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Assessing the Water Pollution Potential of Manufactured Products

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ASSESSING THE WATER POLLUTION POTENTIAL OF MANUFACTURED PRODUCTS

by

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ABSTRACT

A Catalog has been compiled of manufactured products which may, during their normal use or disposal, result in water pollution. The Catalog is in three sections, and the products are grouped in accordance with the Standard Industrial Classification (SIC).

Section I summarizes the pollution potential of each listed product group. Section II provides data on typical chemical compositions for each product group and indicates the types of water-pollutional effects associated with each chemical ingredient. Section III inverts Section II by providing an alphabetical listing of chemicals and the SIC codes in which they occur.

Along with the Catalog, a simple model has been developed to estimate rates of pollutant entry into the waterways via various routes, such as direct discharge, runoff following rainfall, leaching from dumps, discharge to the air and subsequent raindown. A guide including examples is provided on how to use the Catalog and associated models to assess potential water pollution problems arising from finished products in common use.

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SECTION I

CONCLUSIONS

1. Many consumer products, during their normal uses, ultimately reach our Nation's streams, lakes, estuaries, and groundwaters and may have a deleterious effect on water quality. These products, their chemical formulations, and the potential types of associated water pollution, have been cataloged.

2. Multiple pathways exist by which a given product may enter the water. A conceptual framework for evaluating the importance of each of these paths is necessary for the assessment of potential water pollution problems.

3. A simple mathematical model was developed to predict rates of discharge of potential pollutants into the environment from the time of entry into the use stream to the time of ultimate decay.

4. Important data are lacking with respect to product lifetime, amount of product in use, water pollutional effects associated with the chemicals used to formulate manufactured products, and indirect modes of entry of products into the water from dumps, by runoff following rainfall, and through leaching.

SECTION II

RECOMMENDATIONS

1. The Catalog and the associated model should be expanded and computerized to permit accessing of data in many different forms, as appropriate to particular problems, and to facilitate incorporation of new and updated information.

2. The simple two-reservoir model for predicting rates of discharge of potential pollutants should be extended to take into account multiple reservoirs or pathways to the water and changing levels of production rates.

3. Research should be carried out to refine the data base. More precise estimates of product lifetimes may be obtained from literature search and personal interviews. Decay times for products disposed of in dumps or volatilized and washed down by rain may require field experiments. Pathways by which products enter the water should be defined with reference to the entire ecological cycle.

4. The utility of the Catalog and associated models should be tested on a number of specific examples in order to provide a basis for future modification.

SECTION III

INTRODUCTION

One of the characteristics of our advanced technology is the proliferation of consumer products. New products for a multitude of uses are made available to the public every year. Many of these materials, during their normal uses, are discharged to sewers; others are removed from urban and rural land areas by runoff following rainfall; and some migrate to groundwaters by deep soil percolation. These materials may also be disposed of, either deliberately or accidentally, by dumping in sewers or on the land. Regardless of the route followed, many consumer products ultimately reach our Nation's streams, lakes, estuaries, and groundwaters.

The impact on water quality of such a vast array of manufactured products discharged to our Nation's waters is not known in any detail. It is possible that some commonly used products have a deleterious effect on receiving waters, which is not presently known or recognized. It is further possible that harmful effects result from decomposition products or secondary products created by synergism during their normal uses. As a means of identifying such products, a Catalog has been prepared of manufactured products that have water pollution potential, and which may be discharged to streams, lakes, estuaries, and groundwaters.

NEED FOR THE CATALOG

Extensive water pollution is, in part, a result of the proliferation of products containing synthetic organic and inorganic compounds. Many of these compounds and products are toxic or have an adverse effect on ecological life cycles.

To understand the potential magnitude of the water pollution problem posed by the proliferation of consumer products, one needs only to look at the growth in production of two categories of products. Pesticides and surface-active agents--primarily detergents--have shown growth rates far out of proportion to population growth over the past 20 years. The widespread adoption of home laundry units and dishwashers has resulted in an increase in the usage of detergents far beyond that attributed only to the increase in population. Practically all of this detergent load is discharged through our sewers and into our waterways.

Pesticides and surface-active agents are not alone in their increased use. In the past twenty years, the production of synthetic organic chemicals in this country has increased eightfold, to over 120,000 million pounds. Tracing the distribution and end use pattern of these chemicals is enormously complicated. The Catalog represents a first step towards identifying specific manufactured product classes which are or may become potential sources of water pollution.

It is well-recognized that a variety of organic and inorganic materials can cause water pollution, and the results of the discharge of such materials into the water system have been documented in many cases. Water quality criteria may be derived with respect to physical properties (color, odor, temperature, turbidity, etc.); inorganic contaminants (heavy metals, ammonia, fluorides, cyanides, nitrates, nitrites, sulfates); organic contaminants (pesticides, herbicides, oils and greases, phenols, detergents, etc.); chemical properties (pH, hardness, dissolved oxygen, etc.); microorganisms, etc. Corresponding analytical techniques for assessing compliance with the criteria may also be established. Control of pollutant levels, however, requires that potential contaminants be identified at the source. In the case of waste-effluent streams from industrial manufacturing processes such identification is relatively straightforward. In the case of manufactured products, the problem is more complicated. While some analysis of sewage and landfill effluent has been done, there is very little data on the particular products responsible for the various chemical components identified in the effluent streams. Detergents, pesticides, herbicides, and fertilizers, whether discharged to sewers, removed from land areas by runoff, or carried to groundwaters by deep soil percolation, are known product sources of pollutants of various kinds. However, there may be other such product classes for which a deleterious effect on receiving waters has not yet been recognized, or for which a deleterious effect would only be expected if current consumption patterns increase. The Catalog has been compiled to aid in identifying such product classes and to provide a framework for predicting the potential magnitude of possible pollution problems. The Catalog has been organized both by product and by chemical ingredient.

Certain potentially harmful ingredients are used only in very low concentrations in any given product, but are used in a very large number of products. The net cumulative discharge of such ingredients from a variety of products can therefore be significant, although disposal of a single product type may create few problems.

SCOPE OF THE CATALOG

Product Selection.

The Catalog provides an index to finished products to be used for ultimate consumption, which may, during their use or disposal, result in water pollution. The Catalog includes all products which enter the water, either directly or indirectly, in short times or long.

The products have been grouped in conformance with the Standard Industrial Classification (SIC), prepared by the Office of Statistical Standards of the Office of Management and Budget. The SIC, which is based on industries rather than on manufactured products, is not ideal for the purposes of the Catalog. It is so well-known and widely used, however, that there are definite advantages to adapting it to manufactured products. In doing so, each industrial SIC code number is associated with products produced by that industry. The SIC is a hierarchical classification system, in which industries are coded by a number of digits, ranging from two to seven, depending upon the level of detail required for any particular application. For use in classifying products, the SIC cannot be employed in a consistent manner, since the digital breakdown required to identify recognizably distinct classes of finished products varies considerably from one major (two-digit) group to another. Thus, Major Group 21, Tobacco Manufacturers, includes three manufactured product classes, each identified by a four-digit code number - cigarettes (2111), cigars (2121), and chewing tobacco (2131). Within the context of the catalog, no further digital breakdown is required. On the other hand, Major Group 28 encompasses 35 four-digit categories; and each of the four-digit categories covers a very wide variety of products. Thus, speciality cleaning, polishing, and sanitation preparations (2842) include household ammonia, household bleaches, cleaning fluids, floor waxes, furniture polish, disinfectants, ink eradicators, rust removers, shoe polish, and at least thirty other products which are identified by seven-digit numbers in the classification scheme. In preparing the Catalog, therefore, the 4, 5, 6 or 7 digit codes were used as required to identify distinct product classes, characterizable by a small number of typical product compositions.

In using the SIC system for product classification, one also runs into the problem of duplicate counting. Thus, leather dyes and stains, one of the products in Industry No. 2865, are listed separately from leather products. It is thus difficult to separate the amount of leather dye which enters the water supply from home and shop applications, and that which is leached into the water supply from leather products during use and disposal. The same problem arises with respect to synthetic dyes used in household dying and dyes which are gradually released from colored textile products. Similarly, processed food products, such as canned or frozen goods, are considered as a unit, including both the food and the packaging material in the SIC system, while the packaging materials per se are also listed in a separate category.

Water Pollution Potential Evaluation.

Water pollution is not easy to define. Operationally, a manufactured product must be viewed as a potential water pollutant if, during normal use or disposal, it is discharged to sewers or washed into surface waters or groundwaters, and thereby contributes to excessive concentrations of substances, which:(1)

1. Demand large amounts of oxygen for their decomposition;

2. Give rise to infectious diseases;

3. Promote the growth of algae and water weeds;

4. Are acutely or chronically toxic to plants, wildlife, domestic animals or humans;

5. Interfere with natural stream purification;

6. Cause the water to become hard;

7. Make the water corrosive;

8. Give rise to sediments or increased solids;

9. Render the water supply unaesthetic with respect to color, turbidity, odor or general appearance; and

10. Overburden water treatment facilities.

For each of the manufactured product groups in the Catalog, chemical compositions are given wherever possible. Prediction of the water pollution potential associated with the use and disposal or products containing the various chemical substances, however, presents a number of practical difficulties. The water-pollutional effects of any substance depend not only on its chemical composition, but also on its concentration and rate of entry into the water. Furthermore, even in cases where concentrations or rates of discharge are known or can be predicted, there is often no straightforward correlation with potential water pollution problems.

One of the important factors which is difficult to predict is biological concentration of chemicals which become incorporated in simple or complex food chains. A well-documented example of such concentration occurs with DDT. From water containing 0.000005 ppm DDT, fish are found to contain 2 ppm DDT and carnivorous birds 10 ppm DDT. This concentration process has been explained by the near insolubility of DDT in water and its high solubility in lipids and other organic materials found in plants and animals. Heavy metals, which constitute a serious form of pollution because of their stability, are also known to be concentrated by marine organisms. It is not easy to predict, however, what other substances might behave similarly, and what kinds of deleterious effects might be expected.

Another important factor concerns the transformation of chemical components as they enter into the ecological cycle. The mercury problem is one example. Most mercury discharges into our waters are in the form of metallic mercury, divalent mercury, phenyl-mercury, and alkoxy-alkylmercury, all compounds of recognized toxicity. These compounds, however, can be biologically converted to methylmercury, a compound of even higher toxicity. Water pollution problems can develop very slowly by accumulation of dangerous chemicals over many years in the aquatic environment, particularly in bottom deposits. Toxic levels may persist for many years because natural processes that degrade or dissipate toxic chemicals are very slow. This seems to be presently the case with materials such as mercury and chlorinated hydrocarbons.

In preparing the Catalog, cognizance has been taken of the fact that certain types of compounds, which are components of many manufactured products, are recognized contributors to the water pollution problem. These include: phosphates; nitrates; chlorinated hydrocarbons; heavy metals, surfactants; ammonia and amino derivatives; sulfides; cyanides; fluorides; strong bases such as sodium hydroxide, potassium hydroxide and sodium carbonate; and phthalate esters. For most of these compounds, however, the effects are complicated and generally closely tied into the entire ecosystem. Other dangerous chemicals or chemical classes may well be identified in the future. The Catalog can be used as a basis for predicting the prevalence of such chemicals in the waste stream. It can also serve as a guide to future research on potential pollutants.

SECTION IV

CATALOG ORGANIZATION

The Catalog format was designed around the following considerations:

1. It is highly desirable to identify products having water pollution potential at as early a stage as possible in order that appropriate control measures may be initiated.

2. To aid in planning it is important that chemical and other information related to specific manufactured products within each SIC code be readily available.

3. It should be possible to identify cases where potential chemical pollutants appear in small quantities in the formulation of a large number of manufactured products.

4. The categorization of products by four-, five-, six-, and seven-digit SIC numbers must vary somewhat randomly throughout the Catalog in order to achieve adequate detail. Thus, for cigarettes (2111), the four-digit code is sufficient; for hair dyes, which fall into the 2844 category (Perfumes, Cosmetics and Other Toilet Preparations), a seven-digit code will be needed to identify the specific product group.

Given these considerations, the Catalog has been organized in three sections:

SECTION I - SUMMARY

Section I will provide an overview of the pollution potential associated with all manufactured products which, in normal use, are discharged into the Nation's waterways. A sample page is shown in Figure 1. Products are listed by SIC number and name. Usual product uses have been designated by means of the two-digit code shown in Figure 2. This code also helps to categorize products with respect to the pathways followed to the water.

Space is provided for specifying the various rate parameters associated with the model described below. The purpose of the model is to provide estimates of the rates of discharge of manufactured product components or their degradation products into the Nation's waterways. The rates, and the related concentration build-up, are vital to the assessment of the probable magnitude of potential water-pollutional effects. The production rate estimates (R) are derived from the census of manufacturers. An attempt has been made to reduce all production figures to a common base (millions of pounds). However, certain products do not yield to such reduction and are given in other units, e.g., millions of board feet, millions of cars, paint brushes, etc. When (R) has been inferred from

FIGURE 1

SIC NUMBER	NAME	USUAL PRODUCT USES
2841653	Scouring cleansers with no abrasives	7.1
2842	Specialty Cleaning Polishing & Sanit. Preps except Soaps, etc.	7.1
28421	Insecticides	7.1
2842135	Repellent & Attractants (for insects, birds, and other animals)	7.1
2842171	Redenticides	7.1
28423	Specialty Cleaning & Sanitation Products	7.1
2842311	Glass Window Cleaning Preps.	7.1
2842321	Oven Cleaners	7.1
2842331	Toilet Bowl Cleaner & Drain Pipe Solvents	7.1
2842332	Disinfectants for use other than Agricultural	7.1
2842341	Wallpaper, Window Shade & Wallcleaner	7.1
2842351	Rug & Upholstery Cleaners, Consumer	7.1
2842371	Household Ammonia	7.1
2842394	Fabric Softener	7.1
2842395	Laundry Starch Aerosol	7.1
2842396	Laundry Starch, Other Liquid	7.1
2842397	Laundry Starch, Dry	7.1

ANNUAL PRODUCTION RATE (MIL lbs) (R)	PRODUCT LIFETIME (YRS) (L)	$Q_1 = (R)(L)$	k_1L	$k_{12}L$	α_1L	TOXICITY*	OXYGEN DEMAND	SOLIDS	COLOR	ODOR	EUTROPHICATION	OILS AND TARS	HARDNESS	SIC NUMBER
			95	5	0									2841653
			95	5	0									2842
			45	45	10									28421
	.5		45	45	10	X	X	X	X	X				2842135
	2		45	45	10									2842171
						X	X	X	X	X	X	X	X	28423
			25	50	25	X	X	X	X	X	X			2842311
	1		45	10	45	X	X	X	X	X		X		2842321
	1		98	2		X	X	X	X	X	X	X		2842331
	1		85	5	10	X	X	X	X	X	X	X		2842332
						X	X	X	X	X	X	X		2842341
						X	X	X	X	X	X	X		2842351
			95	5	0									2842371
			95	5	0	X	X	O	X					2842394
			95	5	0	X	X	X	X	X				2842395
						X	X	X	X	X	X	X		2842396
														2842397

blank - toxicity data for some or all the constituents of this product are not available

* x - some or all the constituents of this product are known to be toxic under certain circumstances

o - none of the constituents of this product are known to be toxic

FIGURE 2. USUAL PRODUCT USES

Use Category		
9 Personal	9.1	Cleansing
	9.2	Cosmetics
	9.3	Clothes
8 Agricultural	8.1	Chemicals
	8.2	Machinery
7 Housekeeping	7.1	Cleaning
	7.2	Food storage and preparation
	7.3	Maintenance
6 Ingested	6.1	Human
	6.2	Livestock
	6.3	Medicines
5 Transportation	5.1	Personal
	5.2	Mass
	5.3	Special Purpose
4 Construction	4.1	Exposed
	4.2	Indirectly exposed
3 Professional	3.1	Exposed
	3.2	Indirectly exposed
2 Recreation	2.1	Exposed
	2.2	Indirectly exposed
1 Production	1.1	Exposed during use
	1.2	Not exposed during use

other figures, or is given in units other than millions of pounds, an asterisk is used.

There are no readily accessible tabulations of the product lifetime (L); and, in fact, the definition, for purposes of the Catalog does not correspond with the normal concepts used in industry. For example, "product lifetime" is thought of by some sectors of industry as that period of time during which it is profitable to continue producing the particular product. For example, "Kelloggs' Pep" had a "product lifetime" of a decade or two by the industrial concept. For the purposes of the Catalog, however, the average lifetime (L) of Pep would be a matter of months and would incorporate the time between completion of the manufacturing and packaging (i.e., the registering as part of the annual production, R, and the time the cereal was totally consumed. Part of L, then, is made up of warehouse and home-storage time, as well as the time during which the product is actually used.

Due in part to our definition of L and in part to the lack of any systematic tabulation of quantities even qualitatively related to L, we have had to estimate these quantities on the basis of our own knowledge of the products.

Q_1, which is simply the product of R and L, represents the amount of each product in use at any particular time.

The columns headed k_1L, $k_{12}L$, and α_1L represent respectively the percentages of each product which (1) enter the water directly (k_1L); (2) are transferred to secondary reservoirs where they may be indirectly transferred to the water by leaching or carried down by rainfall ($k_{12}L$); and (3) degrade during use or otherwise become chemically transformed. These percentages are not known accurately but can be estimated in most cases to better than an order of magnitude.

The final columns of Section I give a rough indication of the types of water-pollutional effects that might be associated with the use and disposal of each product. Qualitative ratings are provided where available on potential water pollution problems that might result from ingredients of the product which are toxic, have high oxygen demand, lead to increased solids loading, are colored, have an objectionable odor, lead to eutrophication, are oily or tarry, or tend to increase water hardness.

Toxicity is particularly difficult to define since many types of acute and chronic effects on plant life, fish, wildlife, as well as humans are possible and may be significant from the point of view of water quality.

The wide diversity of materials which enters into the manufacture of almost every modern product today offers many sources of potential water pollution. In the first place, the definitions of "water pollution" are not unique and lead to the possibility that any one material or product may contribute on more than one basis. For example, dyes may have toxic properties as well as causing unnatural colors in the water. A particular product may contain dye, contribute to suspended solids, and change the pH of the water all at the same time. In addition, there may be subtle, as yet unrecognized, ways in which a product causes water pollution.

SECTION II - PRODUCT LISTING

In Section II, more detailed information is provided with respect to the pollution potential associated with each of the manufactured products tabulated in Section I. A sample page is shown in Figure 3. Each product category is identified by a heading which gives SIC number and name. One or more typical chemical compositions and weight percentage range are provided, and each ingredient in the formulation is rated for water pollution potential. If any chemical ingredient is a potential water pollutant (denoted by an X in any column), then an X also appears in the corresponding column of Section I.

SECTION III - CHEMICAL COMPOUND LISTING

Section III is, in a sense, an inversion of Section II. A sample page is shown in Figure 4. The ingredients or chemical compounds used in formulating the manufactured products under consideration are listed alphabetically in the first column. The product classes in which such ingredients are found are identified by SIC number in column 2. Column 3 groups each of the ingredients into one of the general chemical classes listed in Table I. The grouping by chemical class is somewhat arbitrary, with the underlying principle that of concern for water pollution. Thus, mercuric acetate is a metal salt, while sodium acetate is a fatty acid derivative. In cases of ambiguity, where a compound may properly be assigned to two classes, both are listed. The reason for providing a general chemical classification is that data are frequently not available for a specific chemical compound, but members of a generic class may tend to exhibit similar water-pollutional effects. Notes on properties that may effect chemical potential are provided in the fourth column of Section III. When TOX or BOD appear under NOTES, additional data related to toxicity and biological oxygen demand, respectively, are given by chemical class in Appendices A and B of Section III.

3942 053	STUFFED TOY ANIMALS										
TYPICAL CHEMICAL COMPOSITION	%	REF.	TOXICITY	OXYGEN DEMAND	SOLIDS	COLOR	ODOR	EUTROPHICATION	OILS AND TARS	HARDNESS	REF.
"Dream Pets"		Cons Rptz. 3/72									
Mixed Sawdust from Evergreens											
Spruce, Fir, Pine, Sugi	all cause derma-titis & allergic reac-tions										
Cotton Fabric (See SIC 2261)					X						CCD
Dye (See SIC 2261)	suspect			X		X					CCD Heukelekian

x - may be an effect
o - no effect
blank - no information

FIGURE 3

COMPOUND	PRODUCT SIC	CHEMICAL CLASS	NOTES	REFERENCE
Abrasives	2841 175 2842 3 2842 498 3941		Examples: Boron Carbide Boron Nitride Corandum Diamond Garnet Tripoli Silicon Carbide	CCD
Acacia (See: Gum Arabic)				
Acetal copolymers	1925 2519 2591 3079 3079 65 3652 3941	Condensation polymers		
Acetic acid CH_3 COOH	2111 2279 2842 332 2842 398 2842 442 2844 351 2844 519 2891 1 2899 3 3861 811 3941	Aliphatic acid	Clear, colorless, acid liquid Very pungent odor Miscible with water Causes severe burns Oxygen demand	CCD CCD CCD CCD Heukelekian

FIGURE 4

TABLE I. CLASSES OF CHEMICAL COMPOUNDS

1. Mineral acids
2. Aliphatic (fatty) acids
3. Aromatic (benzene) acids
4. Rosin acids
5. Alcohols
6. Aliphatic hydrocarbons (petroleum derivatives)
7. Aromatic hydrocarbons (benzene derivatives)
8. Sulfonated hydrocarbons
9. Halogenated hydrocarbons (mostly chlorinated hydrocarbons) (the aliphatic are not persistent; the aromatic are)
10. Alkaloids
11. Ammonia, aliphatic amines and their salts
12. Anilines (any compound having nitrogen attached to a benzene-ring)
13. Pyridines (all sorts of nitrogeneous hetercycles)
14. Phenols
15. Aldehydes
16. Ketones
17. Fluorine compounds
18. Organic sulfur compounds (sulfides, mercaptans)
19. Organometallic compounds (do not degrade easily)
20. Chlorine and hypodilontes
21. Cyanides - because of unusual toxicity
22. Thiocyanates - because of toxicity
23. Synthetic coloring matters
24. Sterols
25. Sugars and cellulose
26. Addition polymers - (do not degrade, since have hydrocarbon or ether backbones)
27. Condensation polymers - degrade, since are polyamides, polyesters
28. Inorganic bases (excepting ammonia)
29. Metals, metal acids and metal salts - only when metal is known to be toxic.

SECTION V

MODEL FOR ESTIMATING RATES OF DISCHARGE OF POTENTIAL POLLUTANTS

In order to provide a realistic basis for a quantitative estimation of the amount of material which enters the water during the normal use and disposition of specific products, we developed a simple model which takes into account rates at which products enter the water via different paths.

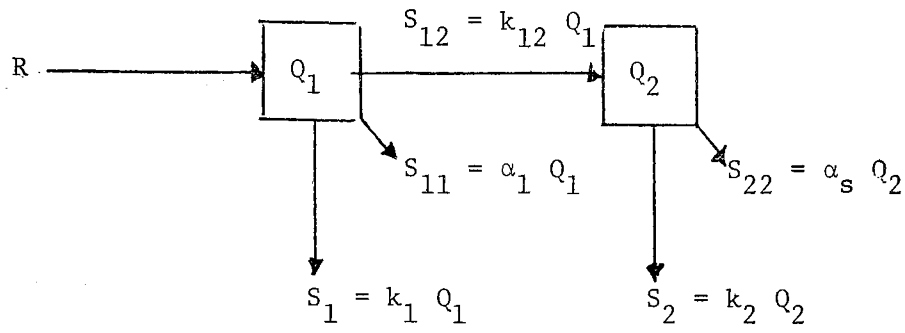
It is only recently that much concern has been placed on determining the ultimate fate of any particular set of manufactured products. Because this is true, statistics which would allow one to evaluate a product for its pollution potential are not generally available. The types of figures one can obtain relate to annual production rates, and the amounts and types of various raw materials used in the production. The production rate represents the maximum rate at which the particular industrial segment could possibly be polluting the waters with manufactured products and their byproducts. However there are many industries which have extremely large annual production figures whose products probably contribute relatively little to pollution problems because of the way the products are used, or decay, before entering the water. Extremely large quantities of gasoline, for example, are produced each year. However, most of it is burned before having access to water; and thus the large annual production figures do not give a direct, and accurate, assessment of gasoline's pollution potential.

In order to evaluate the pollution potential of such products, it is necessary to have a conceptual framework into which apparently diverse kinds of information can be placed for inspection. The model we have developed serves this purpose.

The model is based on two reservoirs, and six rate parameters as indicated in Figure 5. Manufactured products are generated at a rate of R lbs/yr. At any given time, Q_1 pounds of product will be in use in the consumer product market or primary reservoir. As the product is consumed, it may leave the primary reservoir by a variety of routes, three of which are considered in this simple model. The product, or a portion of it, may be discharged to the water directly through sewers or by runoff following rainfall at a rate S_1 lbs/yr. Some or all of the product may degrade during use at a rate S_{11} lbs/yr. A third fraction of the product may be transferred at a rate S_{12} lbs/yr to a secondary reservoir, which might be a dump or the air or a solid surface, from which further discharge or degradation may occur. The amount of product stored in the secondary reservoir at any time is Q_2 lbs, of which S_2 lbs/yr leave the reservoir and enter the water directly; and S_{22} lbs/yr are degraded to another form in the reservoir.

The two-reservoir model is clearly an oversimplification. The amount, Q_2, may, in fact, be the sum of quantities stored in a number of secondary and tertiary reservoirs, the "decay periods" of which vary a great deal. For

FIGURE 5. TWO-RESERVOIR MODEL OF POTENTIAL WATER-POLLUTIONAL PATHWAY



R : Annual production rates (lbs/yr)

Q_1 : Amount of product in use at a particular time (lbs)

S_1 : Rate at which the product enters the water directly (lbs/yr)

S_{11}: Rate at which the product degrades while in use (lbs/yr)

S_{12}: Rate at which the product is transferred to the secondary reservoir (dump, volatilized to be leached by rain, etc.) (lbs/yr)

Q_2 : Amount of product stored in secondary reservoirs (lbs)

S_2 : Rate at which the product enters the water from secondary reservoir (lbs/yr)

S_{22}: Rate at which the product degrades in the secondary reservoir (lbs/yr) example, a portion of the products which make up solid waste may be disposed of in a dump, while another portion may be disposed of through incineration. The incinerated portion may liberate undesirable by-products which are washed down by rainfall in a relatively short "decay period" while that portion residing in dumps is subject to leaching over a much longer period. The model can readily be extended to cover specific cases in more detail; but even in the simple form presented here, useful predictions can be made.

As indicated above, some products in their normal use are disposed of directly into the water. The model assumes that the rate of such disposal is proportional to the amount in use at any time, i.e., the amount in the first reservoir. Some products, such as gasoline, are changed chemically during their use into non-polluting substances. It is assumed that the rate at which this change is made also is proportional to the amount of product in the first reservoir. Some of almost every product is not used but winds up in a dump or other kind of intermediate storage (the second reservoir). The rate of transfer from one reservoir to the next is also assumed to be proportional to the amount of product in the first reservoir. We may thus define further the rates (S) at which the product leaves the reservoirs by the various routes as follows:

$$S_1 = k_1 Q_1 \qquad S_2 = k_2 Q_2 \tag{1}$$

$$S_{12} = k_{12} Q_1 \qquad S_{22} = \alpha_2 Q_2$$

$$S_{11} = \alpha_1 Q_1$$

where the k's and α's are fractional proportionality constants with dimensions of years^{-1}.

The rates of change with time of the quantities Q_1 and Q_2 in each reservoir are given by the difference between the rate at which product enters each reservoir and the rate of loss of product from the reservoir as follows:

$$\frac{dQ_1}{dt} + (k_1 + k_{12} + \alpha_1)\, Q_1 = R \tag{2}$$

$$\frac{dQ_2}{dt} + (k_2 + \alpha_2)\, Q_2 = k_{12}\, Q_1 \tag{3}$$

The quantity $1/(\alpha_1 + k_1 + k_{12})$, which has dimensions of years may be interpreted physically as the average lifetime, L, of a product in the primary reservoir or the average time between manufacture of a product and its discharge from the primary reservoir. Similarly, $1/(\alpha_2 + k_2)$ represents the average decay time, D, for products in the secondary reservoir. In terms of D and L, the solutions to Equations (2) and (3) are:

$$Q_1 = RL\ [1 - \varepsilon^{-t/L}] \tag{4}$$

$$Q_2 = k_{12}\ RLD \left[1 + \frac{D\ \varepsilon^{-t/D}}{L - D} - \frac{L\ \varepsilon^{-t/L}}{L - D} \right] \tag{5}$$

Under steady-state conditions ($t \to \infty$ or $\frac{dQ_1}{dt} = \frac{dQ_2}{dt} = 0$), Q_1 and Q_2 assume limiting values given by:

$$Q_{1,\ lim} = RL \tag{6}$$

$$Q_{2,\ lim} = k_{12}\ D\ Q_{1,\ lim} \tag{7}$$

The limiting values of Q_1 and Q_2 from Equations (6) and (7) may be substituted into the set of Equations (1) to obtain the limiting values of S, the rates of discharge and/or degradation from the two reservoirs.

It may be noted that the total output from the primary reservoir in lbs/yr is given by the sum $(S_1 + S_{11} + S_{12}) = (k_1 + \alpha_1 + k_{12})\ Q_1$. Hence, the fractions of product lost from the primary reservoir via each of the three routes considered are, respectively, k_1L, α_1L, and $k_{12}L$. Estimates of these quantities are provided in Section I of the Catalog. It should be pointed out the percentage error in S_1, the rate of discharge of product directly into the water, will be approximately the same as the percentage error involved in estimating product lifetime, L.

Convenient forms for calculating rates of discharge based on the model are provided in Section VI.

SECTION VI

HOW TO USE THE CATALOG

The Catalog was designed with the following major uses in mind:

1. Identification of manufactured products, which, during normal use and disposal, may contribute to water pollution.

2. Identification of the potentially deleterious chemical ingredients used in the formulation of such products.

3. Alternatively, determination of the manufactured products which typically contain specific recognized or suspected polluting substances.

4. Semi-quantitative estimation of the rate of discharge of products or pollutants into the water and the resultant concentration levels.

Several specific ways in which the Catalog might be used are presented below. Other applications may be expected to develop with increased familiarity.

Section I of the Catalog serves as a summary in which each product group is listed in tabular form according to the SIC code of the corresponding manufacturing industry. Specific ingredients or compounds which cause the pollution are not indicated. This section serves only to draw one's attention to various SIC codes which may, for one reason or another, appear to require more detailed investigation. More explicit data may then be obtained by referring to Section II of the Catalog.

If, for example, a product is suspect, or under investigation for associated water pollution potential, one wants to determine which ingredients of the product are responsible for polluting effects. Section II of the Catalog fills this need by listing typical chemical compositions of products contained in the various SIC codes. There are numerous formulations (many of them proprietary) for most of the products listed in the Catalog. No attempt is made to list all formulations for which data are available. A subjective selection of known formulations was made to be included in the "typical chemical composition" list. In addition to noting the "typical" percentage of each component, the polluting characteristics of each are noted in the same manner as in Section I of the Catalog. References are given for both the "typical composition" and the pollution characteristics data.

Once a particular substance has been identified as a potentially important pollutant, it is often of interest to determine its ubiquity, or the number of products in which it occurs. Section III of the Catalog, which is an inversion of Section II, allows this to be done. Here, the chemicals are listed alphabetically; and the products in which they typically occur are listed by SIC code. It is thus possible to identify each of the product classes which contain, for example, fluorides, various halogenated hydrocarbons, various heavy metals, given toxic or hazardous substances, suspected biorefractories, etc.

The product and chemical formulation information which may be obtained from Sections II and III of the Catalog by direct inspection, can be useful in itself. However, before a very meaningful assessment of pollution potential can be rendered, a more detailed understanding of the routes followed by the pollutant products on their way to the water, and the relative rates at which they are transported is necessary. During the Catalog's development, a simple model evolved which provides a framework for estimating some of these factors.

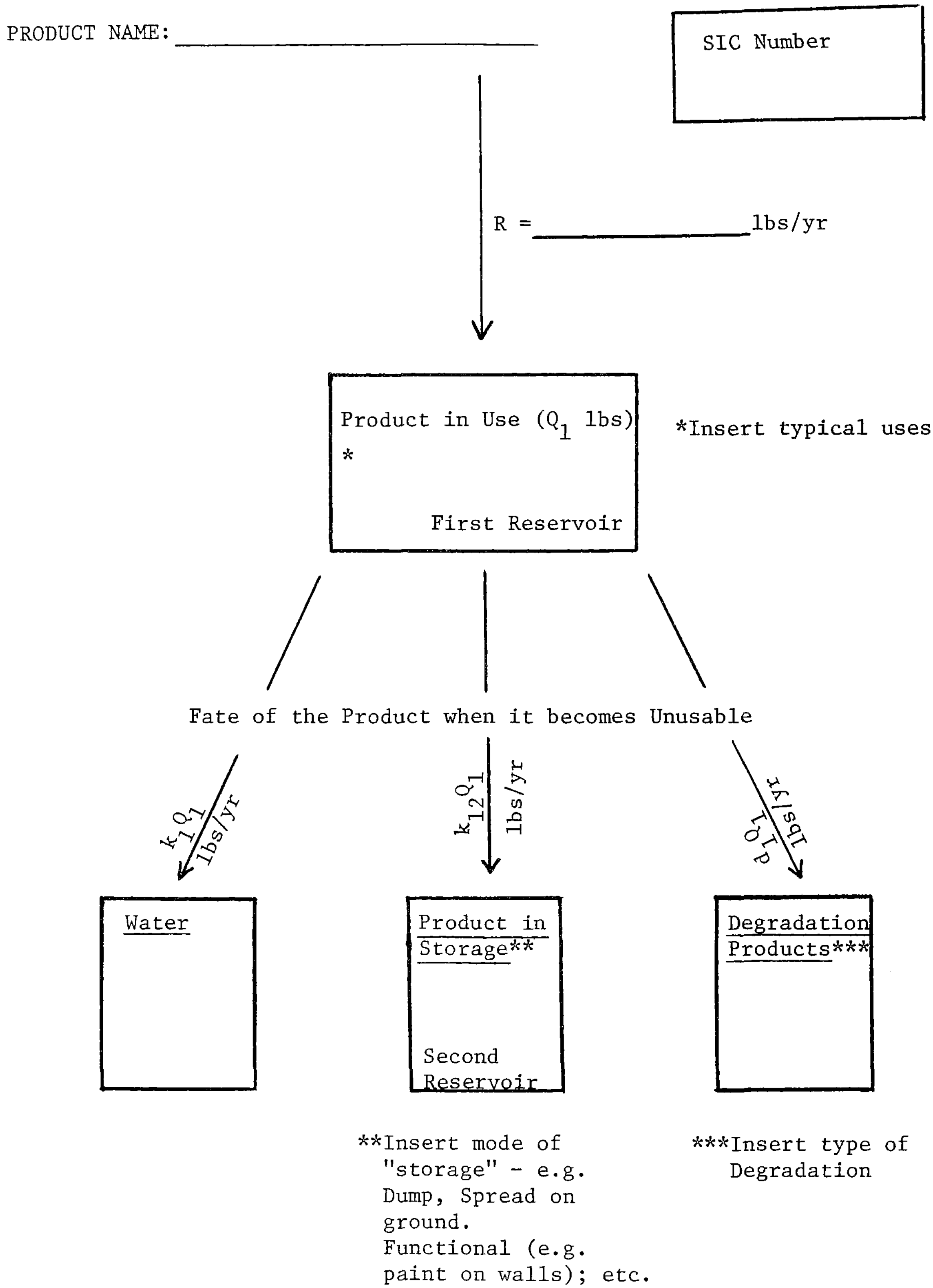
The mathematical framework of the model was discussed in the preceding section. Here, we indicate its method of use.

In Section I, space is allowed for information on annual production rates (R) of the listed product groups. Whenever practicable, production is reported in pounds per year, as required for estimating discharge rates via the model. Section I of the Catalog also includes space for (and in some cases, our own estimates of) the percentage of the total production which, during use and disposal, flows: a) directly into the water, b) into the second reservoir, and c) is chemically decomposed during use.

The model comprises two "reservoirs" which represent, respectively, the amount of a product in use at a particular time, and the amount of a product which is no longer in its initial state of use, but is in some kind of intermediate storage. The first step in using the model for predictive purposes is to define the "reservoirs" for the particular product or product class of interest. From the time a finished product leaves the manufacturer's shelf up to the time when the consumer is through with the product, it may be considered to be in circulation in the "first reservoir." The annual production feeds the first reservoir, and the amount accumulated is equal to the annual production rate (R, lb/yr) times the "lifetime" of the product (L, expressed in years).

The "second" reservoir may be defined by a consideration of the output from the first reservoir. It is helpful to construct a flow diagram of the type indicated in Figure 6 for any product of interest. After the product has been consumed, or is no longer usable, a fraction (k_1L) may be discarded directly into the water at a rate $S_1 = k_1Q_1$. A second fraction ($k_{12}L$) may be stored in various types of "second" reservoirs, which should be specified. The product might, for example, typically be sent to a dump. It might, like fertilizers and herbicides, be spread on the ground from which runoff might occur. It might, like exterior house paint, be functional for a time, although no longer "usable." A given product may enter into several different types of "second" reservoirs; and, in any case, the pollution potential due to outflow, S_{12}, from the set of second reservoirs can be quite complicated to evaluate. Finally, a fraction (α_1L) of the original product may degrade during use at a

FIGURE 6 : FLOW DIAGRAM OF PRODUCT ROUTES



rate $S_{11} = \alpha_1 Q_1$; and a new flow sheet can be constructed for the degradation products.

A form is provided in Figure 7 for calculating the rates at which products leave the first reservoir via the various routes defined in Figure 6.

An example of the use of the forms in Figures 6 and 7 to evaluate the quantity of fluoride which may enter the water from the use and disposal of fluoridated toothpaste is presented here. The first step is to find toothpaste in the SIC manual.(2) It falls under the SIC four-digit code 2844. By scanning the 2844 entries in Section I of the Catalog, toothpaste is coded specifically as SIC 2844 11. A flow diagram is constructed as in Figure 8. In Section I, the annual production rate is given as 177.3×10^6 pounds/year. This figure refers to all toothpaste. We are interested, in the example at hand, in fluoridated toothpaste. A little research tells us that in 1963 fluoride toothpaste had captured 1/3 of the market. Today, we might assume that half the toothpaste sold is fluoridated. Therefore, Figure 8, $R = 88.6 \times 10^6$ pounds/year ($177.3 \times 10^6 \times 1/2$) is inserted. The product use is fairly obvious; and all the toothpaste, except that remaining in the tube, goes directly down the drain. The residual toothpaste, in its containing tube, typically goes to the dump, where it may decay further. Steady-state rate calculations are carried out as indicated in Figure 9, using the following data as provided in Section I.

Lifetime:	$L = 0.5$ yrs
Decay time (in the dump):	$D = 20$ yrs
Percent degraded:	$\alpha_1 L = 0$
Percent entering water directly:	$k_1 L = 95$
Percent stored in the dump:	$k_{12} L = 5$

By referring to Section II of the Catalog, we determine that toothpaste typically contains about 0.2% fluoride.

We see in Figure 9 that the calculated rate of discharge of fluoride directly into the water from use of fluoridated toothpaste is 16.8×10^4 lbs/yr or 461 lbs of fluoride per day for the Nation as a whole. To evaluate this daily rate of fluoride introduction into our waterways, we will estimate the concentration level by comparing it with the amount of water drawn off and replaced during municipal and rural domestic use. The Water Encyclopedia indicates that 19.216×10^6 gallons of water per day are withdrawn, used and replaced for these purposes in the U. S. Assuming 8.3 lbs/gallon, this converts to 1.6×10^{11} lbs/day, indicating an average concentration of:

$$\frac{46.1}{160 \times 10^9} = 2.88 \text{ ppb}$$

FIGURE 7. CALCULATION OF STEADY STATE RATES OF DISCHARGE OF POTENTIAL POLLUTANTS FROM FLUORIDATED TOOTHPASTE

A. Disposal from the Primary Reservoir

Annual production rate of the product	$R =$
% of fluoride (x)* in the product	$\%x =$
Fraction of product discharged directly to the water	$k_1L =$
Fraction of product decomposed during use	$\alpha_1L =$
Fraction of product stored in a secondary reservoir after use	$k_{12}L =$
Product lifetime	$L =$
	$k_1 =$
	$\alpha_1 =$
	$k_{12} =$
Amount of produce in circulation for consumer use (steady state)	$Q_{1,ss} = (R) \quad (L) =$

Rate at which fluoride (x)* is:

Discharged directly into the water $\quad S_1 = (k_1)\ (Q_1)\ \frac{(\%x)}{100} =$

Decomposed during use $\quad S_{11} = (\alpha_1)\ (Q_1)\ (\%x) = \ (0)\ (Q_1)\ (\%x)$

Stored in a secondary reservoir after use $\quad S_{12} = (k_{12})\ (Q_1)\ (\%x) =$

B. Disposal from the Secondary Reservoir

Fraction of product leached or washined directly into the water $\quad k_2D =$

FIGURE 7. (Cont'd)

Fraction of product decomposed in the reservoir	$\alpha_2 D =$
Decay Time	$D =$
Rate constants	$k_2 =$
	$\alpha_2 =$
Amount of product in the secondary reservoir (steady state)	$Q_{2,ss} = k_{12}\ D\ Q_{1,ss} =$
Direct discharge of fluoride* from the secondary reservoir to the water	$S_2 = (k_2)\ (Q_2)\ \frac{(\%x)}{100} =$
Rate of decomposition of fluoride* in the secondary reservoir	$S_{22} = (\alpha_2)\ (Q_2)\ \frac{(\%x)}{100} = 0$ lbs/yr

*Insert the name of the chemical ingredient of interest

FIGURE 8: FLOW DIAGRAM OF PRODUCT ROUTES

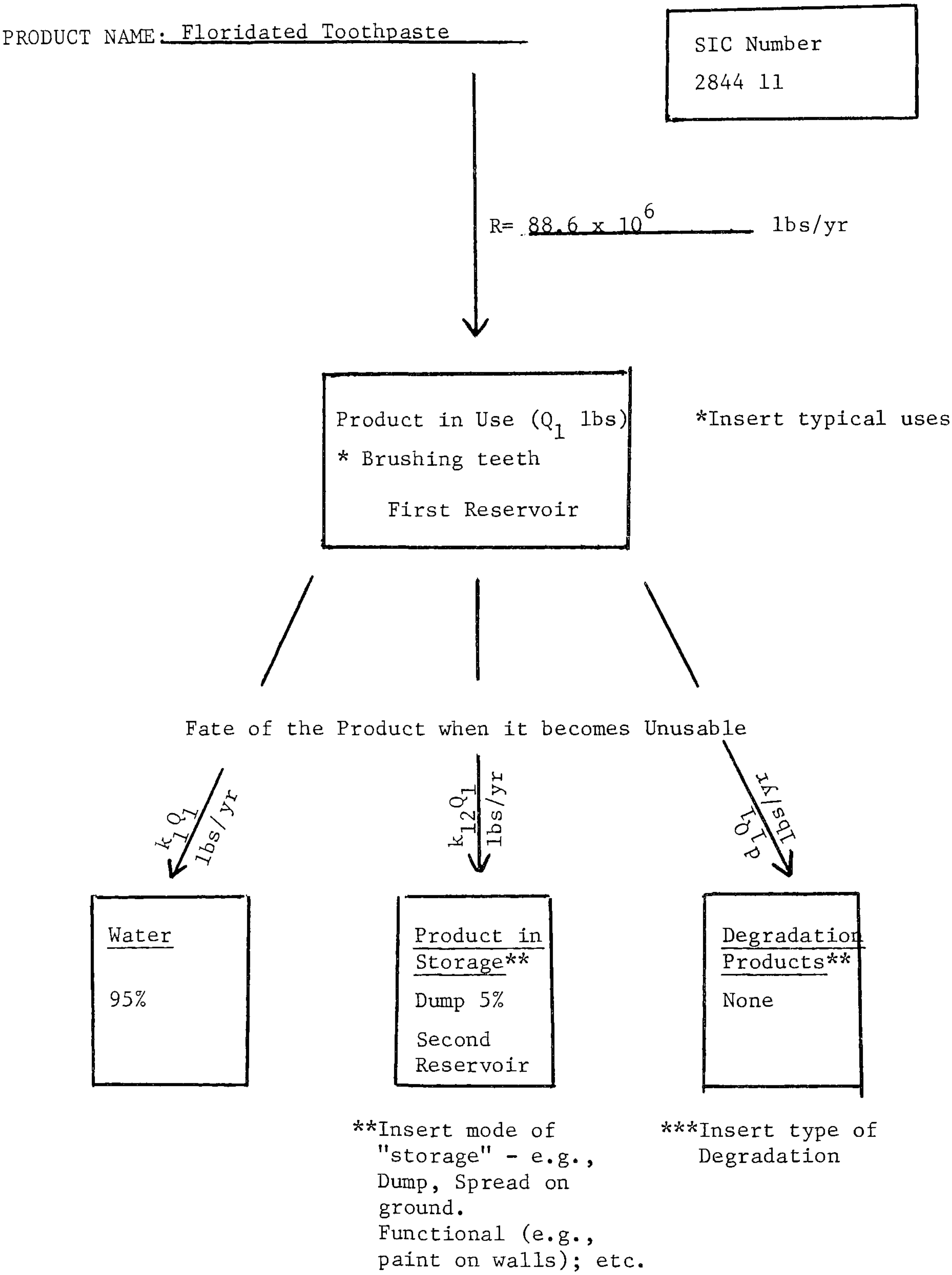


FIGURE 9. CALCULATION OF STEADY STATE RATES OF DISCHARGE OF POTENTIAL POLLUTANTS FROM FLUORIDATED TOOTHPASTE

A. Disposal from the Primary Reservoir

Annual production rate of the product	$R = 88.6 \times 10^6$ lbs/yr
% of fluoride (x)* in the product	$\%x = 0.2\%$
Fraction of product discharged directly to the water	$k_1L = 0.95$
Fraction of product decomposed during use	$\alpha_1 L = 0$
Fraction of product stored in a secondary reservoir after use	$k_{12}L = 0.05$
Product lifetime	$L = 0.5$ yrs.
Rate Constants	$k_1 = 1.9\ yr^{-1}$
	$\alpha_1 = 0\ yr^{-1}$
	$k_{12} = 0.1\ yr^{-1}$

Amount of produce in circulation for consumer use (steady state)

$$Q_{1,ss} = (R)\ (L) = (88.6 \times 10^6)\ (0.5) = 44.3 \times 10^6 \text{ lbs}$$

Rate at which fluoride (x)* is:

Discharged directly into the water

$$S_1 = (k_1)(Q_1)\frac{(\%x)}{100} = (1.9)\ (44.3 \times 10^6)\ (0.002) = 16.8 \times 10^4 \text{ lbs/yr}$$

Decomposed during use

$$S_{11} = (\alpha_1)(Q_1)(\%x) = (0)(Q_1)(\%x) = 0 \text{ lbs/yr}$$

Stored in a secondary reservoir after use

$$S_{12} = (k_{12})(Q_1)(\%x) = (0.1)(44.3 \times 10^6)(0.002) = 8.86 \times 10^3 \text{ lbs/yr}$$

B. Disposal from the Secondary Reservoir

Fraction of product leached or washed directly into the water $\quad k_2D = 100$

FIGURE 9. (Cont'd)

Fraction of product decomposed in the reservoir	$\alpha_2 D = 0$
Decay Time	$D = 20$ yrs
Rate constants	$k_2 = 0.05 \text{ yrs}^{-1}$
	$\alpha_2 = 0 \text{ yrs}^{-1}$
Amount of product in the secondary reservoir (steady state)	$Q_{2,ss} = k_{12}\ D\ Q_{1,ss} =$
	$= (0.1)(20)(44.3 \times 10^6) =$
	$= 88.6 \times 10^6$ lbs
Direct discharge of fluoride* from the secondary reservoir to the water	$S_2 = (k_2)(Q_2)\frac{(\%x)}{100} =$
	$= 0.05(88.6 \times 10^6)(0.002) =$
	$= 88.6 \times 10^2$ lbs/yr
Rate of decomposition of fluoride* in the secondary reservoir	$S_{22} = (\alpha_2)(Q_2)\frac{(\%x)}{100} = 0$ lbs/yr

*Insert the name of the chemical ingredient of interest

The potential outflow of fluoride from the dump is far from negligible, and. in fact, under steady-state conditions Q_2 exceeds Q_1 by about a factor of two. On the other hand, fluoride leached from a dump would probably be tied up with calcium in the soil and is not likely to contribute significantly to the fluoride concentration in the water.

It is instructive to consider the build-up of Q_1 and Q_2 to steady-state conditions. The result of such a calculation, based on Equations (4) and (5) are given in Figure 10. We note that steady-state is closely approached in about a decade for this particular example.

In general, for a constant production rate, R, starting at t = 0, Q_1 rises exponentially to its asymptote, RL; Q_2 lags Q_1 by k_{12} D and follows an "S" shaped curve. Plots of Q_1/R and Q_2/R as a function of dimensionless time $\bar{t} = t/L$ are given in Figure 11 for the case L = 1 yr; D = 10 yrs; and $k_{12}L$ = 0.5.

Generalized plots of Q_1/RL and Q_{12}/k_{12} RDL for D/L = 10, 20, and 40 are given in Figure 12.

One important use for the Catalog and model is to roughly evaluate the total amount of a particular substance which enters the environment through the use of manufactured products. By consulting Section III, one can find the SIC numbers for all manufactured products formulated with any particular chemical. In Section II, the amount of that chemical in the various formulations can be found, while production figures and model parameters are given in Section I.

In general, the Catalog and associated model can be used as a tool to evaluate the relative seriousness of a product's pollution potential as a result of:

A - direct entry into the water through sewers or into streams and waterways,

B - secondary accumulations, as in dumps or other reservoirs, where large quantities may build up, and

C - decomposition or chemical change during use or disposal.

It can further be used to estimate the criticality of a potential pollution problem by determining the time constants associated with it. In addition, it can serve as a predictive tool to estimate the order of magnitude of product quantities which are released into the water by each route.

The amount stored, and the rates at which transfers of products and their component substances takes place from one reservoir to the next, and from reservoirs into the Nation's waters are the real quantities of interest. The rates are proportional to the amount contained in the reservoirs, which in turn depend on the "lifetime" and "decay," or "release" time for the first and second reservoir, respectively. If a large percentage

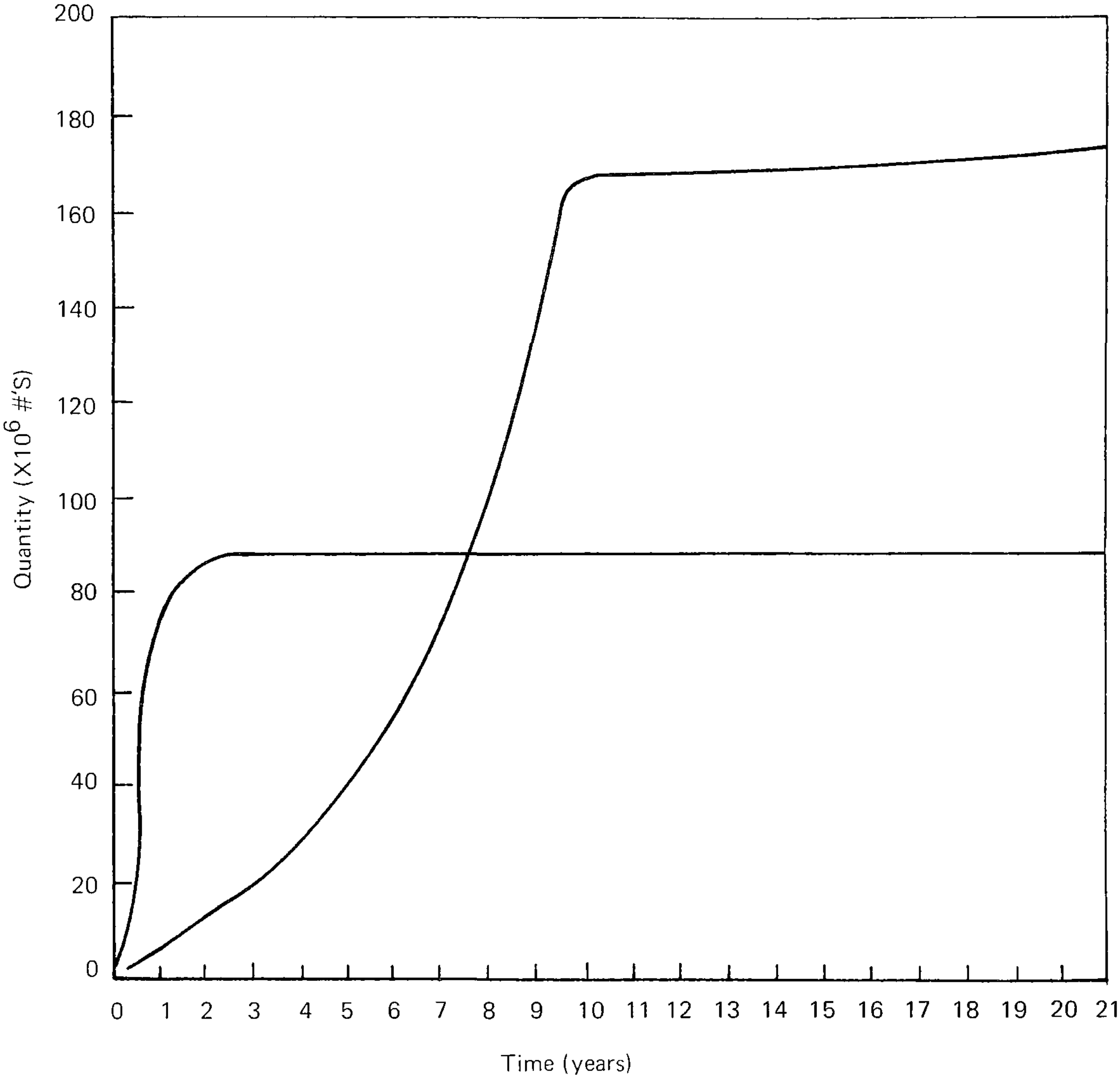

200
180
160
140
120
100
80
60
40
20
0
Quantity (X10^6 #'S)
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Time (years)

FIGURE 10

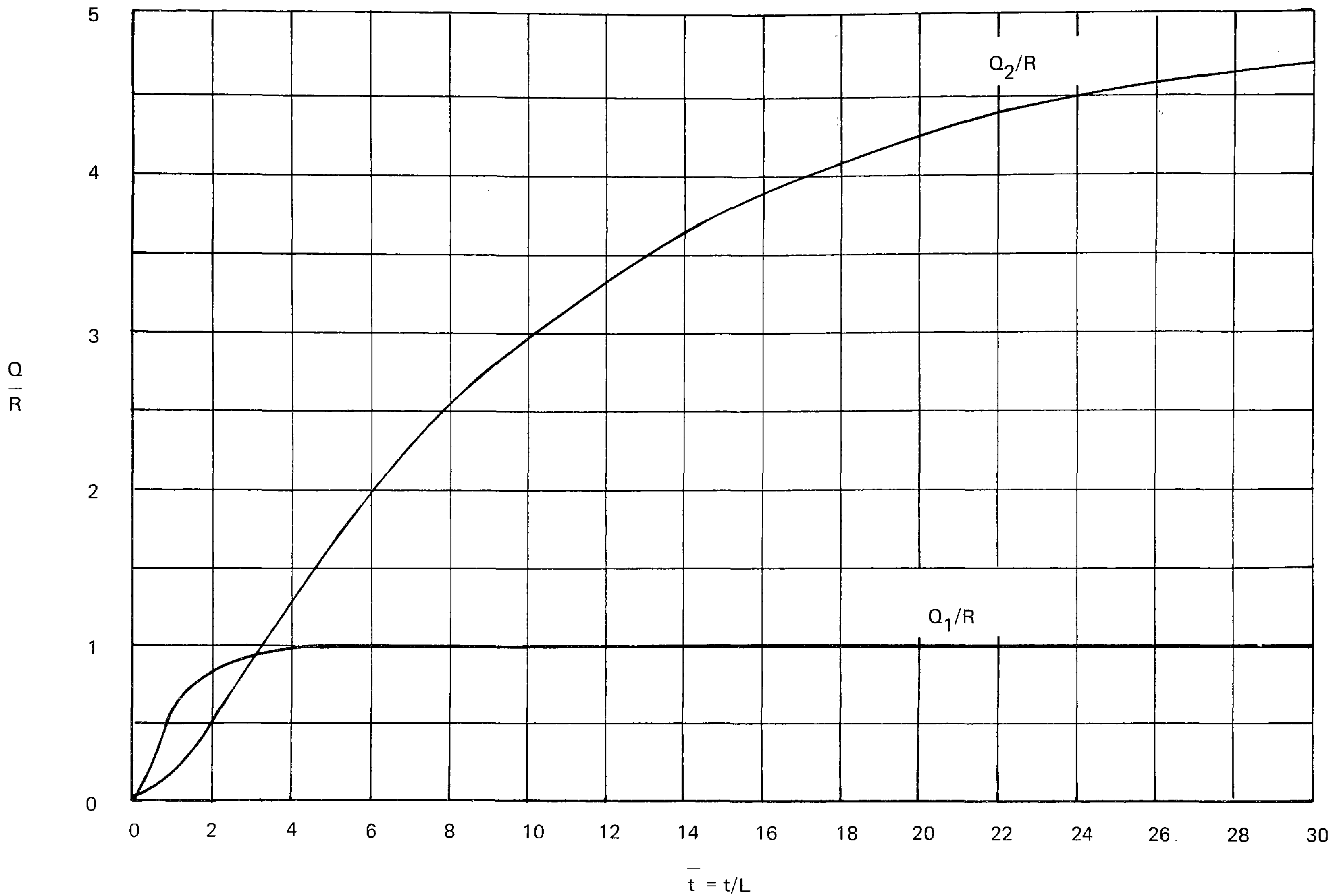
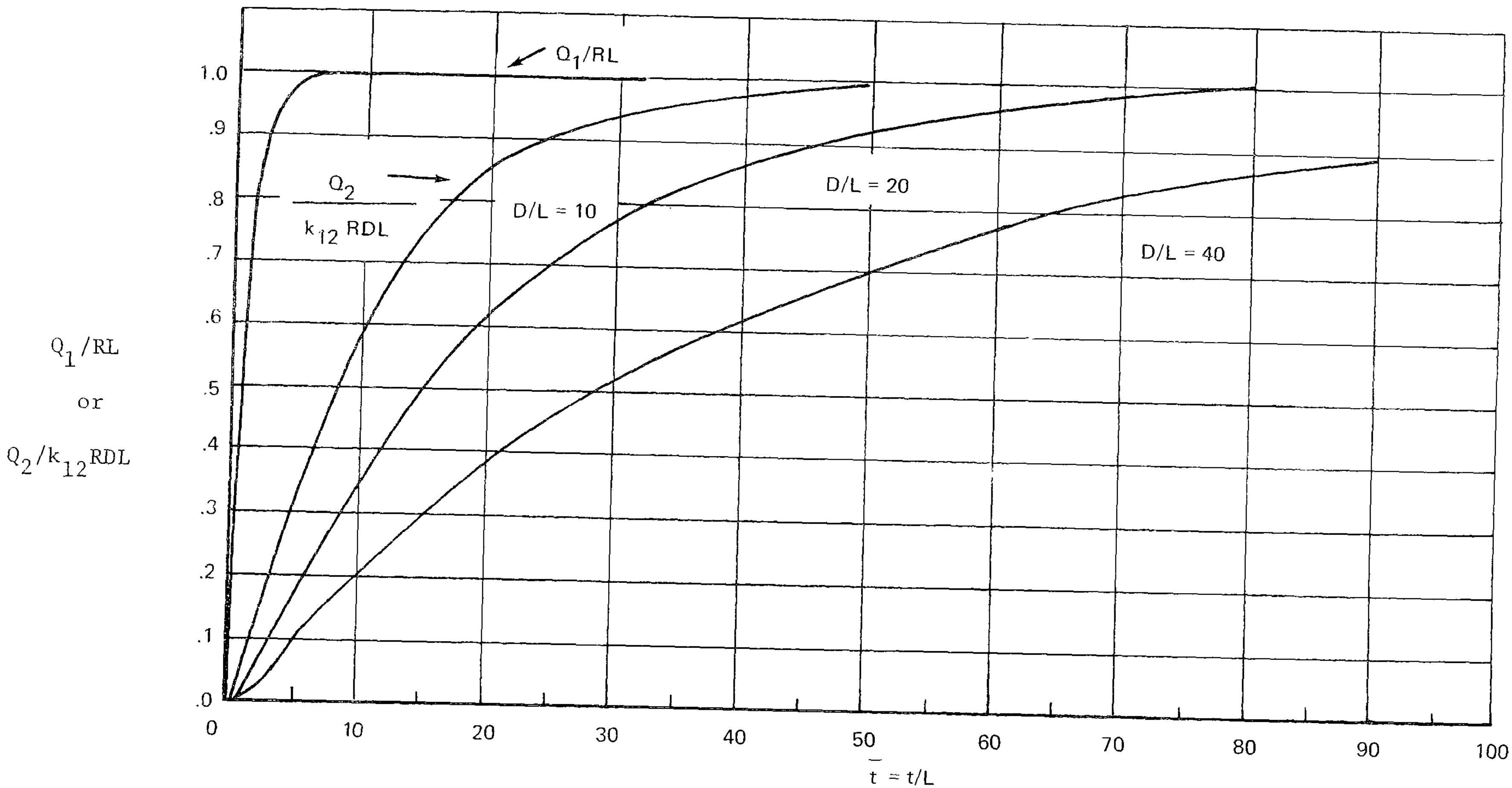


FIGURE 11



Q1/RL
Q2
k12 RDL
D/L = 10
D/L = 20
D/L = 40
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
10
20
30
40
50
60
70
80
90
100
t = t/L
Q1/RL
or
Q2/k12RDL

FIGURE 12

of the product ends up in storage in reservoir two, and it also has a large "decay" time, a serious pollution problem could be building up over a period of years as the stored quantity gradually builds up to an equilibrium value. The problem may not be perceived as such because very small quantities of the polluting material enter the water directly. DDT is an example of one such case where the amount of product entering the water directly each year appears to be relatively small and therefore of little significance. However, due to its persistence (and effectively long "decay" time) it has built up in reservoir two over a number of years to the point where serious consequences are now recognized. The alternative case occurs for products such as toilet bowl cleaners. In this case, nearly all of the product enters the water rapidly and directly. It is necessary to estimate the time scale in which a particular product may represent a pollution hazard. This must be done in order to determine whether it is the direct, short-term effects which are most critical, or whether the potential is for a greater, long-term problem.

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(2) Standard Industrial Classification Manual, 1972, Superintendent of Documents Stock Number 4101-0066.

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27 *Abstract*

A Catalog has been compiled of manufactured products which may, during their normal use or disposal, results in water pollution. The Catalog is in three sections, and the products are grouped in accordance with the Standard Industrial Classification (SIC).

Section I summarizes the pollution potential of each listed product group. Section II provides data on typical chemical compositions for each product group and indicates the types of water-pollutional effects associated with each chemical ingredient. Section III inverts Section II by providing an alphabetical listing of chemicals and the SIC codes in which they occur.

Along with the Catalog, a simple model has been developed to estimate rates of pollutant entry into the waterways, via various routes. A guide including examples is provided on how to use the Catalog and associated models to assess potential water pollution problems arising from finished products in common use.

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