beneath the areas of thicker cinder fill and prefill topographic depressions.

The migration of zinc into the soil seems to be controlled in large part by modern and ancient soils. Figure 6 is a detailed description of boring 2, showing the stratigraphic section, grain size, clay mineralogy, carbonate content, and zinc concentrations. The leaching of carbonates from the soil is the result of soil-forming processes. There are several soil horizons represented in this boring. Soils are represented by horizons A, B, C, D, G, and at the Bedrock surface. The upper soil zone represents general soil-forming periods (including modern) superimposed on slowly aggregating materials. The accretion gley zones in the tills (especially common in unit F, the Smithboro till) are shear blocks of the underlying soil incorporated into the till as the glacial ice advanced across the preexisting land surface.

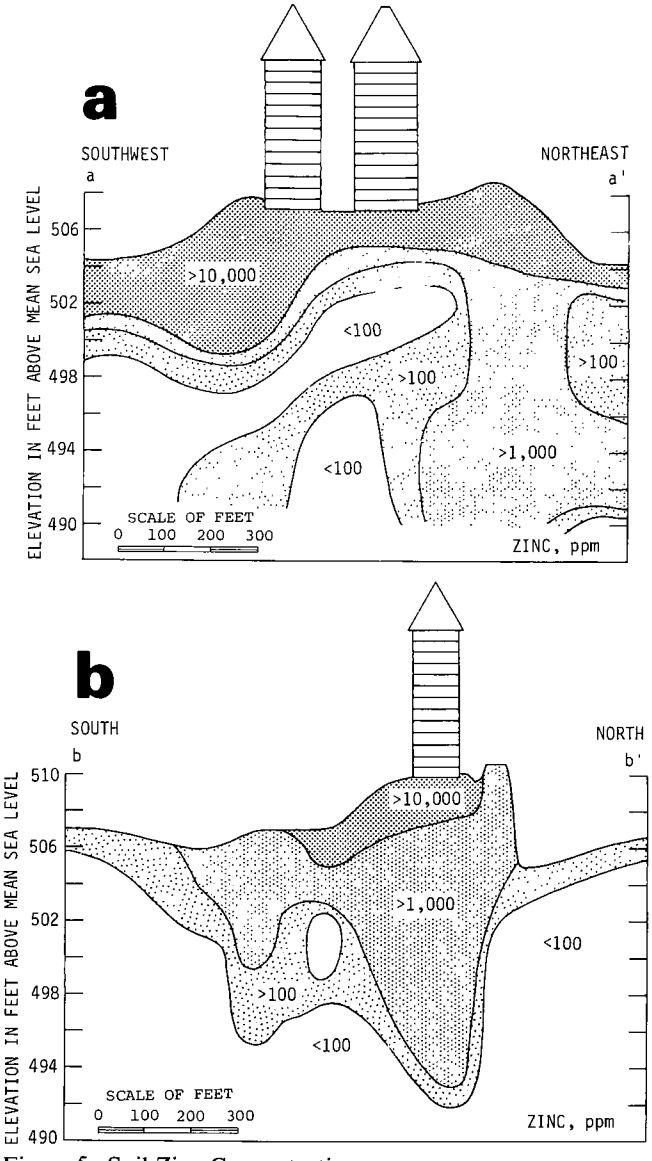

Figure 5. Soil Zinc Concentrations.

Zinc has relatively high mobility in the soil zone which has a pH around 7. Background values of zinc as high as 200 to 400 ppm may sometimes occur naturally in soils. Below the leached soil zone, the pH increases to around 8 and free carbonate is abundant; here the zinc will precipitate as $ZnCO_3$ with very low solubility. Examination of the borings for which analyses are available at this time suggests that the zinc is concentrated within the leached zone of the soils, with the exception of the area directly below the scrubber waste pond. Either the massive concentrations of zinc in the scrubber waste or leaching by the acid water has caused migration into the underlying tills.

Analyses of water samples from the wells at this site are now in progress. In general, zinc concentrations of water from all wells are less than 1 ppm and do not appear to vary significantly from month to month. Preliminary data also suggest that mineral concentrations in the samples stabilize after the second or third month of sampling.

Complete analysis of all soil and water samples should provide the needed data to explain the phenomena controlling the movement of heavy metals from this site.

SPL No.	DEPTH OF SAMPLE ft	UNIT DESCRIPTION	GRAPHIC LOG	ZINC ppm	GRAIN SIZE (total) GRAVEL	SAND	SILT	CLAY	X-RAY DATA (x-ray units per sec) MONTMORILLONITE	ILLITE	CHLORITE-KAOLINITE	CALCITE	DOLOMITE
1	1.0			1600	1	7	71	22	--	--	--	--	--
2	2.0	Peoria			0	4	57	39	82	12	6	--	--
3	3.0	(6-60-34)		71,67	1	6	56	38	84	11	5	--	--
4	4.0	A			1	5	57	38	81	13	6	--	--
	4.5	4.7					--	--	--	--		--	--
5	4.9				1	17	52	31	82	11	7	--	--
6	6.0	Roxana		670,640	1	19	44	37	81	12	7	--	--
7	8.0	(24-40-36)		430	2	30	33	37	87	8	5	--	--
8	9.0	B			2	31	30	39	83	11	6	--	--
		9.3											
9	10.0			500	1	28	36	36	75	15	10	--	--
10	11.0	Berry			2	33	31	36	77	13	10	--	--
11	11.8	(37-31-32)			10	39	29	32	65	26	9	--	--
12	13.0	C			3	51	27	22	57	31	12	--	--
		13.0											
13	14.0	Pearl		270	4	44	38	18	25	56	19	--	--
14	15.0	D 14.5			7	37	37	26	27	57	16	-?	25?
15	16.0	Vandalia		1100		41	33	26	29	54	17	26	15
16	18.0	(38-35-27) E 18.7		45	4	35	36	29	22	53	25	25	18
17	19.0				5	30	45	25	43	38	19	19	14
18	20.0				3	32	40	28	45	36	19	16	14
--	20-20½					--	--	--	--	--	--	--	--
19	21.1				3	28	43	29	50	31	19	27	15
20	22.0			37	4	28	39	33	53	31	16	15	20
21	23.0	Smithboro			3	35	37	28	51	32	17	19	17
22	24.0	(30-41-29)			3	30	39	31	51	29	20	13	17
--	24.5	F				--	--	--	--	--	--	--	--
23	25.0			130,110	4	30	41	29	43	38	19	22	18
24	26.0				5	30	40	30	47	34	19	15	15
25	27.0				8	27	42	31	52	30	18	30	--?
--	28.0					--	--	--	--	--	--	--	--
26	30.0				3	30	38	32	50	31	19	17	16
27	32.0	Smithboro			3	26	38	36	55	26	19	15	16
28	33.0	(29-40-31)			5	29	40	31	46	34	20	18?	--?
29	34.0			33	5	29	41	30	45	35	20	17	11
30	35.0				3	30	38	32	49	33	18	21	18
--	35.5					--	--	--	--	--	--	--	--
31	36.5	36.7			3	27	42	31	51	31	18	22	15
32	37.0	accretion		39	1	22	41	37	76	14	10	12?	--?
33	38.0	gley			1	20	40	40	80	12	8	15	16
34	39.0	38.5		47	14	33	37	30	31	44	25	30	19
35	40.0	accretion			1	18	49	33	57	26	17	15	20
36	42.0	gley		41, 43	4	29	41	30	37	39	24	18	23
37	42.0	accretion		420	3	27	40	33	82	9	9	--	12?
--	43.5	gley			--	--	--	--	--	--	--	--	--
38	44.0	44.1			5	31	43	26	49	36	15	34	28
39	45.0				2	24	39	37	43	39	18	16	30
40	46.0	Lierle		260	2	25	38	37	60	28	12	-?	15?
--	46.5	(25-40-35)				--	--	--	--	--	--	--	--
41	47.0	G		58	2	26	41	33	28	51	21	-?	18?
42	48.0	48.2			4	25	44	31	31	47	22	30	28
43	49.0				4	30	41	29	21	54	25	34	24
44	50.4	(33-42-25)		41	8	32	41	27	25	54	21	61	25
45	51.0			57	0	36	45	19	24	53	23	33	18
46	52.0				1	21	52	27	--	--	--	--	--
47	53.0	Banner			3	21	44	35	21	51	28	33	11
--	53.5					--	--	--	--	--	--	--	--
48	55.0	(31-45-34)			2	18	47	34	20	52	28	37	20
49	56.5	H			4	22	44	34	18	51	31	46	22
50	57.5				4	22	45	33	19	53	28	50	22
--	58-58½					--	--	--	--	--	--	--	--
51	59.0	59.5		79	4	22	44	34	17	52	31	29	20
		Bedrock		(130)									

Figure 6. Description of Boring S-2, Site A.

Preliminary Cost Analysis:

As previously stated, it was decided in the beginning of this project to devote maximum time, effort, and money at site A to gain the needed experience and understanding of the methodologies being applied. Therefore the total expenditures at this site are much higher than would be necessary at other sites of this type. The cost to study a similar site using a minimum monitoring approach would be considerably less.

As of January 1, 1976, approximately 1275 linear feet of piezometer-tube observation wells at 34 different locations have been completed at a total cost of about $6,150 ($4.80/foot). Approximately 1300 linear feet of coring has been done for about $9,150 ($7.05/foot).

As time permits and we gain better understanding of the monitoring methods being tested, the cost effectiveness of the boring technique combined with a minimum number of wells will be determined. Preliminary data suggest that soil coring is a reliable monitoring technique and definitely should be used to locate the proper vertical horizons for installing monitoring wells.

SUMMARY

Work completed at all sites to date has demonstrated that soil coring is an effective tool for mapping the migration patterns of chemical pollutants through the earth materials. This approach also provides field data to verify the effectiveness of various soil types to adsorb or retain different chemical pollutants.

Sufficient comparative data are not available at this time to determine the relative usefulness of the supplemental methods being tested in this study. Temperature surveys, electrical earth resistivity surveys, and vegetation mapping and sampling may prove to be useful in certain shallow geologic regimes. Although color infrared photography is very limited in detecting groundwater pollution, it is a useful tool for soil and vegetation mapping and for detecting surface water pollution.

ACKNOWLEDGMENTS

This study is sponsored by the Solid and Hazardous Waste Research Division of the Federal Environmental Protection Agency (Grant R/803216-01) under the general guidance of Mike Roulier, Project Officer.

A Preliminary Assessment of the Effects of Subsurface Sewage Sludge Disposal on Groundwater Quality*

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INTRODUCTION

The environmental effects of subsurface sewage sludge disposal have not been thoroughly investigated. This is particularly true with respect to effects on ground water quality. This paper presents the results of a preliminary evaluation of the effects of sewage sludge disposal on groundwater quality. The term "subsurface sewage sludge disposal" as used here means the burial of sewage sludge with or without municipal solid waste in trenches, pits or area type landfills.

A study conducted at Oceanside, California[1] on leachate from municipal solid waste and mixed sewage sludge/municipal solid waste was completed in 1973. This study concluded that other than a lower pH and higher BOD in the leachate from mixed sewage sludge/municipal solid waste no other differences occurred. A continuing study of sewage sludge only disposal was initiated in 1972 by the U.S. Department of Agriculture, Agricultural Research Service at Beltsville, Maryland. The data from this study[2] show groundwater has been affected after only 19 months. The testing has been limited to chloride and nitrogen compounds.

These studies did not allow projection of the total effect of subsurface sewage sludge disposal on groundwater resources. The Oceanside study, for example, was limited to leachate analysis only. The data then could only yield a determination of potential pollutants. The USDA study did not include analysis for toxic metals. Toxic metals analysis at the USDA field plots will be started in the near future.

Sewage sludges, however, are being generated in ever increasing quantities and state regulatory agencies must determine what methods of sludge disposal are acceptable. In order to provide a broader data base on which to issue guidance to state regulatory agencies, Environmental Protection Agency's Office of Solid Waste awarded a contract to SCS Engineers in Long Beach, California to monitor the effects of subsurface sewage sludge disposal on groundwater quality. This paper will briefly describe and report the results of that contract, drawing comparisons where appropriate to a similar and somewhat more comprehensive study of municipal solid waste only sites.

Project Description

One objective of this project was to determine differences in groundwater contamination resulting from subsurface sewage sludge disposal at eight land disposal sites where location and operational conditions ranged from optimal to unacceptable.

Further, a similar and somewhat more comprehensive study of ten solid waste sites was being conducted. Thus the second objective of the study was to compare these two sets of data to determine if differences in groundwater contamination occurred between solid waste only and sewage sludge land disposal practices.

Site Selection and Description—The acceptability of any given site relative to groundwater protection is dependent upon many interrelated factors such as permeability, depth to groundwater, subsurface soil, geologic characteristics, climatology, etc. The major factors considered in site selection for this study were as follows:

Factor	*Range*
Soils/Geology	Sand to clay
Precipitation	59 to 115 cm/year
Operation	poor to excellent
Age	3 to 5 years

It was expected that all sites would generate some leachate given a minimum annual precipitation of 59 cm. It was also expected that sites with clayey soils and excellent operations would show less groundwater contamination (if any) compared to sites with sandy soil and/or poor operations. Other factors such as quantity of waste received, depth of wastes disposal and depth to groundwater would also be expected to influence the affect a specific site could have on groundwater quality. In selecting sites to cover the above factors, a wide geographic distribution was necessary. The approximate location of study sites is shown in Figure 1. The sludge quantities received at mixed sites varied from 1 to 18% of the solid waste received on a weight basis (dry weight for sludge and as received weight for solid waste). At sludge only disposal sites the loading rates varied from 2241-5603 tonnes/ha (1000-2500 tons/ac) on a dry weight basis. Further description of the sludge and solid waste received at each site is given in Table 1.

Monitoring Program—Wells were drilled at each site to sample leachate (if present) and groundwater downgradient from the disposal site. Samples for background water quality were obtained from nearby existing wells. The general well locations are shown in Figure 2. Two wells, one shallow and one deep, were established to sample grandwater downgradient, local conditions permitting.

* Based in part on the results of a study conducted for the Environmental Protection Agency by SCS Engineers of Long Beach, California, under Contract No. 68-01-3108

Figure 1: Location of Sludge Monitoring Sites

Table I: Waste Characteristics for Sites Studied

Criteria	Site 1	2	3	4	5	6	7	8
Sludge Type	Raw primary and secondary	Raw primary and secondary	Raw primary and secondary paunch manure	Raw primary and secondary	Raw Digested and incinerated sludge ash	Digested and septic tank pumpings	Raw primary and secondary and Zimpro sludge	Raw primary and secondary
Solids Contents	25-30%	20-25%	25-40%	18-25%	20-25%	3-5%	40% Zimpro 20% where down	15%
Annual Sludge Quantity	13,555m^3	26,224m^3	Variable	7,300m^3	125,700m^3	8,000m^3	15,200m^3	19,900m^3
Total Annual Solid Wastes Quantity	76,500m^3	354,100m^3	None	None	760,420m^3	127,700m^3	585,000m^3	None
Proportion of Sludge to Solid Waste Received (Volume basis)	17%	7%	Sludge Only	Sludge Only	10%	6%	26%	Sludge Only

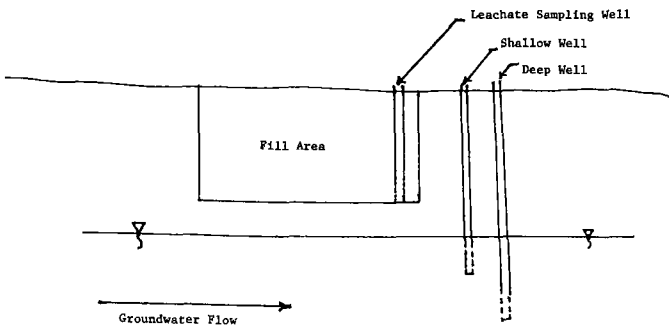

Figure 2: Generalized Location of Monitoring Wells

Starting one month after the wells were established three samples of leachate and groundwater downgradient and one sample of background water were taken during a five month period in 1975 from May to November. An additional sample was obtained in June of 1976 from most wells. The relationship of samples taken during this time period to the hydrologic cycle is unknown. This sampling program was admittedly limited, however, it must be remembered that the objectives were limited to (1) determining types of contamination occurring, (2) compare contamination from sewage sludge to contamination from solid waste only. The data for the latter being generated by a somewhat more comprehensive monitoring program. In addition to the water samples, sludge at each site was analyzed, once in 1975 and once in 1976.

Before presenting the results obtained, it may be beneficial to briefly discuss the method of data presentation. Figure 3 shows a theoretical distribution over time for some contaminant concentration in both background and downgradient groundwater. The variation over time shown is a function contaminant source. The curve representing downgradient groundwater varies then, according to the quality and quantity of leachate produced over time. The variation shown for background water quality is exaggerated compared to "normal" uncontaminated groundwater. This was done for illustrative purposes. From examination of this figure, it is obvious that when only three or four samples downgradient are compared to one or two samples of background groundwater, as in this study, examination of individual data points can be confusing. In order to avoid a confusing picture, I have averaged all available data points from each well. In this manner it is possible to subtract background levels from downgradient levels and display the "average" increase. This method is obviously subject to inaccuracy, however, since normal background variation is generally quite small the probability of showing an increase which is not real is minimal.

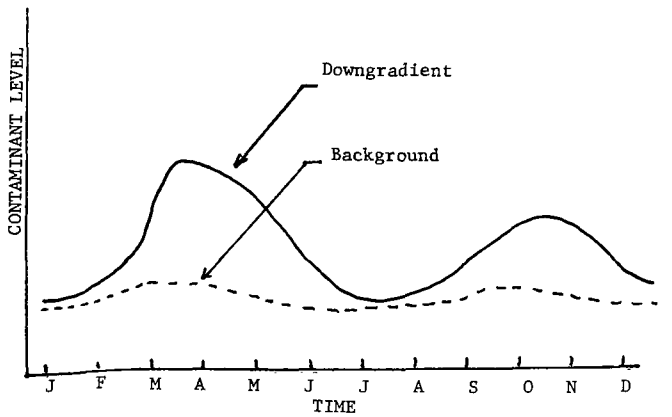

Figure 3: Theoretical Variation of Contaminant Levels in Groundwater Over Time

Results and Discussion—The presentation of results is being limited to heavy metals. This is because contaminants such as sulphates, chloride, etc., have rarely exceeded their suggested drinking water standard. Secondly, although increases in such parameters often exceeded industrial standards, discussion of groundwater contamination is most often related to drinking water standards. Because standards on groundwater do not exist, I will in general only, refer to increases above background levels. Where it is necessary for comparative purposes, increases will be compared to drinking water standards.

The data generated in this study will be presented in the following sequence: the source of metals, the leachate characteristics; and the nature of groundwater contamination. Where appropriate the discussion will compare these data to unpublished data from a similar but somewhat more comprehensive study of solid waste only land disposal sites.

Source of Contaminants—The total content of selected metals for the sludge presently entering each site is given in Table II. Due to the lack of historical sludge data we are forced to assume that the metals content of the sludge analyzed was representative of that entering the site during its lifetime. This assumption is probably reasonable for sites one thru five where industrial input is apparently limited.

Table II: Metals Content of Sludges

	ppm (dry weight basis)			
Site	Cd	Cr	Fe	Pb
1	4	111	4,100	170
2	9	65	13,000	220
3	3	150	4,700	170
4	10	120	23,800	110
5	22	780	67,000	1,100
6	3	2,750	75,000	100
7	23	43,300	6,700	1,000
8	1	33,300	2,000	90

The range of leachate concentrations of selected parameters is shown in Table III. These are compared to leachate concentrations from municipal solid waste only sites. The municipal solid waste only leachate analysis comes from the draft final report of U.S.E.P.A. contract 68-01-2923 submitted by SCS Engineers of Long Beach, California. The ranges for sewage sludge only and mixed sewage sludge/solid waste are not separated as no differences were apparent. The only apparent difference is a higher upper limit of metal contents at sludge sites. No conclusion, however, can be drawn due to the limited amount of data and site to site variability. In general, it appears that the effect of leachate on groundwater quality should be the same whether the leachate is from municipal solid waste, sewage sludge or a combination of both.

Table III: Range of Leachate Characteristics

	Leachate Source	
Parameter	MSW *	SS +
TKN	11-758	115-2513
Cl	139-568	3-1201
COD	165-13,000	3,000-20,000
Cd	.007-.05	.009-.1
Cr	.65-.33	.14-21
Fe	15-679	14-172
Pb	.09-.29	.1-1.55

* Municipal Solid Waste Only - 5 sites SCS Contract No. 68-01
\+ Sewage Sludge W/Wo MSW - 6 sites SCS Contract No. 68-01-3108

This, however, does not appear to be the case. Data from this study and the previously mentioned study of solid wastes only show contamination of groundwater has occurred at all sites based on indicator prameters such as specific conductive and chemical oxygen demand (COD). Unlike solid waste only sites,

however, the subsurface sewage sludge sites show a definite trend toward contamination of groundwater with heavy metals. Data for selected metals are shown in Table IV.

Table IV: Average Increase Over Background Level of Selected Parameters

Site	Parameters			
	Cd	Cr	Fe	Pb
	Increase in ppm			
1		.02	.46*	.03
2		.65*	539*	.79*
3		.65*	28*	.09*
4		.02		.07*
5			1.10	
6			.29	.02
7		.10*	3.8*	
8	.10*	.38*	374*	.34*

* Increase is at or above applicable Drinking Water Standards

In examining the data in Table IV, a logical conclusion would be that sites 5 and 6 are sanitary landfills and all other sites are dumps. This, however, is not the case. Using "Sanitary Landfill Design and Operation" as a guide, site 5 would be called a sanitary landfill and site 6 a dump. The latter is largely due to poor operation. Further, site 3, which shows rather significant contamination, would also be classified as a sanitary landfill. I should point out that the reference used discusses factors related to the potential for ground water contamination but does not give specific recommendations. Classifying any site then is a matter of professional judgment. I believe that few people would disagree with the above classification of sites 3, 5 and 6. Because metals contamination as shown in Table IV was found at disposal sites accepting sewage sludge and generally not at solid wastes only sites, suggests that some factor or factors other than concentration are responsible for the observed results. Such factors could be chelation or other changes in chemical equilibrium brought about by the presence of sludge. It must be remembered that the groundwater samples obtained here were within 61 meters (200 feet) of the landfills studies. The data do not predict what effect this contamination could have on groundwater users further downgradient. This question will require further study.

This study was designed to determine the types of contaminants found in groundwater as the result of subsurface sewage sludge disposal. In developing this study it was assumed that no greater effect would be observed than would occur from municipal solid waste only. This was not found to be the case. The limited scope of this study, however, does not justify abandonment of subsurface sewage sludge disposal. It does, however, justify greater emphasis in groundwater resource evaluation for sites which will accept sewage sludge.

It is obvious that more work is needed in the area of subsurface sewage sludge disposal to better define the extent of the problems and provide solutions. A contract has been awarded to SCS Engineers to conduct further study of the sites discussed. Detailed information is being obtained on soils, geology, etc. to better define the cause and effect relationships that exist.

At the present time, good site selection practices should include a comprehensive ground and surface water resource evaluation. This should include quality, quantity, direction and rate of flow, present and potential use downgradient from the disposal site. Where the water resource has a "high" value site design and operation should offer protection of the water resources.

Groundwater investigations are expensive to conduct, difficult to evaluate and can provide answers only after years of study. We, therefore, cannot expect definitive solutions rapidly. We can, however, periodically adjust our activities as more information becomes available.

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Control Program for Leachate Affecting A Multiple Aquifer System Army Creek Landfill, New Castle County, Delaware

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Site History

Between 1960 and 1968, New Castle County, Delaware utilized an abandoned sand and gravel pit as the primary disposal site for municipal and industrial wastes. The landfill location in Northern Delaware is shown on the map in Figure 1.

From records and test borings, it was determined that a modified area fill method was used to emplace the refuse material. During the land-filling operation, daily covering was probably not practiced. This, coupled with less than adequate compaction within the areas, caused differential settling and an uneven finished surface when the fill was closed.

The final lift was emplaced in 1968, and the completed fill encompassed a volume of 1.9 million cubic yards (1.42 million cu m) of refuse, about 30 percent (or 600,000 cubic yards, 450,000 cu m) of which was beneath the seasonal high water table. Refuse thicknesses over the 47-acre (19 ha) site ranged from about 6 to over 35 feet (2 to 11 m).

Late in 1971, water in a residential well, located 900 feet southwest of the landfill, developed quality problems such as a distinctly disagreeable odor and permanent staining of porcelain fixtures. Gradually, this condition became more pronounced and the water supply was abandoned. Further analyses conducted by the Delaware Geological Survey and New Castle County Public Works Department indicated the presence of leachate in the ground water. In early 1972, intensive field study was begun by the county, through its consultant Roy F. Weston, Inc., and the Delaware Geological Survey to determine the hydrogeologic controls responsible for this problem.

Hydrogeologic Description

The surficial geology in the old gravel pit consists of medium and coarse-textured, channel-bedded, unconsolidated sands that demonstrate substantial textural variability within a short vertical section. The origin of these sands has been related to glacial meltwaters having seasonal discharges.[2] The deposits were placed in shallow, relatively narrow braided channels with numerous ice floes. These deposits have been formally named the Columbia Formation and within the study area form a continuous surficial layer up to 60 feet (18 m) in thickness with the formational base varying between +20 to -20 feet (+6 m), present mean sea level. Dragline excavations in the gravel pit during quarrying had terminated at a basal quartz conglomerate. It has been determined from air photos that in at least two places within the gravel pit this basal conglomerate was removed by excavation and the bottom of the gravel pit was continued into the underlying aquifer sands of the early Cretaceous Potomac Formation.

The Potomac Formation of Early to Late Cretaceous age[1] consists of unconsolidated sands, silts, and clays genetically emplaced as channel deposits by southerly flowing meandering streams.[3] Figure 2 is a "hydrogeologic-stratigraphic" column for this area. A fairly consistent Potomac layer underlying the post-Cretaceous erosion surface consists of variable thicknesses of clay. Due to the lensatic depositional nature of the Potomac Formation, this upper clay layer varies in thickness and textural character throughout a cross section of the landfill to a northerly direction. In this area the clay layer is sandy or completely absent, while immediately south of the landfill the layer varies in thickness from 30 feet to over 100 feet (9 to over 20 m).

Hydrologically, the Potomac upper clay functions as a confining zone for the underlying aquifer, which has been named the upper Potomac aquifer.[4] Pump tests conducted in this upper 50-100 feet (15-30 m) thick aquifer zone yield transmissivity values in the range of 45,000 to 70,000 gpd/ft (560 to 870 sq m/day), and storativity values in the 10^{-4} to 10^{-5} range. Leakage coefficients of 0.028 to 0.033 ft (0.85 cm to 1.0 cm) have been computed for the confining clay. The lower aquifer, although a coarser sand, is relatively thin in this area, and transmissivity values of less than 1,000 gpd/ft (12 sq m/day) are common.

The upper aquifer zone has been heavily developed for ground water since the early 1960's. In the immediate area pumpage had exceeded 8-10 mgd (30,000 to 38,000 cu m/day) during this decade. Consequently, the natural southerly groundwater gradient has been steepened to the south, and the rate of ground-water movement has been greatly accelerated. As a result, Potomac potentiometric heads have declined to about 20 feet (6 m) below sea level.

Contamination History

In mid-1972, upon discovery of contimination in a residential well, an initial investigation was launched to determine the extent of the leachate-affected area. Figure 3 is a map showing the leachate plume as first determined by monitoring several drilled observation wells. This earliest monitoring well network was soon expanded about the periphery of the landfill and included a significant down-gradient area. These wells served to facilitate the monitoring of leachate migration in selected areas of the aquifer near existing residential and municipal wells, including a major well field belonging to a water company. As a result of the expanded monitoring network, by early 1973 the

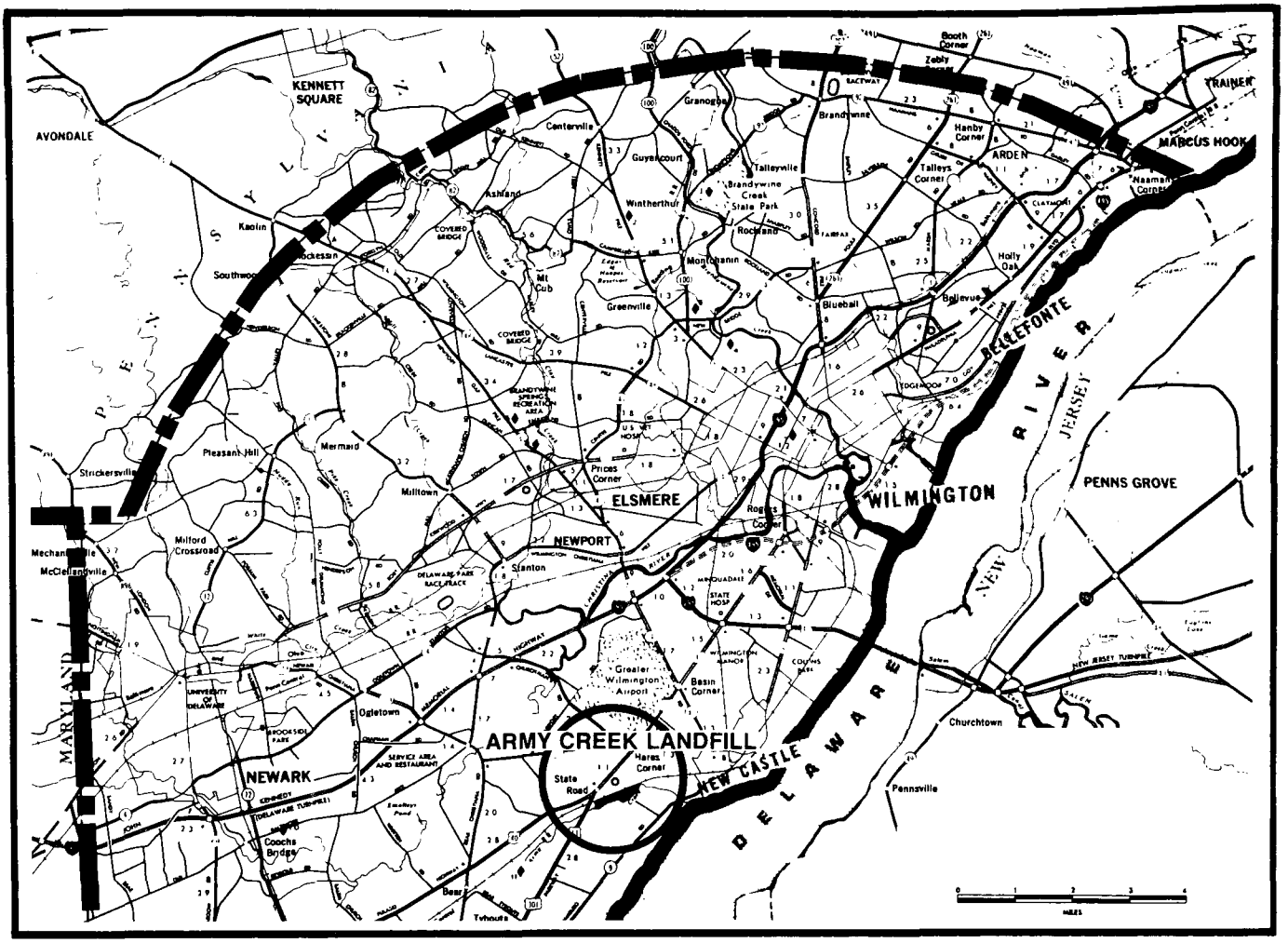

Figure 1: Location Map of Army Creek Landfill

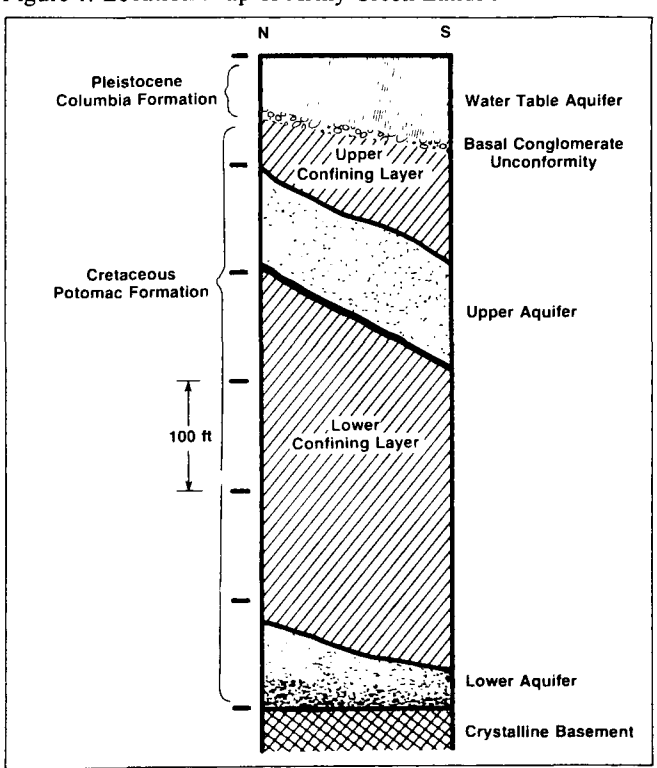

Figure 2: Hydrogeolic-Stratigraphic Column for Army Creek Area

migration of the leachate plume was found to be farther down-gradient than was originally thought.

Based on aquifer characteristics of the Potomac, the rate of contaminant migration was computed. The permeability of the channel sands of the Potomac is greater 500 gpd/sq ft (20 cu m/day sq m). The hydraulic gradients, as can be inferred from the potentiometric surface map in Figure 4, vary from about 0.015 ft/ft immediately sough of the landfill to 0.02 ft/ft, as the gradient steepens nearer the production wells. An average rate of movement of 0.5 feet per/day (15 cm/day) is reasonable for the area close to the landfill and increases to 1.5 ft/day (46 cm/day) down-gradient closer to the pumping centers of the nearby wells.

As leachate enters the upper Potomac aquifer, barring attenuation of select constituents, it was expected to reach the water company's pumping wells within 10 years if no corrective procedures were undertaken.

Leachate Quality

The quality of landfill leachate generated by saturated decomposition of domestic refuse depends upon such variables as waste composition and sorting, compaction, moisture capacity, temperature, and age of the refuse. Thus, the actual concentrations of chemical species in various leachates vary greatly. A young landfill will generally produce a leachate characterized by very high concentrations of dissolved organic and inorganic substances. Both the Chemical Oxygen Demand (COD, a measure of dissolved organics) and the Total Dissolved Solids concentration (TDS, a measure of dissolved inorganics) are typically in the thousands of parts per million for the raw leachate.

The concentration of most environmentally significant metals greatly exceeds the recommended EPA limits for such substances in potable water. The leachate concentration rapidly decreases as it migrates down-gradient from the landfill by such processes as dilution, bioassimilation, chemical oxidation, and adsorption.

The background water quality in the Potomac aquifer has a low dissolved solids concentration. The range of inorganic constituents in natural Potomac waters is listed in Table 1, along with comparison values from selected observation wells located within and down-gradient of the landfill.

Counter-pumping Program

The installation of a network of monitoring wells was completed in early 1973, so that the ground-water area affected by migration of leachate could be fully identified.

Figure 5 shows the line of contaminant migration identified in late 1973. This line is an approximate location based upon specific parameters used as standard indicators. These parameters included physical appearance of water, e.g. color and odor, and COD, total iron, manganese, and chlorides. The concentration of iron and manganese in aquifer waters is such that they are useful as quality parameters. Their gradual increase over background conditions has, therefore, indicated: (1) remobilized metals under nonequilibrium conditions and/or (2) fresh dissolved metals carried in solution. The COD levels within the landfill were normally high (see Table I). A few hundred feet south in monitoring wells nearest the landfill the COD levels had dropped significantly, indicating that organic decomposition of the landfill was subsiding or, more likely, that fresh, oxygenated recharge waters were fully oxidizing the organics within the Potomac aquifer through interformational leakage.

Through an analysis of the initial flow network in the Potomac aquifer and computed well interference from selected observation wells, an interim contaminant control was designed. The control consists of an artificially depressed drainage divide within the upper Potomac aquifer, down-gradient from the landfill at about a third of the linear distance to the water company well field. The drainage divide, as designed, was composed of a two-part well interference system. Counter-pumping wells were systematically located within the channel sands of the upper Potomac aquifer to create the initial divide. Secondly, the water company wells were throttled back to initiate head buildup down-gradient. The counter-pumping recovery wells have been in operation since November 1973. At the time of completion in early 1974, the wellfield was pumping a total of 3.54 million gallons of contaminated water per day (13,400 cu m/day).

The divide has been effective in preventing contaminated waters from flowing into the steepened gradient of the water company's wells. In plan view, the divide consists of roughly an L-shaped ground-water mound south and east of the landfill as shown in Figure 6. The flow lines again indicate the preferred flow path of a particle within this network.

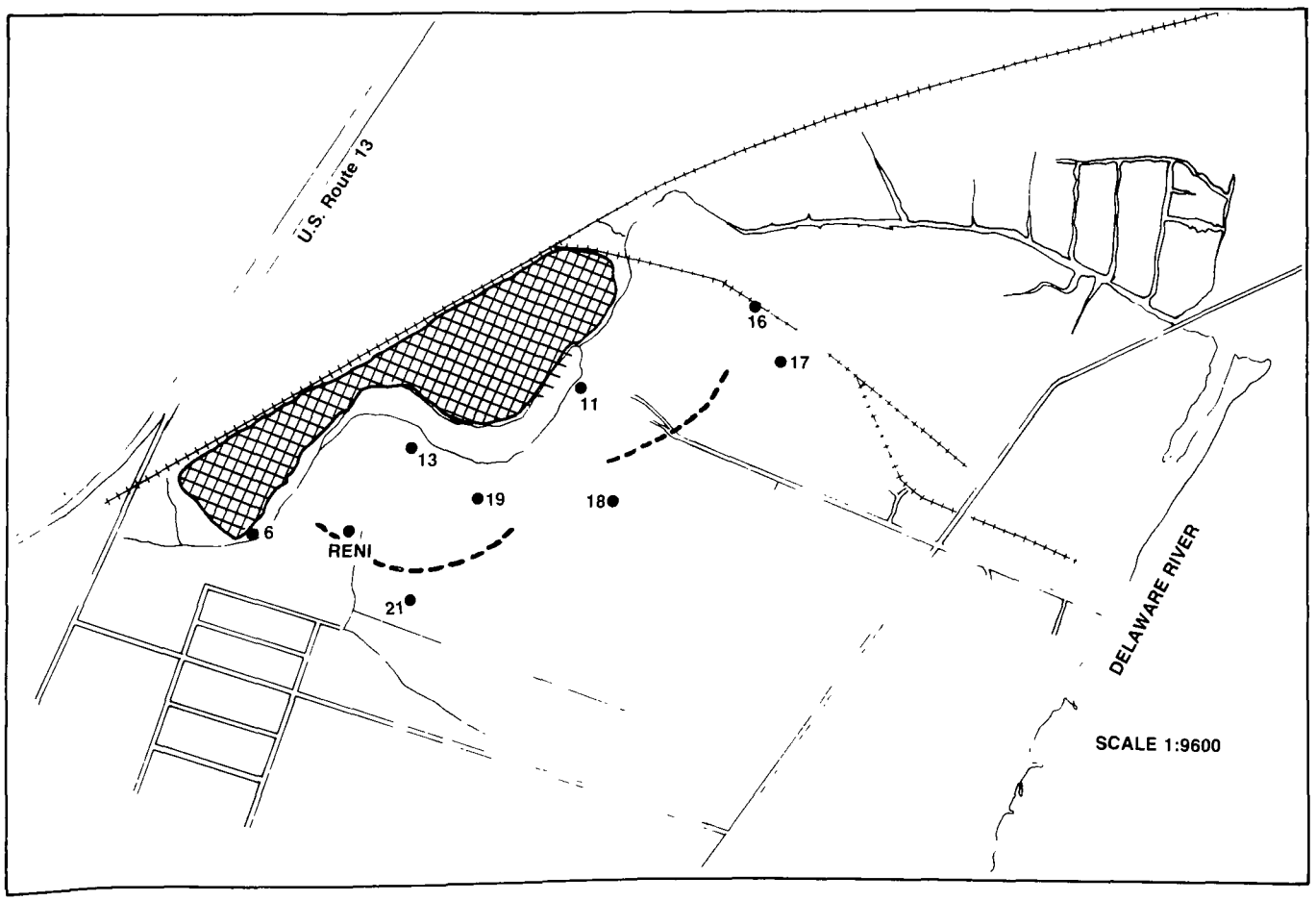

Figure 3: 1973 Contamination Front

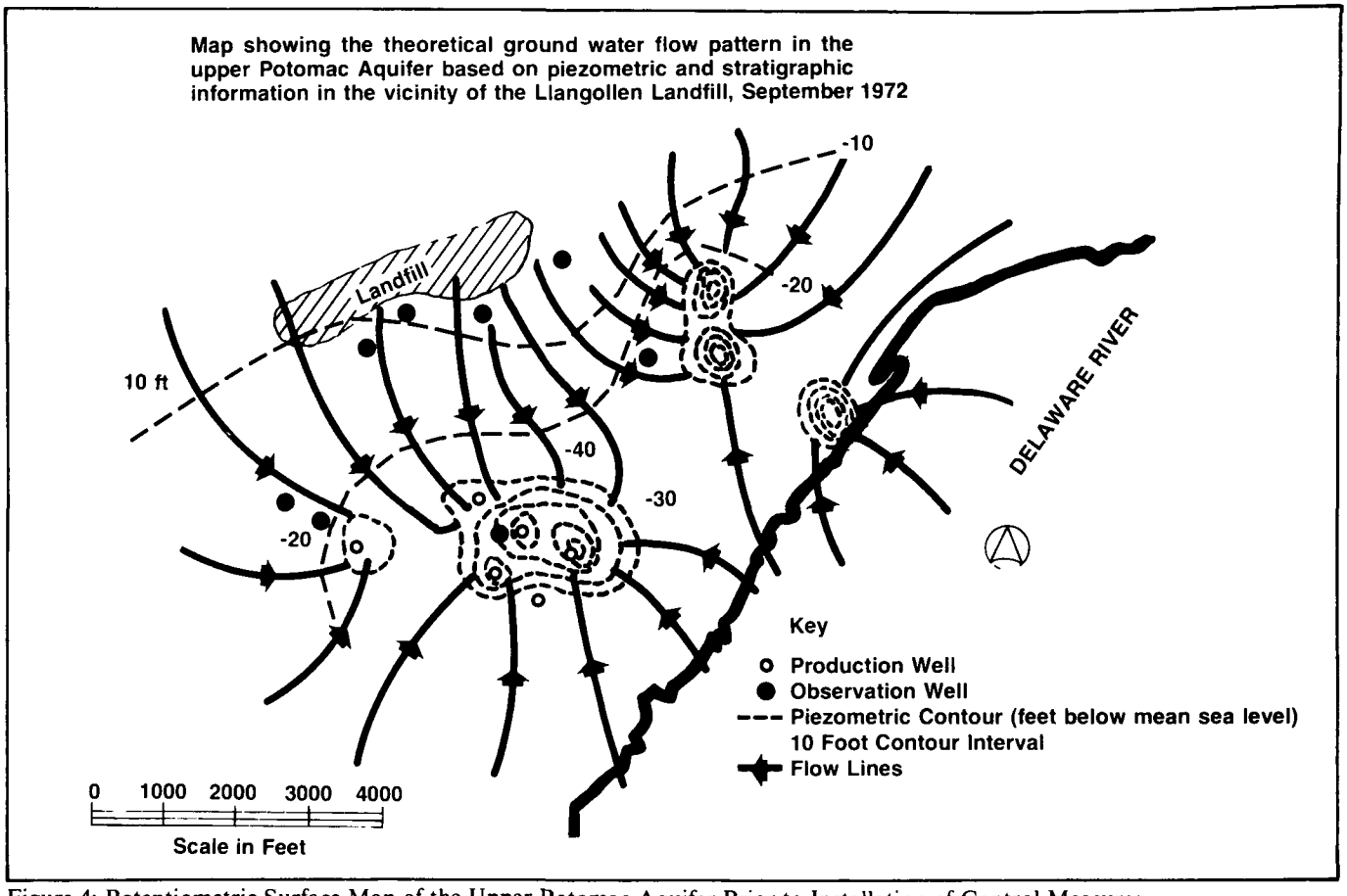

Figure 4: Potentiometric Surface Map of the Upper Potomac Aquifer Prior to Installation of Control Measures

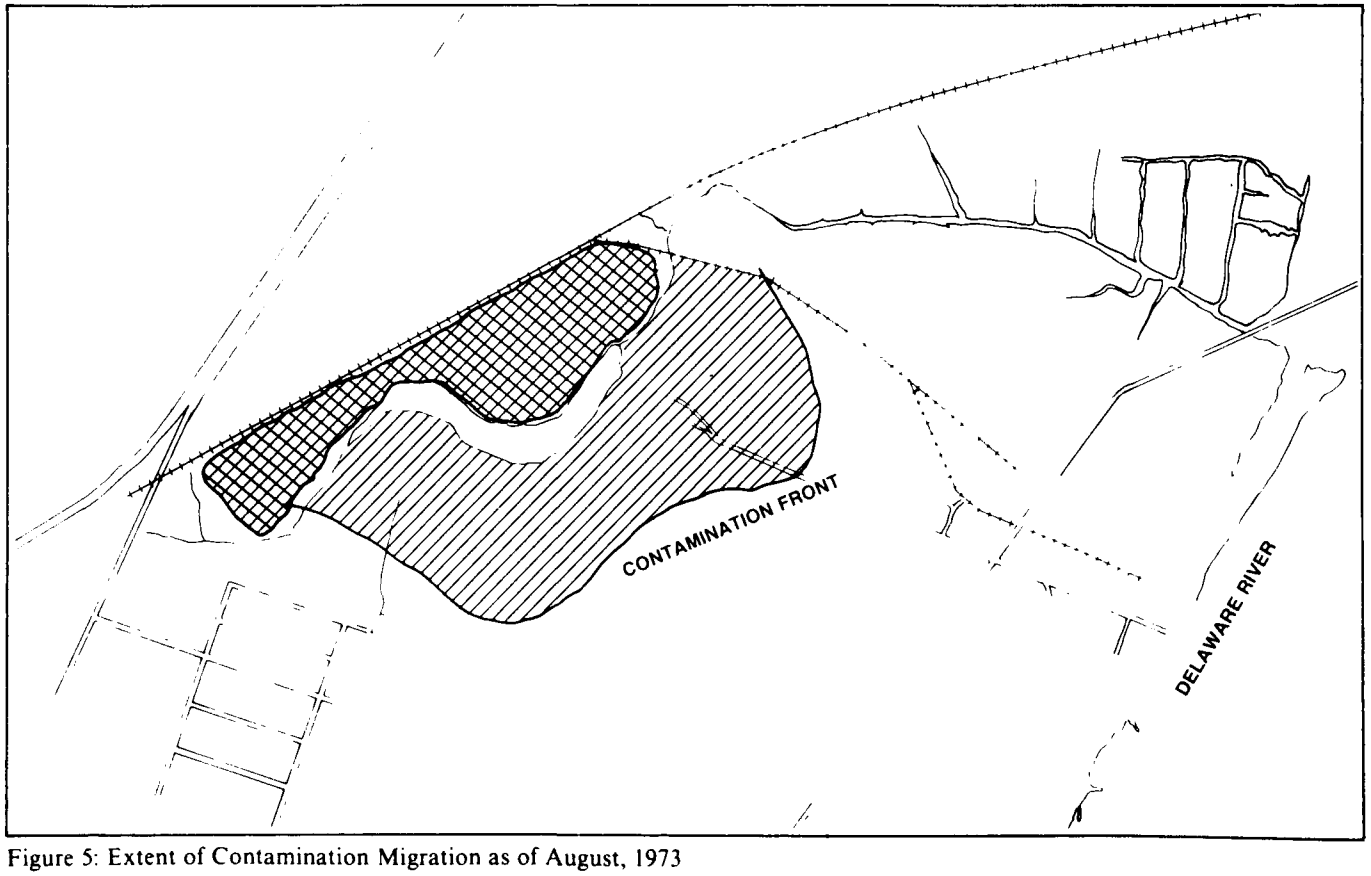

Figure 5: Extent of Contamination Migration as of August, 1973

An added feature to the divide is the physical removal of contaminants at that point. The leakage characteristics through the Columbia Formation south of the counter-pumping network then allow fresh recharge to enter the aquifer. The recovered contaminated water is allowed to settle within a perched retention pond south of the landfill. Through mild oxidation, certain contaminants are removed and the overflow infiltrates the Columbia Formation and the Delaware Estuary.

In cross section, the development of the drainage divide during the history of the leachate containment is shown in Figure 7. Line A shows the piezometric gradient form north to south between the landfill and the community wells. Line B shows the same traverse line after initiation of the control measures in late 1973. Since that time, the piezometric gradient has risen and declined with respect to increased recharge, seasonal demand, chemical and bacteriological encrustation of the recovery wells, and later rehabilitation; still it has remained fairly constant in position and effectiveness to this day.

Table I: Concentration of Specific Chemicals and Contaminants Near Army Creek Landfill

	Background Quality Potomac Aquifer	Water table Beneath Landfill	Potomac Aquifer 400 ft. Downgradient from Landfill
COD	(ppm) 14	5617	170
TDS	(ppm) 26	3606	933
NH_3N	(ppm) .55	113.4	72.2
NO_3N	(ppm) 1.75	—	—
Cl	(ppm) 9.2	436	236
ΣFe	(ppm) .20	550	47
Phenols	(ppm) <20 ppb	18	01
Sp C (μ mhos cm^{-1})	1.20	2500	1900

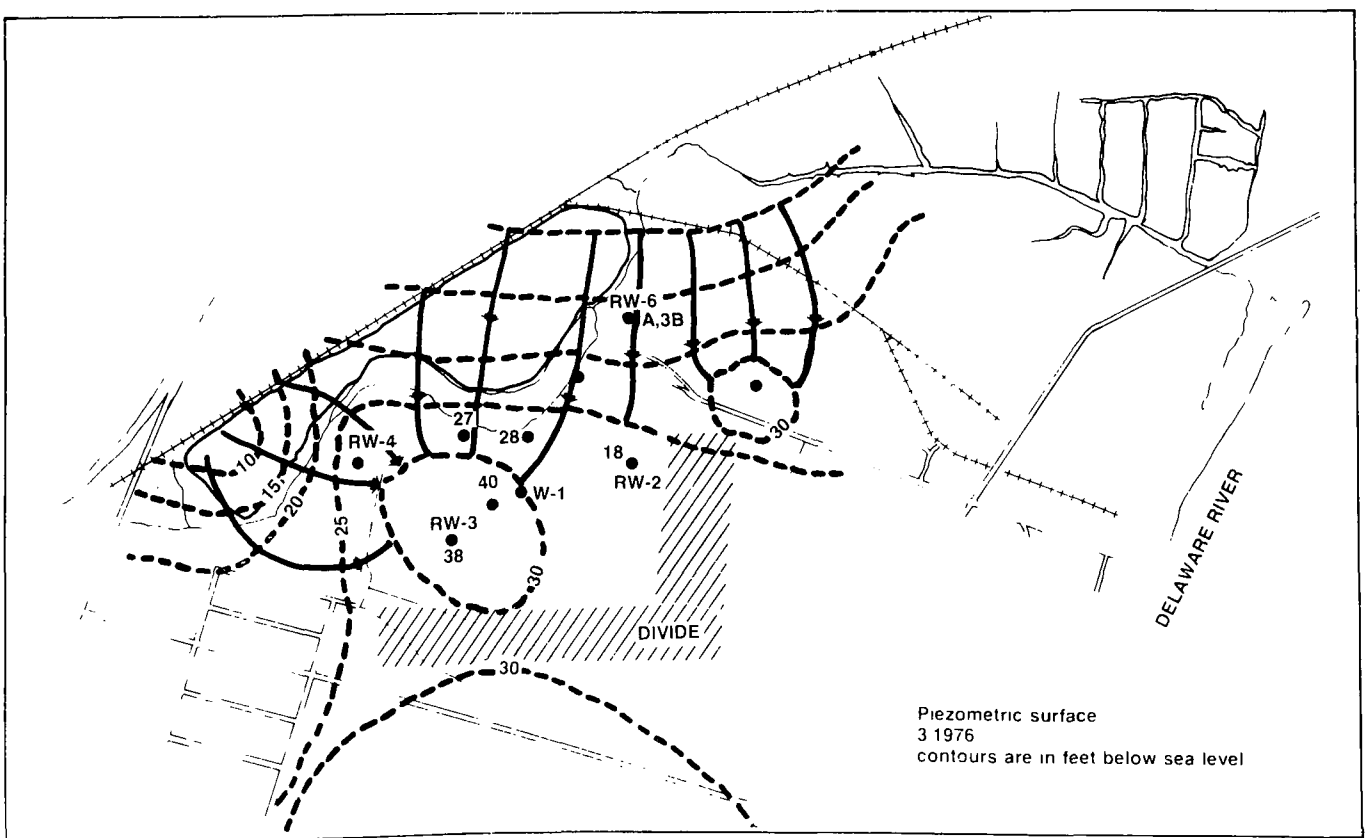

Figure 6: Location of Recovery Wells at Army Creek

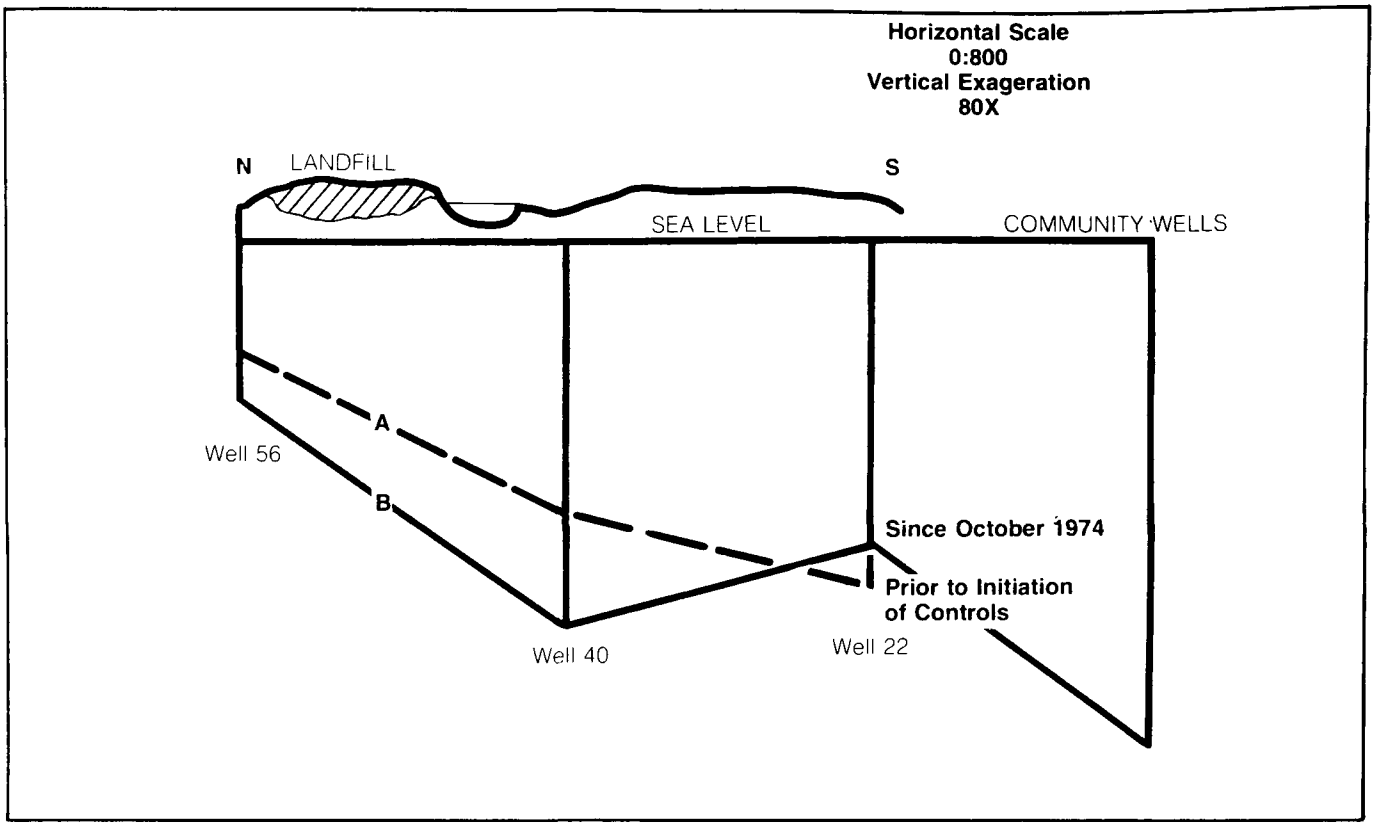

Figure 7: Cross Section through the Piezometric Surface "Drainage Divide"

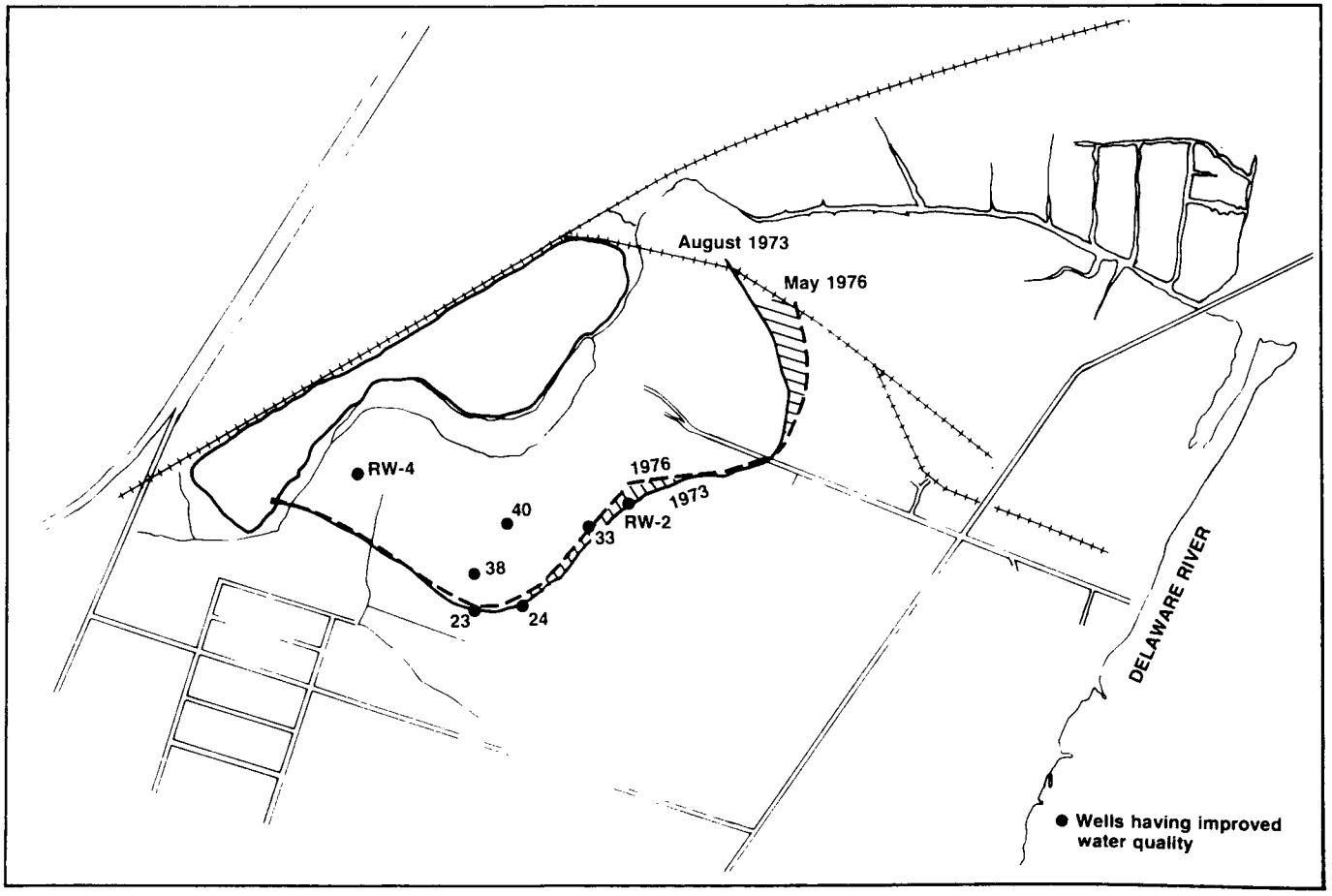

Figure 8: Extent of Contaminant Migration as of May, 1976

CONCLUSION

The counter-pumping measures at the Army Creek Landfill have been successful. Figure 8 shows an interpretive line of contaminants based upon spring 1976 data. In certain fringe area monitoring points, the groundwater quality has actually been shown to improve, although it is still below U.S. Public Health Service limits and EPA interim standards for potable water.

Although successful, the present containment program is just that—a containment program. No resulting aquifer rehabilitation in the affected area can be expected unless the source of the contaminant problem is removed or effectively neutralized.

To date, approximately 1.35 million dollars have been spent in an effort to contain contaminant migration and preserve the ground water which, in coastal Delaware, is the primary source of drinking water. Although the present counter-pumping measures have been successful, it is evident that a more permanent solution must be reached. To this end, New Castle County has directed efforts toward an economically sound and environmentally acceptable solution.

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The Potential for National Health and Environmental Damages from Industrial Residue Disposal

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INTRODUCTION

According to current estimates by the Office of Solid Waste Management Programs, 344 million metric tons of industrial wastes are produced annually in the United States, with a yearly growth rate of about three percent. This is more than twice the combined quantities of municipal solid wastes and sewage sludge. We also estimate that at least ten percent of all industrial wastes are potentially hazardous. This, of course, raises a serious environmental issue, which received special attention with the publication of an EPA Report to Congress in 1973.[1] The Report concluded that the prevailing methods of hazardous waste management are largely inadequate and result in the uncontrolled discharge of hazardous residues into the environment, thereby threatening the public health and welfare.

Types of Documented Damages

The Office of Solid Waste Management Programs has compiled hundreds of case studies of damages resulting from improper industrial residuals management; some of these have been published.[2,3,4,5] In the course of this data gathering effort, we have recognized six major routes of environmental transport through which the improper land disposal of hazardous wastes can result in damage: (1) groundwater contamination via leachate; (2) surface water contamination via runoff; (3) air pollution via open burning, evaporation, sublimation, and wind erosion; (4) poisoning via direct contact; (5) poisoning via the food chain; (6) fire and explosion. These forms of damage were discussed, and illustrative case studies were presented in a previous publication.[6] As examples of potential human health injuries from industrial waste disposal, we would like to mention only two of the more recent incidents that have come to our attention:

- A case of suspected chronic mercury poisoning on a farm in Illinois is currently under litigation. It involves a family of six who exhibited the typical symptoms of Minamata disease after prolonged drinking of well water from an aquifier which had been contaminated by the disposal of industrial wastes three quarters of a mile away.
- A previously reported case of solvent disposal in a Maryland sand and gravel quarry has recently resulted in litigation. The suit involves three members of a family living near the quarry who have sustained pancreatitis, a condition associated with chronic solvent exposure.

Tabulation of Damage Data

The Office of Solid Waste Management Programs has compiled an inventory of over 400 cases of damage resulting from waste disposal practices. The majority of case studies in the inventory relate to industrial processing waste disposal; however, damages from the disposal of pesticides and pesticide containers have also been incorporated. The primary sources for this data gathering effort were State environmental regulatory agencies.

Based on 421 industrial and pesticide waste-related damage case studies compiled to date, we have prepared a number of tabulations which may help in reaching some preliminary conclusions about prevailing damage trends.

Table I summarizes the damage mechanisms involved in the analyzed case studies by disposal method. It indicates that groundwater contamination is the most common type of damage reported, followed by surface water contamination. Moreover, in most cases of established groundwater contamination, actual water supply wells (as compared to monitoring wells) have been affected. The table also shows that "other land disposal," which generally refers to promiscuous dumping or dumping on land not designated for this purpose, is the most significant source of damage. Surface impoundments and landfills contribute in about equal measure; however, these disposal methods together account for about as many damage incidents as "other land disposal." It should be noted that the data summarized in the table are not nationally representative since 65 out of the 421 cases studied were obtained from an incomplete survey of one State that already has a permit system for landfills and surface impoundments. The most flagrant environmental offenses generally occur in those States that do not have regulatory programs for industrial waste disposal. Further, such States generally do not have adequate documentation of damages.

Table II shows the contaminants identified in damage incidents by disposal method. It should be emphasized that in most documented damage cases chemical analysis of the contaminants is incomplete. This is mainly due to the expensive nature of thorough laboratory analysis, especially when organic contaminants are involved. Despite its incompleteness, the table is informative because it identifies a wide range of harmful and potentially harmful contaminants. The largest category, miscellaneous organics (identified in 86 separate incidents), includes some known and suspected carcinogens.

Finally, two other interesting observations derived from the tabulation of case studies should be noted. One is that in 63 percent of the incidents of damage, the causative waste disposal action occurred on the property of the waste generator, although in many instances the damage had spread off-site when it was discovered. The second observation relates to the time frame of discovery of damage. Sixty percent of the available damage incidents were discovered during the past five years; however, the acts of waste disposal responsible for the damage may have occurred years or even decades earlier.

Table I: Mechanisms Involved in Incidents of Damage by Disposal Method[a]

Disposal Method	Surface Impoundments	Landfills, Dumps	Other Land Disposal b)	Storage of Wastes	Smeltings, Slag, Mine Tailings
Number of Cases	89	99	203	15	15
Damage Mechanism (number of cases)					
Groundwater (259)	57	64	117	10	11
Surface Water (170)	42	49	71	-	8
Air (17)	3	5	9	-	-
Fires, Explosions (14)	-	11	3	-	-
Direct Contact Poisoning (52)	1	6	40	5	-
Wells Affected[c] (140)	32	28	74	4	2

a) The tabulation refers to 421 cases studied thus far. The numbers in the matrix add up to more than 421, because several damage incidents involved more than one damage mechanism.
b) Haphazard disposal on vacant properties, on farmland, spray irrigation, etc.
c) Not included as a damage mechanism.

Note: The data presented in this table have been derived solely from case studies associated with land disposal of industrial wastes.

The Potential Nationwide Impact

Most hazardous waste-related human health injuries result from months and years of chronic exposure at trace concentrations of the toxicant. The health effects are insidious and almost impossible to trace back to the causative agents. Yet, even in the absence of positive identification—and especially quantification—of health injuries, there should be serious concern about any large-scale release of toxicants, carcinogens, and other harmful materials into the environment. In the following, we shall relate industrial waste generation data to information on waste disposal practices, in order to indicate the potential for nationwide health and environmental damage.

The Office of Solid Waste Management Programs has studied 14 key industries to gather data on waste generation rates and disposal practices. These industries, which are thought to generate most of the nation's potentially hazardous wastes, are indicated in Table III, together with a partial listing of their waste components. The 14 industry categories generate about 206 million metric tons (wet) of process and pollution abatement residuals, of which about 35 million metric tons can be considered potentially hazardous, chiefly on the basis of toxicological considerations. The annual growth in the generation of potentially hazardous wastes is estimated at three percent for the next decade.

In order to gain an understanding of the nationwide potential for industrial waste disposal-related health and environmental damages, we have made an assessment of the environmental adequacy of current disposal practices, as these relate to the estimated 35 million metric tons of potentially hazardous residuals indentified in the aforementioned industry categories. The assessment of environmental adequacy was based on the disposal practices employed by typical manufacturing facilities, i.e., those which employ average disposal technology relative to other plants in the same industry. The modes of disposal have been categorized as environmentally adequate or inadequate, whenever possible on the basis of each contractor's judgment, which was largely arrived at by numerous plant visits. However, in many instances contractors were not able to make such a judgment but simply categorized the prevailing disposal practice into a series of progressively less adequate methods. An example of such a progression would be "secure landfill—approved landfill—landfill—dump." In such instances the authors made the determination of environmental adequacy. The judgment was made conservatively for the purposes of this analysis. In the example cited above, disposal at "approved landfills" was termed environmentally inadequate, because the Office of Solid Waste Management Programs has on file numerous case studies demonstrating damage at landfills which have been approved by State and local authorities only on the basis of a lack of alternatives.

Table II: Contaminants Involved in Damage Incidents by Disposal Method (Cases Studied: 421)

Disposal Method / Contaminant	Total	Surface Impoundments	Landfills, Dumps	Other Land Disposal*	Smelting, Slag, Mine Tailings	Storage
As	19	5	4	10		
Cd	5	3	1	1		
Cr	33	11	9	12	1	
Cs	1		1			
Cu	20	6	4	7	3	
Fe	40	10	20	6	4	
Hg	11	1	1	9		
Mn	26	3	15	4	4	
Ni	13	5	2	5	1	
Pb	22	5	6	8	3	
Zn	22	9	5	5	3	
Cl^-	27	11	6	9	1	
CN^-	19	6	4	9		
F^-	8	5		3		
NH_3	14	6	2	6		
NO_3^-	16	6	2	7		1
$SO_4^=$	18	9	2	5	2	
Inorganic Acids	27	9	4	10	4	
Misc. Inorganics	83	21	25	29	6	2
PCBs	3		1	2		
Petrochemicals	27	10	5	10		2
Phenols	31	9	10	12		
Misc. Organics	88	19	25	39		5
Bacteria	11	1	2	8		
Pesticides	71	1	6	57		7
Radioactive	9	2	3	1	1	2
Unspecified Leachate	25	5	18	1	1	
Total	689	178	183	275	34	19

*Disposing on vacant properties, on farmland, spray irrigation, etc.

Table IV categorizes the prevailing disposal practices on the basis of estimated environmental adequacy and indicates the percent of total wet weight attributable to each disposal practice. The table shows that the prime disposal method employed for potentially hazardous industrial wastes is lagooning in unlined surface impoundments, accounting for nearly half of the total of these wastes disposed. Lined impoundments which were considered adequate receive less than 0.1 percent of the total. Land disposal in dumps or on other non-secure land surfaces receives the second largest quantity. Together, these forms of land disposal account for over 80 percent of the total. Incineration is the third major disposal practice now in use, with uncontrolled incineration accounting for almost twice the amount adequately handled through controlled incineration. The result is that over 90 percent of the approximately 35 million metric tons (wet weight) of potentially hazardous wastes generated yearly by 14 key industries is handled by disposal practices which do not seem adequate to provide protection of public health and the environment. This estimate may be somewhat pessimistic, because a small portion of unlined surface impoundments and non-secure landfills may be located in areas which preclude the escape of pollutants into the environment. However, this estimate may not be exaggerated if one considers that the locations for landfills and dumps have been traditionally selected on the basis of economic rather than environmental considerations. Waste disposal usually takes place on land that has little or no value for other uses, such as marshlands, abandoned sand and gravel pits, old strip mines, limestone sinkholes, etc. Most of these sites have hydraulic connections with natural waters. Similarly, most industrial surface impoundments are unlined and were not sited on the basis of hydrogeological considerations. Therefore, one could venture to say that up to 90 percent of potentially hazardous wastes are disposed of by questionable methods and are ultimately susceptible to escape into the environment.

Table III: Partial Listing of Waste Components of Fourteen Industries

	Batteries	Electronic Components	Electroplating	Inorganic Chemicals	Leather Tanning & Finishing	Organic Chemicals*	Paints	Petroleum Refining	Pharmaceuticals	Primary Metals	Rubber & Plastics	Special Machinery	Textiles Dyeing & Finishing	Waste Oil Re-Refining
Ammonium salts								X		X				
Antimony				X			X							
Arsenic						X		X	X	X			X	X
Asbestos				X			X							
Barium							X				X		X	X
Beryllium		X						X				X		X
Biological wastes									X					
Cadmium	X	X	X	X			X	X		X	X	X		X
Chlor. hydrocarbons			X	X		X	X				X			
Chromium	X		X	X	X		X	X	X	X	X	X	X	X
Cobalt							X	X			X			
Copper	X	X	X		X		X	X	X	X	X	X	X	X
Cyanide		X	X	X				X		X		X		
Ethanol waste, aqueous									X					
Explosives (TNT)						X								
Flammable solvents		X				X	X							
Fluoride				X						X				
Halogenated solvents		X							X					
Lead	X		X	X	X		X	X		X	X		X	X
Magnesium														X
Manganese		X								X	X		X	X
Mercury	X			X			X	X	X	X	X			
Molybdenum								X			X			X
Nickel	X			X				X		X	X		X	X
Oil			X					X		X		X		X
Organics, misc.						X					X			X
Pesticides (organo-phosphates)						X								
Phenol			X					X		X	X	X		X
Phosphorus			X	X										
Selenium								X	X	X				
Silver	X		X					X						
Vanadium								X			X			
Zinc	X	X	X	X	X		X	X	X	X	X	X	X	X

*Including pesticides and explosives

Table IV: Estimated Environmental Adequacy of Disposal Practices for Potentially Hazardous Wastes*

DISPOSAL PRACTICE	PERCENT OF TOTAL WET WEIGHT OF POTENTIALLY HAZARDOUS WASTES
ENVIRONMENTALLY INADEQUATE **	
Unlined Surface Impoundments	48.4
Non-Secure Landfills	30.3
Uncontrolled Incineration	9.7
Deep-Well Injection	1.7
Landspreading	.3
Use on Roads	<.1
Sewered	<.1
Total	90.4
ENVIRONMENTALLY ADEQUATE	
Controlled Incineration	5.6
Secure Landfills	2.3
Recovery	1.7
Lined Surface Impoundments	<.1
Wastewater Treatment	<.1
Autoclaving	<.1
Total	9.6

*Based on annual generation in 14 key industries during the period 1973 1375.

**Criteria for environmental adequacy defined in text.

There are other circumstances which underscore the significant potential for nationwide damages from industrial waste disposal. One is that most manufacturing industries are located in the "wet regions" of the nation, where groundwater and surface water contamination are most likely. Figure 1 illustrates this point by superimposing the major areas of industrial activity on a contour map combining rainfall and evapotranspiration data. The areas of maximum rainfall and minimum evaporation are generally in the eastern third of the nation, where most manufacturing and consequently industrial waste disposal takes place.

A similar map (Figure 2) shows where the nation's principal underground aquifiers are located in relation to industrial concentration. One can draw three general conclusions from this map. The first is that most areas of high industrial concentration are underlain by principal aquifers. The second is that some of the most heavily used aquifers are located in dry regions of the nation, where the risk of groundwater contamination from land disposal practices is relatively small. The relatively small risk is counterbalanced by the fact that any contamination of these scarce water resources would result in particularly severe environmental and economic damage. The third conclusion derived from this map is that many groundwater aquifers in highly industrialized areas are not currently exploited as major water resources. This interpretation is somewhat misleading, since the map does not designate those areas where groundwater usage is only moderate now but is expected to increase significantly. From an environmental perspective, of course, the risk of groundwater contamination should be viewed with concern, regardless of current usage rates.

In spite of the large rate of generation of potentially hazardous wastes and the prevailing questionable disposal practices, the documented cases of health and environmental damage are relatively small. However, for every waste disposal site documented as a source of environmental contamination, we estimate that there are thousands which are situated and operated in a similar manner. The vast majority of such sites are not monitored for the escape of pollutants into the environment. Virtually all of the case studies in our damage inventory were discovered after damages had already occurred. Specifically in the case of groundwater contamination, the problems usually manifest themselves only after years—and sometimes decades—of environmental insult. The abatement of damage—if technically feasible—may take even longer and could be too costly to implement. A good case in point is the groundwater contamination in Colorado described in Reference 3, where just a comprehensive *study* of the problem—excluding abatement—may cost up to 78 million dollars.

CONCLUSIONS

- The prevailing hazardous waste disposal practices have often resulted in the release of harmful (e.g., toxic, carcinogenic) materials into the environment, causing injury to human health and also environmental and economic damages.
- The area of most serious concern is the impact of these disposal practices on human health. The effects are mostly chronic, following years of exposure at trace amounts of the toxicants.
- Of over 400 hazardous waste disposal-related damage incidents documented by the Office of Solid Waste Management Programs, the majority relate to groundwater contamination. Most cases of detected groundwater contamination affect water supply wells.
- In groundwater contamination cases, years or decades may elapse before the damages become evident. After-the-fact abatement is extremely costly, if at all feasible.
- Of the approximately 35 million metric tons of potentially hazardous wastes generated in 14 key industry may not be adequate to prevent their escape into the environ ment.
- Over 80 percent of potentially hazardous wastes go to landfills, dumps, and surface impoundments. Most of these were located and designed on the basis of economic rather than environmental considerations.
- Most areas of industrial concentration, and consequently disposal sites, are located in wet regions of the nation, where precipitation exceeds evapotranspiration potential, increasing the likelihood of soil infiltration and runoff.
- Most areas of industrial concentration are underlain by groundwater aquifers which are vulnerable to pollutants.

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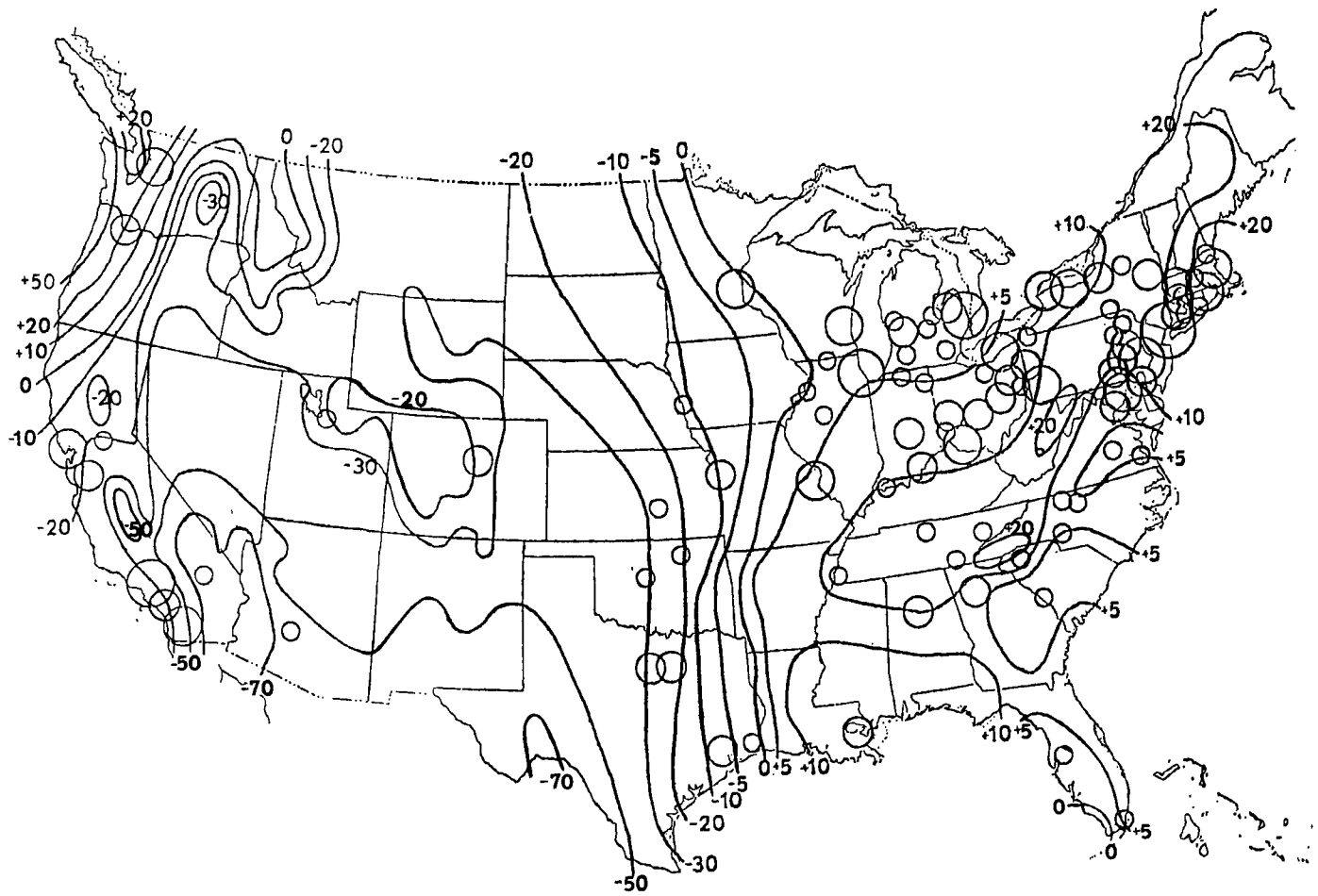

KEY

Industrial Centers of the U. S. (Based on Manufacturing Employment: 1963)*

- >1,000,000
- 400,000 – 999,999
- 120,000 – 479,999
- 48,000 – 119,999
- 24,000 – 47,999

Contours represent mean annual precipitation (inches) minus potential evaptranspiration.†

*National Atlas, 1970

†Proc. of joint conference on recycling municipal sludges and effluents on land. Champaign, U. of Ill., 1973. p. 117.

Figure 1: Precipitation—Evapotranspiration Potential Contours and Industrial Centers of the Conterminous U.S.

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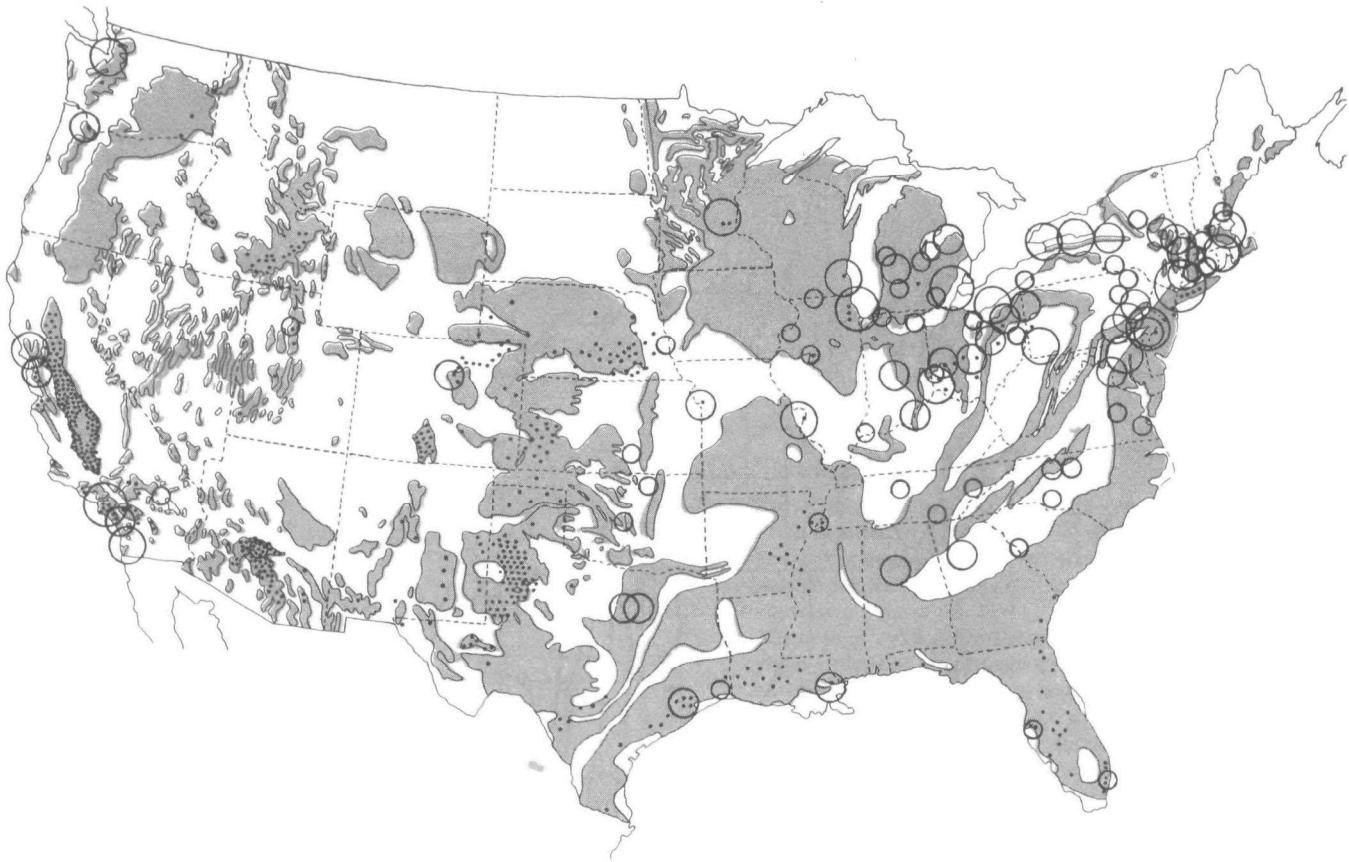

KEY

Industrial Centers of the U.S.

(Based on Manufacturing Employment: 1963)*

> 1,000,000

480,000 – 999,999

120,000 – 479,999

48,000 – 119,999

24,000 – 47,999

Each dot represents withdrawal of 81,000 acre-feet or 100 million cubic meters annually, equivalent to 72 million gallons per day.*

Shaded areas represent groundwater areas (major aquifers) of the U.S.†

* National Atlas, 1970

† Water Atlas of the United States, 1973

Figure 2: Major Aquifers, Well Withdrawals, and Industrial Centers of the Conterminous U.S.

Health Effects— Land Application of Municipal Wastewater and Sludge

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INTRODUCTION

The number, size and complexity of wastewater and sewage treatment plants is increasing constantly. Whether or not there are potential health hazards arising from the treatment process itself and various proposed methods of disposal of the sludges produced is largely unknown. The problem is nationwide.

Currently, 12 billion gallons of wastewater and 17,000 dry tons of sludge will be treated and processed daily. It is estimated that by 1985, 22 billion gallons and 23,000 dry tons of sludge will be treated and processed daily (Table I).[1]

The Federal Water Pollution Control Act (FWPCA) as amended in 1972 (PL 92-500) requires that all publicly owned treatment works install secondary treatment by July 1, 1977. Consequently, the quantity of wastewater to be treated and sludge to be disposed of will increase. The Marine Protection Research and Sanctuaries Act of 1972 (PL 92-532) requires permits for dumping of wastes in the ocean, including municipal sludge. Section 102(g) requires that permit applicants consider appropriate locations and methods of disposal, including land-based alternatives. This impacts sludge disposal practices and identifies a need for R&D to improve sludge disposal alternatives.

The FWPCA also requires that an assessment of alternative treatment technologies be made before a construction grant is awarded (Sec. 201g).[2] Alternatives that must be considered are land treatment of wastewater and sludge recycling (Sec. 201(d)). As a result, there will be many new technologies that may pose health risks and must be addressed.

The Safe Drinking Water Act (PL 93-523), Section 1444 (a)[1] and 1444(a)[2] requires R&D associated with any project which will demonstrate health implications involved in the reclaiming, recycling and reuse of wastewaters for drinking water. This too impacts on sludge disposal. Methods used in the past are now restricted by specific laws or regulations. Current research programs have emphasized a shift of philosophy from ocean dumping to the development of improved technologies for returning the sludge to the environment (land) in an ecologically acceptable manner with minimal health risks. Many State agencies are reluctant to approve use of agricultural land for the treatment and disposal of wastewater and sludge, because of the lack of information on the health hazards associated with such practice.

It is essential that the health risks associated with sludge processing, utilization and disposal be identified and adequately studied.

Types of Sewage Treatment, Disposal and/or Utilization Methods

Sewage treatment can be divided into three phases: primary, secondary, and advanced. In the primary phase, the waterborne constituents are separated from the water stream by screening and sedimentation or flotation. Conventional secondary treatment removes up to 90% of the organic matter in sewage by making use of a biological active mass. The two principal techniques used in the secondary phase are trickling filters and the activated sludge processes. Stabilization ponds can be used to treat sewage to the secondary phase of treatment or they can be used to supplement other processes. Physical-chemical methods may be used to remove colloidal matter, color, odor, acids, alkalis, heavy metals and oil. To return water of more usable quality to receiving lakes and streams, new methods for removing pollutants are being developed. These advanced waste treatment technologies can include coagulation and sedimentation which will increase the removal of solids from effluent after primary and secondary treatment. Filtration, microscreening, ammonia stripping, carbon adsorption, electrodialysis, ion exchange and reverse osmosis can be used to remove nutrients, refactory organics and dissolved solids. Disinfection can be associated with primary, secondary and advanced waste treatment.

The sludge produced during the treatment can be handled by any of a number of processes, including anaerobic and aerobic digestion, lagooning, pasteurization, centrifugation, drying by sand beds, heat (thermal) drying, composting, incineration; liming and chlorination. Thermoradiation and radiation are also being developed as disinfection processes.

Many alternatives are available for the disposition of the liquid phase. Most treatment works effluents are directly discharged to surface waters. Other means for disposal or use of effluents include: (1) discharge to the land for further treatment; (2) recharge of the groundwater; (3) irrigation of agricultural crop land; (4) wastewater effluent discharge into waters used for recreational purposes; and (5) subsequent industrial reuse. Direct reuse of effluents for potable water supplies is not practical currently due to the many potential public health factors.

Of the many methods of processing and disposing of sludges from wastewater treatment plants, no single method is capable of solving all problems. Each disposal method has advantages; each works well under a given set of local conditions while another approach may be better suited to a different set of circumstances.

The major decision in selecting sludge disposal alternatives relates to the desired or allowable final form of the material when introduced into the receiving environment. All sludge processes are directed at economically converting the material withdrawn from the liquid treatment phase into a form satisfactory for release to the environment. The alternatives currently available are: (1) incineration; (2) composting; (3) landspreading for land reclamation or agricultural enhancement; (4) landfilling; and (5) by-product recovery.

Table I: Sludge Information Summary

1. Quantities of sludge (estimated)

dry tons/day

	Current	Secondary Treatment (next 10 years)
Domestic	10,000	13,000
Industrial users of municipal plants	7,000	10,000
Total municipal sludge	17,000	23,000

2. Current disposition of sludge

Method	% Total Sludge	Reliability of Estimate
Landfill	25%	Good
Ocean dump	15%	Good
Incineration	35%	Good
Land application	25	Good
Croplands	(20%)	Poor
Others	(5%)	Poor

*Derived from background information to the Technical Bulletin on Municipal Sludge Management (1).

3. 1972 Land Spreading Survey (Liquid Sludge Only)

EPA Regions II, III, IV, V, and IX
Mailed 1909, Responded 745 (39%)

Region	Currently Used	Will Use	Do Not Use
II (NJ,NY)	6%	6%	88%
III (DE,MD,PA VA,WV)	27%	5%	68%
IV (AL,FL,GA, KY,MS,NC, SC,TN)	18%	12%	70%
V (IL,IN,MI, MN,OH,WI)	36%	9%	55%
IX (CA,HI,NV)	14%	6%	80%
Total	25%	8%	67%

Size MGD*	Currently Used	Will Use	Do Not Use
1-10	27	8	65
10-100	15	9	76
Greater than 100	7	13	80

4. Total Costs for Various Sludge Methods

Includes operating and construction costs

$/Dry Ton

	1 MGD	10 MGD	100 MGD
Land Application	127-168	53-71	57-84
Landfill	171-208	77-116	63-98
Incineration	250-320	111-174	79-120
Ocean Dumping	376-417	93-134	56-93

* MGD = million gallons/day

Present Knowledge Concerning Presence and Survival of Pathogenic Agents and Toxic Chemicals in Various Phases of Sewage Treatment, Disposal, and/or Utilization Methods

A. *Biological:* Information on pathogen removal typical of various municipal wastewater treatment processes is presented in Table 2.[2,3,4,5]

Primary treatment by settling, which still constitutes the whole of municipal wastewater treatment for many communities, removes little of the pathogens in wastewater. Secondary treatment by trickling filters, activated sludge, or stabilization ponds can markedly reduce the number of pathogenic enteric bacteria, viruses, tubercle bacilli, and parasites in sludge depending on the process used. Resulting effluents will contain a quantity of each kind of microorganism present in raw sewage depending on the efficiency of the particular process.

Table II: Percent Removal of Pathogens by Sewage Treatment Processes

	Trickling Filter	Activated Sludge	Anaerobic Digestion	Chlorination
		%		
		Enteric Bacteria		
Total Counts	70-95	70-99		96-99
Coliform	82-97	91-98		99-99+
Fecal Strep	84-94		-	
Typhoid Group	84-99+	Present: 95-99.2	Not Found: 25-92.4	98-99
Shigella		97-98		
Cholera	-	Not Found		
Microbacterium	66-99-	Slight to 87		
Salmonella	84-99+	96-99		
		M. Tuberculosis		
M. Tuberculosis	Survive: 66-99	Survive: 88	Survive: 69-90	Survive 99+
		Entero Viruses		
Polio	Slight-90+	60-90+	Slight-99+	Slight
Coxsackie	Slight-90+	60-90+	Slight-99+	to
ECHO	Slight-99+	60-90+	Slight-99+	Considerable
Infectious Hepatitis				
		Parasites		
Tapeworm Ova	18-26	Not Removed	97	No Effect
E. Histolytica Cysts	11-99+	No Reduction	Removed	
Ascaris Lumbricolides Ova	-	-	45; Reduce	
Taenia Saginata	62-70	Little Effect	Very Slow	
Trichuris	-	91.8-100	-	
Schistosoma Japonicum	Reduced:	Excellent Hatching Medium	90(25-35 days)	
S. Mansoni	-	-		
Hookworm	100	81.5-96		

*Derived from data reported by Kabler (1959) and others; (2,3,4 & 5)

The efficiency of disinfection (chlorination being the most widely used method) of the effluents discharged varies considerably under different physical and chemical conditions. The data available have shown that sewage effluents after secondary treatment and after chlorination contain reduced numbers of viruses and intestinal parasites.

There are insufficient data regarding the survival and destruction of pathogens during sewage sludge incineration. It should be expected that, under conditions of good incineration practices and equipment, pathogens would not survive and be found in the sludge residue or emitted from the incinerator stacks. However, under conditions of poor combustion, pathogens may survive.

Studies have shown that the pathogen content of sludge is similar to that of municipal solid waste, thus the pathogen survival in land-filled sludge can be considered similar to that in landfilled municipal solid waste providing that environmental factors—temperature, moisture, and pH are comparable.[6]

B. *Presence of Persistent Toxic Chemicals:* The concentration of toxic chemicals in municipal wastewater effluents and sludge are related to the kinds and amounts of industrial discharges as well as street runoff directed into the municipal treatment systems.

Conventional methods of wastewater treatment do not completely remove many potentially hazardous chemicals. The con-

centration of contaminants in receiving waters has been shown to increase in downstream communities as water is used and reused and as the percentage of unremoved residual refractory chemicals grows.

When sludge is properly incinerated, small but measurable quantities of specific metals can be found in the stack emissions, scrubber water and residue of incinerators. The metals identified are arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel and vanadium. Aside from the potential hazards associated with atmospheric exposure to these metals (for mercury—performance standards exist), other hazards may be posed by these metals upon ultimate disposal of the scrubber water and residue. Many of these metals are known to accumulate in the human system.

Small but measurable quantities of specific organic compounds dieldrin, chlordane, DDT and polychlorinated biphenyls are also found in some sludge and would be destroyed under optimum combustion conditions, but under conditions of poor combustion could be emitted from the stacks of municipal sludge incinerators. These compounds are known to accumulate in the human system and many are known to be mutagenic and carcinogenic.[7]

Health Implications of Sewage and Effluent Disposal

The methods presently employed or under consideration for the reclamation and/or disposal of sewage effluent and sludge may contribute to adverse health effects unless measures are carried out to curtail exposure to pathogens and toxic chemicals.

A. *Biological:* Application of sewage sludge to soil has been shown to increase the number of soil microbes.[8]

Application of sewage (primary or secondary) effluents or sewage sludge to the land may present a potential health hazard because of the presence of human or animal pathogens. Among the most common pathogens found in sewage effluents are the bacterial pathogens Salmonella, Shigella, and Mycobacterium; the entero-viruses, adenoviruses, and possibly hepatitis virus; the amoeba cysts, and helminth ova. Some studies have suggested that many micro-organisms are retained at or near the soil surface. Their movement through the soil is not considered to be a problem.[9],[10] Only recently has quantitative information on virus survival appeared in the literature.

Irrigation with sewage has been found to be associated with vector-borne disease such as malaria and encephalitis; severe annoyance by blood-sucking insects; as well as typhoid fever, cholera, and other gastrointestinal diseases.[11] Vegetables irrigated with either raw sewage or primary-treated and chlorinated effluents have been found to contain Salmonella and Ascaris ova.[12] Grass samples sprinkled with raw sewage yielded Salmonella.[13] Enteric viruses such as polio-, coxsackie-, echo-, and infectious hepatitis may be spread through sewage contaminated vegetables.[14]

Where animals have access to raw sewage and treatment plant effluents, the possibility of their contracting certain diseases may exist.[15] In cattle, these diseases include bovine tuberculosis, anthrax, tapeworm, etc.

Health implications may be associated with: (1)the municipal wastewater effluent as it passes over or into the soil —on crops, animals, or man; (2) groundwater contamination; (3) aerosolization of wastewater and particulate matter containing pathogens; and (4) ponded areas, open lagoon storage sites, or contaminated air/soil interface. Where not adequately designed, mosquitoes may breed, flies and other insects, migrating birds and rodents may have access and serve as mechanical carriers of disease organisms.[16]

Pathogen Concentrations in Wastewater and Sludge

The number of pathogens found in municipal wastewater and sludge varies widely depending on the time of year and the community. Estimates of virus concentrations from field studies have indicated concentrations up to 7000 plaque forming units (PFU)/liter for raw sewage to about 50-1600 PFU/liter for chlorinated secondary effluents.[10]

It has been demonstrated repeatedly that many pathogens, especially viruses, survive conventional waste treatment processes including chlorination, although they are reduced in number. Berg[17] points out that primary and secondary treatment processes reduce the numbers of viruses only slightly. Although some laboratory studies have shown good reduction, field evaluations are, at best, erratic.

Current research being conducted by the U.S. Department of Agriculture, Agricultural Research Station at Beltsville, Maryland, has shown that potentially infective stages in the life cycles of parasites persist in sewage.[18]

In actual practice, disinfection probably plays the most important role in reducing pathogen concentrations in wastewater. However, much of the classical data on disinfection does not reflect real world conditions. Disinfection as practiced for wastewaters is often less effective for pathogens, especially viruses, than it is for indicator bacteria. Table 3 contains data which supports this contention.[3], [19], [20]

Table III: Effect of Wastewater Treatment on Various Organisms[3]

	Total Reduction in Treatment Plant (Log_{10})	Reduction by Chlorination Only (Log_{10})
PLANT #1 *		
Fecal Coliform	3.7	2.1
Fecal Streptococci	2.4	2.0
Salmonella †	1.4	0.5
Enteric Viruses ¶	0.4	0.3
PLANT #2 δ		
Total Coliform	6.8	5.5
Fecal Coliform	5.8	3.6
Klebsiella α	5.2	3.7
§2 Bacteriophage		0.9**

* Standard-rate trickling filter; chlorine residual approximately 1.5 mg/l

† Presumptive. M-bismuth sulfite broth with MF procedure

¶ Three days on BGM cells after concentration (19)

δ High-rate trickling filter; chlorine residual approximately 4 mg/l with improved mixing

α Large number confirmed as Klebsiella on differential media

** After Kruse, et al. (20)

Pathogens in Soils

The application of municipal wastewater and sludge to soil has been studied to some extent with regard to pathogen mobility and destruction in soils.[21] Studies by Sagik, *et al.,* provide current information.[22] Basically, pathogen removal in soils is a function of the characteristics of the soil. Heavily textured clay soils, through adsorption and filtration, can remove viruses, bacteria and the larger pathogens, on or near the soil surface. Desorption and transport of viruses may present a more long-range problem.[23]

Those pathogens which are collected on or in soil can be inactivated after land application. Exposure to ultraviolet light, oxidation, and desiccation are the most important destructive mechanisms. Temperature and soil moisture also appear to be important factors.[24] Conversely, there is ample literature

indicating that some pathogens can survive these natural destructive effects in soil for relatively long periods.

The extent that pathogenic organisms can survive on soil and vegetation is important.[25] It has been shown that coliform organisms survive longer in soil than on vegetation .[18] Virus survival on soil is currently receiving attention by Sagik *et al.*[26] and Duboise *et al.*[23,24] It is unlikely, however, that coliform organisms can survive longer than viruses.

It is also important to consider pathogen concentration on or near the soil surface. Consideration should be given to the effects of long-term application of non-degradable organic materials that may clog the soil surface or tie-up soil adsorption sites; the effect of cation species and concentration with respect to soil tightness and adsorptive capacity; the effects of high pH on soil filterability and reduced adsorption capability; and lastly, the reduced treatment capabilities of soil for pathogens after shock loading of a toxic effluent (from spills).

These possibilities suggest some potential public health implications. Human contact with organisms on soil surfaces may result if winds, machinery, or other human activity such as walking reaerosolize the organisms and make them accessible for inhalation. Runoff, either during intense effluent application or precipitation, may cause significant numbers of concentrated pathogens to enter surface waters. This problem can be minimized by proper design of the application site.

Pathogenic Aerosols

In evaluating the potential problems associated with pathogenic aerosols consideration must be given to wastewater pathogen concentration and treatment effectiveness, the amount of wastewater and the degree of aerosolization, the distance from receptor populations and the prevailing meteorological conditions.

It is reasonable to postulate that, if disinfection of sewage is not relatively efficient and if pathogenic organisms are aerosolized, even very low numbers of these organisms may be a potential public health hazard. In order to evaluate this situation, models have been developed describing the potential human risk for a variety of wastewater pathogen conditions, meteorological conditions, and treatment schemes.[3] Field validation of these predictions are becoming available.[27, 28, 29]

Although the potential problem of pathogenic aerosols have been identified, research is necessary to allow better definition and assessment of the potential problems.

It is interesting to relate the potential aerosol problem to spray area design criteria. Predictions through modeling indicate a 3-log reduction in virus concentration can be achieved with a buffer zone of less than 200 meters.[30] For comparative purposes, it can be shown that filtration followed by disinfection with adequate mixing will provide approximately a 3-log reduction in the virus concentration.

B. *Chemical Considerations:* The presence of toxic substances both inorganic and synthetic organic chemicals in wastewater and sewage sludge is related to the kinds and amounts of urban and industrial discharges to the sewage treatment systems as well as the persistence of the compounds with respect to both chemical and biological degradation. The composition and character of urban activities and industrial processes are ever changing and, so too, municipal sewage wastes vary in their chemical composition.

1. *Inorganics:* Applying sludge as a fertilizer or soil conditioner entails the risk of increasing the metals content of crops. This may be detrimental or beneficial to the quality of the crop for food. Direct ingestion of contaminated crops, or drinking water derived from groundwater polluted by leaching or surface water polluted runoff are possible exposure modes.

Most of the elements are found in wastewater, and if no controls are exerted on what is discharged into sewers, they could be found at undesirable levels in sludge. The inorganic toxic substances that may be found in sludge that are of greatest concern to health are the heavy metals—arsenic, cadmium, lead, mercury, selenium and zinc.

Arsenic, Lead, Mercury and Selenium

Contamination of soils with arsenic, lead, mercury, selenium, much beyond the normal range in soils is unlikely if the application of nitrogen, cadmium, zinc, copper, and nickel is regulated to control sludge application rates.[31]

Cadmium and Lead

Cadmium is the element of greatest concern from sludge use on agricultural land because it is toxic to man and accumulates in the kidneys and liver, with deleterious effects after a certain threshold has been reached. Animal studies have indicated that an accumulation of 200 ppm in the renal cortex is the level at which susceptible individuals would experience kidney damage. The World Health Organization established a provisional tolerance of 400-500 μgCd/week; this is equivalent to 57-71 μgCd/day. Estimates of the daily dietary intake of Americans vary widely, but the most recent FDA surveys indicate that the level is almost up to the World Health Organization (WHO) tolerable dietary intake. The cadmium level in the diet does not appear to pose a short-term health problem, because the daily intake at present estimated levels will not result in accumulation of 200 ppm in the renal cortex for the average life span. Neither, does it seem likely that judicious use of sewage sludge will significantly increase the average daily dietary intake of the U.S. population as a whole. However, it could increase for certain local populations who primarily consume local crops grown on sludge treated land. Also, the margin of safety is small (safety factor 4) and parts of the population may not be average in regard to dietary intake and sensitivities. In addition, heavy cigarette smoking can add greatly to the daily intake of cadmium.[31]

Another concern is for cadmium and lead ingested directly by animals grazing on pastures contaminated with sludge. Experiments are under way to evaluate the effects on cattle grazing on sludge-amended pastureland and consuming sludge directly. Preliminary results indicate that there is some increase in lead and cadmium levels in the liver and kidneys but no indication that there is any imminent danger of significantly increasing man's intake of the metals. It would seem like a reasonable precaution to avoid sludge spreading on pastures pending receipt of data from research on the effects of sludge application. Restrictions against animals grazing sludge-treated pastures until the sludge has been thoroughly washed off the grass or the levels of the lead and cadmium in the sludge exceed 1,000 mg/kg dry sludge and 20 mg/kg dry sludge, respectively, are described in the U.S. EPA proposed Municipal Sludge Management Technical Bulletin.[1] These restrictions appear to be providing some protection against excessive increase of cadmium and lead in the daily diet.

The application rate of sludge-borne cadmium to agricultural crops should be controlled until the permissible levels in food crops have been established and until research can define the plant uptake by various species and varieties of plants under varying environmental and management conditions. The rates of application that are being advocated by the U.S. Department of Agriculture, Agricultural Research Service, or by the Wisconsin State guidelines appear to minimize accumulations of cadmium in foods. They are probably restrictive enough that many industrial cities will find that land spreading is not an economically feasible disposal method for them, but some large cities may be able to comply. Dedicated land could have less stringent restrictions than those for agricultural lands as long as products to be marketed meet any present or future standards of FDA, USDA, or State departments of agriculture.[31]

2. *Organics:* Numerous efforts have been made to gain a better understanding of toxic hazards of modern synthetic organic

chemicals that find their way into wastewater and sludge. However, there are many difficult sampling and analysis problems in concentrating, extracting, and identifying such compounds many of which still may be unknown breakdown products of more complex chemicals that have undergone partial biodegradation. In 1960, researchers at the Taft Sanitary Engineering Center were able to identify fewer than 40 percent of the soluble organics remaining in biologically treated sewage and these were described only in general terms such as ether treated extractable matter, protein, tannin, lignin or alkyl benzene sulfonate.[32] No such systematic effort has been reported in the literature since then, except for certain specific compounds like PCBs and organochloride pesticides. However, EPA is presently conducting a study to identify toxic materials in the effluent.

The conventional methods of wastewater treatment leave many potentially hazardous chemicals unchanged. Many of the organics found in drinking water may also be found in sludge. EPA has compiled a list of about 300 specific compounds identified in drinking water.[33] The concentration of some contaminants has been shown to increase in downstream communities as water is used and reused and as the percentage of unremoved residual refractory chemicals grows.

Petroleum products and refinery wastes are among the sources of many possible mutagenic and carcinogenic substances that may appear in municipal sewage sludge. Various polynuclear aromatic hydrocarbons have been recovered from sewage sludge among them the known carcinogens 3,4,—benzpyrene and 1,-2—benzathracene. Carcinogenic aromatic amino compounds such as beta-naphthylamine and benzidine originate in dye and rubber works and may be released to sewer systems together with nitroanalogs used in the production of amino compounds such as aminoazodyes, amino stilbenes and tri- and diphenyl methane dyes. Pharmaceutical factories, textile dying plants, plastic production and similar industries are sources of these organics. Some of the chemical intermediates such as orthochloronitrobenzene have been found in the Mississippi River in appreciable quantities and appear to be quite stable. Chloronitrobenzene for example, discharged to the Mississippi at St. Louis, Mo. was still detectable in the drinking water drawn at New Orleans, Louisiana hundreds of miles and many days flow downstream.[34] Very little research has been done to determine the fate of toxic chemical substances in the pasteurization of sludge. Pasteurization has been proposed as the method for rendering sewage sludge microbiologically acceptable for increased land use. However, until recently, the possible adverse health effects from toxic chemicals which may persist in pasteurized sludge has been ignored.

Few data are available on the concentrations of synthetic organic chemicals in municipal sludges except for PCBs and chlorinated pesticides. Table 4 summarizes data obtained in the few studies available.[35] Using routine pesticide analytical procedures, all the chlorinated organics examined for were found, with levels ranging up to 352 ppm for PCBs, 1.1 ppm for the DDT family, 32.2 ppm for chlordane, 1.4 ppm for dieldrin and 16.2 ppm for aldrin. More up-to-date and extensive data on PCBs, pesticides and other persistent organics in sludge are needed.

Disposal of sludge by incineration where persistent organics and PCBs are found would result in effective destruction under optimum combustion conditions, but under conditions of poor combustion could result in emissions from the stacks of sewage sludge incinerators.

The utilization/disposal of sludge on croplands and pasturelands emphasizes the need for definitive data on plant uptake of synthetic organic chemicals. Uptake studies have shown that edible parts of plants contain these organics, but at levels 5 to 20 percent of the levels in the soils used. In general, root crops take up more chlorinated organics from the soil than other types of crops. However, studies have shown that chlordane, heptachlor and dieldrin are translocated from the soil into soybeans and stored in the oil of the seed.[36] Although the levels found were low, these data show that sludge can be a source of recycling of organic contaminants back into the food chain.

Table IV: Pesticide and PCB Content, Dry Sludges[35](ppm)

Contaminant	Range		Sludges Examined
	Min.	Max.	
Aldrin (1)	ND	16.2	5
Dieldrin(1)	0.08	1.4	7
Chlordane(1)	3.0	32.2	7
DDT + DDD(1)	0.1	1.1	7
PCBs(2)	ND	352.0	69

(1) Examined in 1971
(2) Examined in 1971, 1973, 1975
Jelinek et al., 1976 (35)

Uptake of PCBs by plants was recently reported in the document *Background to the Regulation of Polychlorinated Biphenyls (PCB) in Canada.*[37] The levels of PCB found in corn grain as a result of sludge application ranged from less than 5 ppb to 95 ppb (Aroclor 1254).

Direct contamination of growing plants above ground is also a potential problem with sludge application to croplands and pasturelands. Recent USDA work for FDA showed that dried grass contained about 5% by weight of sludge, when the grass had been mowed 80 days after it had been sprayed with the sludge. This means about 30% of the applied sludge remained on the grass. It is noteworthy that the grass in this study was grown in the East, not an arid section of the country. This work indicates a significant potential for contamination by persistent synthetic organics such as organochlorine pesticides and PCBs as a result of application of sludges containing these organics.[35]

The recent discovery (April 1976) of PCBs in a family cow's milk in Bloomington, Indiana is illustrative of the potential consequences of sewage sludge application to pasture when industrial discharges contaminate the sludge. The family cow grazed on pasture to which 12 tons per acre of city sewage sludge had been applied in November 1975. Subsequent analysis of the sludge samples from that plant showed 105 ppm and 240 ppm PBBs (Aroclor 1016 dry weight basis). The cow's milk contained 5 ppm PCBs on a fat basis [38] This is well above FDA's tolerance of 2.5 ppm PCBs in milk on a fat basis. Transfer of PCBs to the cow was probably related to grazing habits resulting in consumption of the contaminant without uptake of pasturage.

Problems may arise when sludges high in PCBs are applied to pastures that are grazed soon after the application or to forage crops before harvest. Applying sludge to hay crops after cutting may not present a problem because much of the new growth takes place at the top not from the bottom. Technology for pretreatment control of PCBs in sludge is available and can be accomplished by source control. Research now in progress through an interagency agreement with the U.S. Department of Agriculture, Agricultural Research Service, should provide more information on the fate of PCBs in soil. Feeding experiments in progress will also provide more information on the effect of ingested PCB on the potential contamination of beef tissues.

Health Implications of Municipal Wastewater and Sludge Disposal

The evidence that intestinal pathogens and parasites are transmitted by municipal wastewater irrigation indicates the possible danger for pathogens as it passes through or over the soils.[39] Cases of cysticercosis have been reported near Tucson, Arizona where cattle were grazed on pastures that had been irrigated with municipal wastewater effluent.[40]

Municipal wastewater contaminated drinking water has been proven to cause outbreaks of infectious hepatitis.[41]

Aerosols from around municipal wastewater treatment plants[42] and irrigation fields[43] containing intestinal bacteria have been found to be dispersed over distances of up to 1300 meters.[44]

Many diseases have been related to municipal waste treatment water and many insects of public health importance have been found in aquatic habitats associated with municipal wastewater irrigation.

Pasteurization or equivalent treatment of wastewater sludge and effluents appear to be the only effective method for pathogen and parasite kill. Although the process is used in European countries, R&D is needed to define temperatures for effective kill.[45] Energy consumptions appear to be minimal for the heat requirements for pasteurization. However, until such treatment becomes available in the United States a comprehensive research program is needed to assess the impact of municipal wastewater sludge and wastewater effluent utilization upon public health.

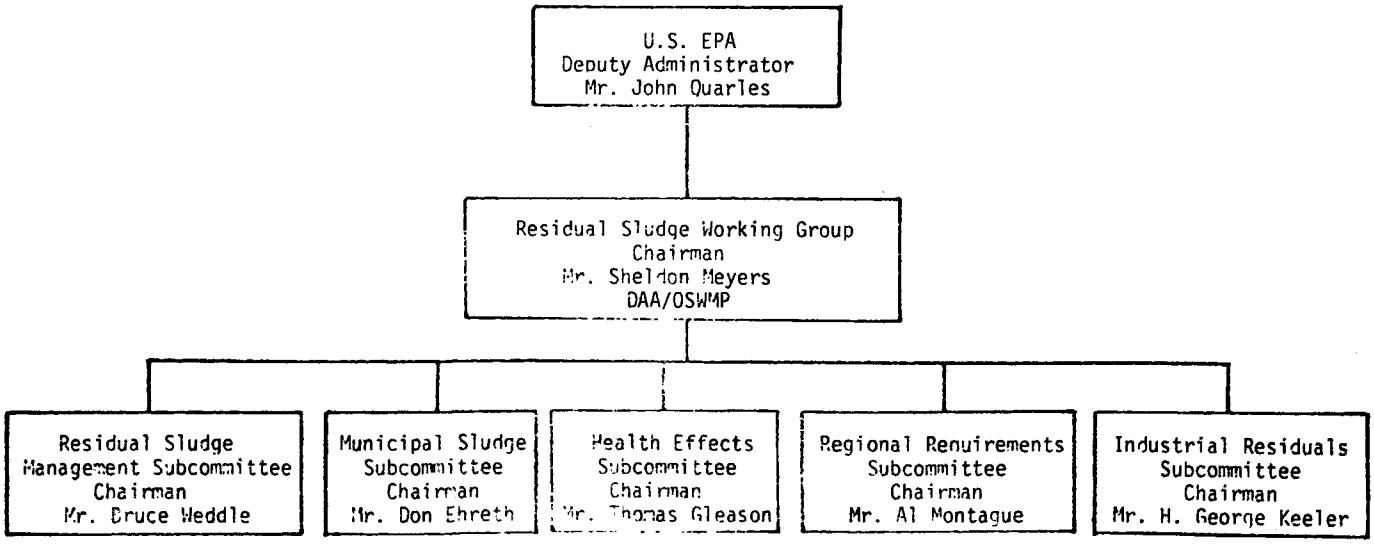
Consequences of Sewage Sludge and Wastewater Recycling to the Land

Current practices result in about 60 percent of the municipal wastewater and sludge produced being placed on or in the land, FWPCA (PL 92-500) and Agency policy require that land application be considered as a viable alternative for municipal wastewater treatment. This emphasis on use of the land places a burden on EPA, States, and local agencies and municipalities to ensure that the methods used do not result in creation of health hazards and are otherwise ecologically sound. Many of the questions raised concerning potential health problems are currently unanswerable with existing information. They can only be answered by an R&D effort which carefully coordinates the control technology, health and ecological efforts and socio-economic aspects. Stated in broad terms, the following questions need to be answered.

1. What is the fate, effect and persistence of metals, organics and micro-biologicals (pathogens, parasites, and viruses) applied to the land (aerosols, leachates) under various climatic, meteorological, and soil compositions (clay, sand, etc.)?
2. What are the potential health and ecological risks involved when municipal wastewater and/or sludge are applied to agriculture lands? Constituents of concern are trace metals, organics, micro-biologicals (pathogens, viruses, parasites) and nutrients, such as nitrogen.
3. How much municipal wastewater and sludge can be applied to agricultural land before health and ecological hazards result?
4. What is the extent and significance of ecological impact on the environment from applying municipal wastewaters and/or sludge to the land (insects, wildlife and migratory birds, grazing animals, groundwater and aquatic life, both marine and fresh)?
5. What are the environmental benefits to be gained and risks we are willing to accept by applying municipal wastewater and sludges to the land?
6. What are the long-term environmental insults to the land, man, and the ecosystem?
7. Can pretreatment of industrial discharges to municipal systems be effective in managing metal content of sludge and effluents? If so, how can the resulting industrial sludge be managed in an environmentally safe manner?
8. What is the fate, persistence and effect of aerosol transport of pathogens (bacteria, viruses, parasites) and chemicals from a municipal treatment plant under various meteorological and climatic conditions? (Includes both conventional facilities and land application.)
9. What is the scientific basis for establishment of safe buffer zones for protection to populations living near municipal wastewater treatment plants?

The Office of Solid Waste Management Programs (OSWMP) has been designated as the lead office within EPA for coordinating the development of policy, planning, and guidance in the area of the utilization and disposal of residual sludge. Sheldon Meyers, Deputy Assistant Administrator for Solid Waste Management Programs, is the Chairman of the newly-formed Residual Sludge Working Group. This working group is composed of five subcommittees (see Table 5). Each subcommittee was charged with basically the same mission.

Table V: Residual Sludge Working Group Organization



1. Define the problem(s) facing the municipalities (urban and rural), the regulatory Agency, the farming community, etc.
2. Establish what is known by EPA, USDA, FDA, and others toward resolving the problem(s).
3. Identify the gaps requiring research.
4. Develop a program plan leading to a successful solution for sludge disposal (guidelines, policy, models, etc.).

The Health Effects Subcommittee addressed the problems of heavy metals uptake by crops, parasites, viruses and the transmission of other pathogens from sludge to man. It identified the current level of R&D effort by the Agency in this area; the problems to be resolved and the policy issues that need to be addressed by the Agency. The final output of the subcommittee was a preliminary assessment of the public health problems for the Administrator; identification of what Federal involvement is needed and recommendations for guidance on municipal sludge utilization. These recommendations were reviewed by the Residual Sludge Working Group in October of this year and forwarded to the Administrator for approval.

CONCLUSION

It is obvious that a potential for producing adverse human health effects is associated with the practice of applying wastewater or sludge to agricultural lands, and that the primary areas of concern relate to potentially toxic chemicals and to pathogenic organisms. The extent of the risk relates to the many variables relating to application such as soil/sludge factors, plant factors and climatic effects, and to the treatment the wastes have received.

The uncertainties associated with the practice of applying wastewater and sludge to the land, especially for agricultural purposes, make it imperative that a continuing vigorous research program be pursued.

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Health Effects of Municipal Refuse Disposal

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A wide variety of waste from industries, residences, and municipalities has been and will continue to be disposed of on the land. Current practices range from simple dumping of refuse on a readily available piece of property to controlled disposal of waste on designated sites which are designed to minimize the potential for contamination of local water resources.

Solid waste land disposal sites (SWLDS) are sources of local water resources contamination because of the generation of leachate caused by water percolating through the solid wastes. Precipitation falling on a SWLDS either becomes runoff, returns to the atmosphere via evaporation and transpiration, or infiltrates into the SWLDS. This infiltrating water ultimately will form leachate (water that has percolated through the wastes and, through leaching, picked up soluble and suspended contaminants).

The process of leachate formation and subsequent contamination is dependent upon the amount of water which passes through the solid waste. Water which infiltrates the surface of the cover material, assuming daily and final cover are applied, will first be used for soil evaporation and plant transpiration. Any excess water will percolate into the layers of solid waste. Additional surface runoff from surrounding land, moisture contained in the solid or liquid wastes placed in the SWLDS, moisture from solid waste decomposition, water entering during waste placement in the SWLDS, and ground water entering through the bottom or sides of the SWLDS also contribute to the generation of leachate.[1]

According to the latest available estimates, 120 million tons of residential and post-consumer commercial solid wastes are disposed of on the land in the United States annually.[2] The largest component of municipal solid waste is paper, but substantial food waste, yard waste, glass, metals, plastics, rubber, and liquid wastes are also included. Pesticides containers, paint cans, batteries, various cleaning agents, dead animals, disposable diapers, grease and oils, and wastes from the health professions are among the typical potentially hazardous wastes received at municipal sites. Not included in this 120 million tons are sewage sludge, industrial chemicals and tailings, septic tank pumpings, street sweepings, discarded automobiles, construction and demolition wastes, and landclearing wastes. Many of these wastes, such as industrial chemicals, are disposed of in the SWLDS without the operator's knowledge.

As noted before, the amount of infiltration from precipitation that falls on a landfill is the major factor affecting the quantity of leachate that can be generated, unless, of course, poor site location was at fault. Therefore, the extent of the potential problem of water resources contamination resulting from leachate is greatest in areas where average annual precipitation exceeds the loss by evapotranspiration. Such areas are generally found east of the Mississippi River and in the coastal region of the Pacific Northwest. About 70 percent of the municipal SWLDS found in the United States are located in these water surplus areas. These are also areas of high industrial and residential density. Thus, the local water resources of many cities are located near areas where potential contamination due to land disposal sites might occur.

Leachate generation information has been compiled over a one-year period at five different municipal land disposal sites under an EPA study conducted by SCS Engineers (1975).[3] The principal criterion for their selection was that they received only residential and commercial wastes. It should be noted, however, that many land disposal sites do accept some industrial wastes and/or sewage sludge, and many others fail to monitor or record what they do accept. Site location, age, size, type, and annual precipitation were recorded for each study site (Table I). Site age and method of operation were the major differences between the five sites. Raw leachate was easily obtained in large quantities, which, if not collected and treated, could pose a serious threat to ground and surface waters. Organic, heavy metal, and conductivity data for undiluted, surface leachate are presented for each study site (Tables 2-6). These tables indicate the mean and the range, and compare the number of parameter values, which were above the standard, to the total number of analyses for each parameter.

Table I: Leachate Study-Site Characteristics

Site location	Age (years)	Size (acres)	Type*	Annual precipitation (inches)
Washington	2	83	SLF	57
Pennsylvania	2.5	17	SLF	41
Indiana	3.3	20	SLF	43
Tennessee	5	7	conversion+	44
California	20	52	conversion+	40

*SLF - sanitary landfill, following the definition described by the ASCE with regard to public health and safety.[3]
+Conversion - a site, which has been previously operated as a dump and now, mainly due to cosmetics (addition of cover material), has the appearance of a sanitary landfill.

From the data presented, certain factors concerning the composition of leachate are evident. First, younger sites (less than five years old) exhibit strong organic content (chemical oxygen demand) and high conductivity. As the site ages and as decomposition declines. COD and conductivity decrease. COD is an important parameter for its usefulness in determining the relative degree of solid waste decomposition, leachate treatment

technique, detection of contaminant migration, and organic contamination. Conductivity is important in determining the relative degree of solid waste decomposition and detection of contamination migration.

Table II: Washington

EPA drinking water standards primary	secondary	Parameter	Average	# of values above standard	Range
	.3	Fe	495	12/12	84-1,126
	1.0	Cu	.45	1/9	.01-1.13
.05		Pb	.15	7/7	.07-.31
.01		Cd	.007	1/5	.001-.012
.05		Cr (total)	.073	1/5	.025-.22
	-5.0	Zn	13.6	8/9	3.2-33
.002		Hg	.0034	3/5	.001-.008
.01		Se	.027	4/5	.005-.1
		COD	14,258		4,963-30,933
		conductivity	4,636		3,350-13,500

*All values in mg/l, except conductivity (micromhos/cm).

Table III: Pennsylvania

EPA drinking water standards primary	secondary	Parameter	Average	# of values above standard	Range
	3	Fe	679	10/10	18-1,550
	1.0	Cu	2	0/8	.01-.65
.05		Pb	.18	5/6	.017-.31
.01		Cd	.02	4/6	001-.073
.05		Cr (total)	.19	6/6	.09-.29
	-5.0	Zn	9.1	4/8	.53-28.2
.002		Hg	.018	5/6	.001-.061
.01		Se	.08	5/6	.01-.33
		COD	11,274		7,650-17,654
		conductivity	5,795		3,730-8,300

*All values in mg/l, except conductivity (micromhos/cm).

Table IV: Indiana

EPA drinking water standards primary	secondary	Parameter	Average	# of values above standard	Range
	3	Fe	618	10/10	208-1,237
	1.0	Cu	.43	2/7	.01-1.54
.05		Pb	.26	7/7	.2-.33
.01		Cd	.015	3/5	.006-.038
.05		Cr (total)	.11	4/5	.01-.175
-	-5.0	Zn	1 62	0/7	.88-2.25
.002		Hg	.0635	3/5	.001- 008
.01		Se	127	4/5	01-.3
		COD	12,292		10,341-16,721
		conductivity	7,148		5,875-9,300

*All values in mg/l, except conductivity (micromhos/cm)

Table V: Tennessee

EPA drinking water standards primary	secondary	Parameter	Average	# of values above standard	Range
	.3	Fe	15.2	10/10	6.5-34.5
	1.0	Cu	.25	0/8	.016-.48
.05		Pb	.16	7/8	.02-.33
.01		Cd	.008	2/5	.004-.01
.05		Cr (total)	.10	6/6	.06-.133
	-5.0	Zn	7.2	3/7	.54-27.2
.002		Hg	.036	5/6	.0006-.16
.01		Se	.116	5/5	.02-.21
		COD	2,900		845-8,669
		conductivity	8,035		6,550-10,080

*All values in mg/l, except conductivity (micromhos/cm).

Table VI: California

EPA drinking water standards primary	secondary	Parameter	Average	# of values above standard	Range
	.3	Fe	25.0	11/11	9.9-120
	1.0	Cu	.19	0/8	.004-.38
.05		Pb	1	5/7	.01-.16
.01		Cd	.008	2/6	.0013-.01
.05		Cr (total)	.034	1/6	.01-.09
	-5.0	Zn	3.7	1/8	.07-20.8
.002		Hg	.012	4/5	.001-.032
.01		Se	.06	4/5	.001-.112
		COD	168		79-420
		conductivity	2,666		2,050-6,300

*All values in mg/l, except conductivity (micromhos/cm).

The leachates contain measurable quantities of specific metals. The Environmental Protection Agency *Interim Primary Drinking Water Standards*[4] and proposed secondary standards are presented in the tables for comparison against reported values of contaminants in SWLDS leachates.

From an analysis of the data from this study, several conclusions can be drawn. First, copper is not present in concentrations in this leachate above EPA maximum contaminant levels. Second, the zinc concentration found in this leachate decreases as the age of the SWLDS increases. Third, the amount of cadmium and chromium appear to vary greatly from site to site. Fourth, iron is present at each site above secondary standards. And fifth, lead, selenium and mercury are present at each site in concentrations above EPA maximum contaminant levels, regardless of site age.

Since maximum contaminant levels are exceeded by certain heavy metals present in leachate, consideration must be given to the overall damage and the individual effect that each contaminant presents. As leachate is generated by solid waste land disposal sites, contamination of ground and surface waters may occur. This leads directly to the problem of contamination of drinking water supplies either by contamination of surface supplies or by contamination of an aquifer or well field.

When water supplies are contaminated with leachate containing heavy metals, the mechanism leading to health hazards is bioaccumulation. Many living organisms, including man, are known to accumulate specific toxicants (chemical pesticides, industrial organics, heavy metals) from the environment. This capability is widespread and the amount accumulated may

range from barely detectable concentrations to concentrations that greatly exceed the amount present in the environment, depending on the contaminant and organism involved.

Bioconcentration is considered to be accumulation at a rate which results in a concentration of contaminant greatly exceeding that to which the organism was exposed. The degree of bioconcentration can be described by a concentration factor: the ratio of the concentration of chemical recovered from the organism to the concentration to which the organism has been exposed. This concentration factor may be influenced by several factors such as (1) nature of the contaminant, (2) amount of contaminant in the water,[5] (3) duration of exposure to the contaminant,[6] (4) rates of storage and excretion of the species, (5) size and age of the organism, (6) reproductive condition of the animal,[7] (7) the organ analyzed, and (8) the manner in which the contaminant is accumulated—directly from the water or from the food chain.

It is important to note here that the health effects from SWLDS leachates are not limited to drinking water but may also occur through the food chain due to the ingestion of other organisms (fish, aquatic plants) that habitate an environment contaminated by SWLDS leachates.

Classic examples of the effect of bioconcentrated toxicants are the painful and fatal Itai-Itai disease, caused by chronic cadmium poisoning, and Minamata disease, causes by chronic mercury poisoning. In both diseases, the contaminants are concentrated by fishes from industrial wastes discharged into coastal waters. Continued consumption of the contaminated fishes by man permitted accumulation of concentrations sufficient to produce these diseases.

In relation to general water quality, the initial entry of contaminants into a body of water not only degrades it, but also may weaken or kill the biota. Persistent contaminants, which could result from long-term discharge of SWLDS leachate into a stream, may concentrate and increase over time in the biota or sediments. Some portion of the contaminant may be accumulated and concentrated in living organisms; another portion may be sorbed onto sediments from which it is accumulated by benthic organisms. Death and decay of these organisms would permit recycling and re-entry of contaminants into the water.

In addition to bioaccumulation, certain metals, such as iron, may coat the bottom sediment so that feeding on the bottom is not permitted. SWLDS leachate can thus cut off the food supply from benthic organisms.

Cd, Hg, Pb, Cr^{+6}, and Se are the metals found in SWLDS leachate which are important in the areas of toxicity and dietary essentiality (Table 7). The normal healthy adult levels for these metals vary widely (Table 8). Here, it is important to note that the effects of toxic dosages of many of the heavy metals are evident only after long periods of exposure as in the Minamata Bay mercury poisonings.

Chromium

Chromium is the seventeenth most abundant element in the earth's crust. Although chromium has oxidation states ranging from Cr^{-2} to Cr^{+6}, only the trivalent and hexavalent forms are found in nature. Chromium is found in air, soil, some food, and most biological systems, it is rarely found in natural waters. It is also recognized as an essential trace element for humans.

Trivalent chromium, at normal blood pH, exists in large, insoluble macromolecules which precipitate and become biologically inert. Hexavalent chromium, on the other hand, is irritating and corrosive to the mucous membranes, is absorbed via ingestion, through the skin, and by inhalation. Hexavalent chromium forms complexes with organic compounds which may, unlike trivalent chromium, become cumulative in human tissue.

Knowledge of the harmful human health effects of hexavalent chromium come almost entirely from the occupational area. Symptoms of excessive dietary intake of chromium in man are unknown, and marginal chromium deficiency is of greater nutritional concern than overexposure. Since lifetime tolerable levels of chromate ion are not known for man, it is recommended by the Committee on Water Quality that public water supply sources for drinking water contain no more than .05 mg/l total chromium.[8]

Table VII: Toxicity and Dietary Essentialily of Metals*

	Dietary essentiality established	Dietary essentiality suspected	Dietary essentiality unknown
Toxic only in exceptional cases	Cr^{+3} Fe		
Toxic in certain occupational cases	Zn		
Toxic at levels well below most metals		Se	Cr^{+6}
Serious cumulative body poisons			Cd, Hg, Pb

*Clark, T. P. Hydrogeology, geochemistry, and public health aspects of environmental impairment at an abandoned landfill near Austin, Texas. M.A. Thesis. university of Texas at Austin, May 1972. p.55.

Table VIII: Average Level and Primary Physiological Sites of Concentration of Metals

Metal	Average level in healthy adult human body, 154 lbs.	Primary sites of concentration
Cr^{+3}	.02-.04 ppm	cell components
Cr^{+6}	unknown	liver, kidney, respiratory problems
Fe	4-5 g	blood hemoglobin
Zn	1.4-2.3 g	kidney, liver, eyes
Se	.1-.2 ppm	liver, kidney
Hg	.05-.2 ppm	kidney, liver, lungs
Pb	.3 ppm	kidney, liver, lungs
Cd	.2-.8 ppm	liver and kidney

*Clark, Hydrogeology, geochemistry, p.56-60.

Levels of total chromium in the SWLDS study leachates ranged from .01 to .29 mg/l with a mean of .1 mg/l. Since most of the reported levels are below the recommended standard, the possibility of an adverse health effect due to total chromium from this leachate appears remote. But since lifetime tolerable levels of chromium are not known, caution should be used when a drinking water supply may be affected.

Iron

Iron is the fourth most abundant element in the earth's crust. It is an essential trace element required by both plants and animals. In some waters it may be a limiting factor for the growth of algae and other plants. Iron is vital to the oxygen transport mechanism in the blood of all vertebrate and some invertebrate animals.

Granick[9] has estimated that the normal adult man contains about 5 grams iron. Most body iron exists in complex forms bound to proteins, as in the heme compounds, hemoglobin and myoglobin. Outside of several rare excess iron storage diseases, iron toxicity in man is seldom encountered. Iron deficiency is one of the most frequently diagnosed deficiency diseases in man and usually is brought about by chronic blood loss or dietary insufficiencies.

Limitations are placed on the iron content of water mainly to prevent objectional staining of laundry, cooking utensils and porcelain fixtures such as sinks and bathtubs. Iron also imparts objectional tastes and favors the growth of bacteria. Mainly because of the effect on taste and staining, the EPA has proposed a secondary level of .3 mg/l iron.

Levels of iron in the SWLDS study leachates ranged from 6.5 to 1,550 mg/l with a mean of 366 mg/l. The reported values at each site were high enough to cause concern about staining of fixtures and laundry and giving a bad taste to the water. Data indicate that younger sites have very high values while older sites have been flushed out by infiltrating water. Because high iron values are detectable by color and taste, iron serves as an indicator of contamination from SWLDS.

Zinc

Zinc ranks as the twentieth most abundant element in the earth's crust. It is usually found in nature as the sulfide; often associated with sulfides of other metals, especially lead, copper, cadmium, and iron.

Zinc is an essential and beneficial element in human metabolism, and is relatively non-toxic to man.[10] The daily adult intake averages 0 to 15 mg. Because of undesirable aesthetic effects produced by zinc in water, an EPA standard of 5 mg/l has been proposed.

Levels of zinc in the SWLDS study leachates ranged from .07 to 33 mg/l with a mean of 7 mg/l. Since these levels are below reported levels found in drinking water supplies which caused no harmful effects, it is believed that the zinc in this leachate does not pose a health problem.[11]

Selenium

Elemental selenium is amorphous, crystalline or metallic in form and usually occurs in nature in the sulfide ores of heavy metals.

Any consideration of the toxicity of selenium to man must consider the essential dietary requirement of the element in amounts estimated to be .04 to .1 mg/kg of food. The daily intake of 1 mg selenium per kilogram of body weight may produce chronic toxicity in man. The continued ingestion of food selenium as low as .2 mg per kilogram of body weight may be harmful.[12]

The mechanisms of selenium toxicity is uncertain, and the precise ways in which selenium interferes with tissue structure function remain unclear. A water supply containing 9 mg/l produced chronic selenosis in humans. Parents showed some mild symptoms, but the children showed partial loss of hair, discoloration of finger nails, and loss of metal alertness. Upon discontinuation of the water supply, the hair and finger nails regrew and the children showed increased metal alertness.[13] Thus, EPA primary standards recommend a maximum contaminant level of .01 mg/l of selenium in drinking water supplies.

There is also evidence that selenium can pass through the food chain and accumulate in fish. Based on studies on a reservoir in Colorado that contained bottom sediments high in selenium, Barnhart reported that mortalities of fish stocked in the reservoir were caused by selenium.[14]

Levels of selenium in the SWLDS study leachates ranged from .001 to .33 mg/l with a mean of .08 mg/l. Levels greatly exceeding the standard (.01 mg/l) were found at each study site. Since these reported levels exceed the standard, concern for this toxic element should be a factor when considering a water supply well in the area of a SWLDS, especially since .07 mg/l gives rise to selenium toxicity.

Mercury

Mercury is a silver-white, mobile liquid metal at ordinary temperatures. Biologically, it is a nonessential, nonbeneficial element recognized as an element of high toxic potential. The toxic properties of mercury and its compounds have formed the basis for its widespread use for medical and agricultural purposes.

There have been clinically recognized poisonings from mercury or its compounds and, although its toxic properties are well known historically, dramatic instances of toxicosis in man and animals have occurred. Recently, the Minamata Bay poisonings is a prime example.[15] Toxic effects vary with the form of mercury and its mode of entry.

Mercury intoxication may be acute or chronic. The mercurous salts are less soluble than the mercuric salts and consequently are less toxic. For man, the fatal oral dose of mercuric salts ranges from 20 mg to 3 grams.[16] Symptoms of acute inorganic mercury poisoning include gastoenteritis and vomiting followed by symptoms of systemic poisoning and circulatory collapse. Chronic mercury poisoning results from exposure to small amounts of mercury over extended time periods. Chronic poisoning from inorganic mercurials most often has been associated with industrial exposure, whereas poisoning from the organic derivatives has been the result of accidents or environmental contamination. Alkyl compounds are the derivatives of mercury most toxic to man, producing illness, irreversible neurological damage, or death from the ingestion of only a few milligrams.[17]

Since mercury added to water is subject to biochemical change, the total mercury level should be the basis for a mercury criterion, instead of any particular form in which it may be found within a sample. Also, due to bioconcentration, mercury limits must accommodate the food chain transport path from lower organisms to man. Therefore, EPA primary standards recommend a maximum contaminant level of .002 mg/l of mercury in drinking water supplies.

Levels of mercury in the SWLDS study leachates ranged from .0006 to .16 mg/l with a mean of .027 mg/l. Mercury levels exceeding the standard (.002 mg/l) were found at each study site. Because mercury effects result from exposure over extended periods of time, harmful effects could take place if mercury in this concentration reached drinking water supplies.

Lead

Lead is a toxic metal that tends to accumulate in the bones of man and other animals. As far as is known, lead has no beneficial or desirable nutritional effects. Although seldom seen in the adult population, irreversible damage to the brain is a frequent result of lead intoxication in children. Lead intoxication most often is from eating lead-containing paint still found in older homes.

The concentration of lead required to produce symptoms of plumbism are variable, but in general are more precisely known than for other cumulative body poisons. Chronic lead poisoning symptoms are loss of appetite, weakness, lesions, neuromuscular damages, brain damage, and circulatory damage.

Like other heavy metals, lead may act as an enzyme inhibitor. There are suggestions that lead may disrupt biochemical functions such as glucose transport and detoxification mechanisms.[18] Lead appears to operate at a large number of biochemical sites, and experiments with lead distribution patterns in

higher animals have indicated similarities to the distribution observed in lower species. Lead accumulation is most noted in the liver, bones, kidneys, spleen, lungs, and hair. For these reasons, the EPA maximum contaminant level of lead permissible in drinking water is .05 mg/l.

Levels of lead in the SWLDS study leachates ranged from .017 to .33 mg/l with a mean of .17 mg/l. Reported values are higher than the standard (.05 mg/l) but are less than the estimated maximum safe level of lead intake (300 micrograms/day), assuming a daily water intake of 2 liters/day.[19]

Cadmium

Biologically, cadmium is a nonessential, nonbeneficial element which is recognized to be an element of high toxic potential.

Airborne cadmium has been reported to be a promoter of human hypertension and possibly related to cardiovascular disease. Waterborne cadmium has been related to hypertension. Despite the amount of evidence amassed showing chronic toxic effects of cadmium, the prognosis of chronic cadmium poisoning remains poor, and as yet no specific treatment of the disease is available. The fact remains that there is little if any significant improvement in persons already affected with chronic poisoning, and once taken up in the body cadmium is practically never excreted. The most significant case of cadmium poisoning was the recent outbreak of Itai-Itai disease in a small Japanese farming and fishing village.[20] The cause has been linked to cadmium uptake by major food staples which were contaminated by irrigation water from a river where cadmium wastes had been discharged.

Along with selenium and mercury, cadmium shares the place of the most stringently restricted metals in drinking water standards. The EPA maximum contaminant level for cadmium is .01 mg/l.

Levels of cadmium in the SWLDS study leachates ranged from .001 to .07 mg/l with a mean of .01 mg/l. Some reported values were above the standard (.01 mg/l), but most values are below the reported daily intake of .026 mg/day, assuming a daily water intake of 2 liters/day.[19]

CONCLUSION

The study indicates that undiluted, raw leachate contains substances that are potential threats to human health. Although raw leachate contains concentrations of heavy metals in excess of the drinking water standards, it is not clear how likely it would for these recorded levels to be found in drinking water supplies or for contamination to reach the human body. Before leachate reaches an aquifer, it is subject to the purifying affect of the unsaturated zone (attenuation or dilution). The usual odor and/or color of municipal leachate would be a significant deterrent to using water contaminated by it for human needs. Further study of the environmental affects of leachate are being undertaken by the EPA.

It is clear that if solid waste is placed directly into ground water, or if leachate is allowed to drain directly into surface water, it can cause severe damage. It can destroy life in a water resource by coating the bottom sediment so that feeding by the animal population is precluded—iron is a prime example. Toxic metals can build up in the aquatic life and destroy their use by man—selenium and mercury are examples. Therefore leachate generated by improperly located and managed solid waste disposal sites can destroy drinking water resources making it necessary to locate new sources, at considerable cost.

Finally, in evaluating the data from this study, it should be kept in mind that data were obtained from the monitoring of five municipal solid waste disposal sites that received only municipal and commercial wastes. Many SWLDS never question or document types of incoming waste. Many sites accept some type of hazardous waste (inorganic and organic chemicals, electroplating sludges, petroleum wastes, pharmaceuticals, etc.) and/or municipal sewage sludges, which tend to be high in organics and heavy metals. This study can only report values that have been observed in strictly municipal SWLDS. The monitoring of SWLDS which accept hazardous wastes and/or sewage sludge is presently being undertaken by EPA.

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