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A risk assessment approach for evaluating the environmental significance of chemical contaminants in solid wastes

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17-1 INTRODUCTION

Increasing attention is being given to the environmental significance of chemical contaminants in solid wastes.* This is the result of an increasing awareness that improper disposal of liquid and solid wastes on land can result in significant environmental degradation. The "Love Canal" situation

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*For the purposes of this discussion, "solid wastes" are defined as municipal and industrial solid wastes, as well as the concentrated liquid wastes from certain manufacturing operations, which are typically disposed of by land application or burial. The approaches discussed in this chapter are equally applicable to assessing the environmental significance of land disposal of domestic wastewater sludges.

in Niagara Falls, NY, is just one of many examples across the United States in which land disposal of wastes has caused or has the potential to cause significant environmental degradation. As recently as two years ago, based on a survey by Green *et al.* (Ref. 17-1), there- were no federal, and, with a few exceptions, no state regulations governing the disposal of hazardous chemical wastes on land. In an effort to remedy this situation the U.S. Congress and many State Legislatures have passed laws enabling pollution control agencies to develop regulations governing solid waste disposal. The U.S. EPA, in accord with the provisions of the Resource Conservation and Recovery Act (RCRA), is attempting to develop regulations that would minimize environmental contamination from land disposal of solid wastes.

One of the key requirements of RCRA is the classification of solid wastes with respect to their potential environmental hazards. There is considerable controversy, however, about the validity of the U.S. EPA's planned approach. The basic approach advocated by the U.S. EPA for classifying solid wastes by toxicity involves a single leaching test with arbitrarily established concentration limits for contaminants in the leachate. As discussed by Lee (Ref. 17-2), this approach is not technically valid for assessing the environmental hazard associated with solid wastes primarily because the transport and transformation (environmental chemistry) of the solids-associated contaminants can be markedly different for each specific environment, and usually play a dominant role in determining the hazard associated with the introduction of the solid into the environment. The environmental chemistry of contaminants is influenced by many factors, as discussed later in this chapter, and must therefore be evaluated on a site-specific and solid waste-specific basis. No single leaching test will properly simulate chemical behavior for all cases. In addition to causing municipalities, industry; and others to spend unnecessarily large amounts of money for controlling wastes that would not cause environmental degradation, implementation of such an approach into public policy may result in instances of inadequate protection being provided as a result of improper classification of the environmental hazard associated with contaminants present in solid wastes (Lee, Ref. 17-2). This chapter presents general guidance that is useful not only for the development of appropriate leaching test and hazard assessment procedures for solid waste disposal evaluation, but also in the site-specific application of these approaches.

Some groups within the U.S. EPA and Corps of Engineers have attempted to make site-specific assessments of the hazard associated with solids (dredged sediment) -associated contaminants by determining the bulk content of potentially hazardous chemicals in the solid. It has been well documented, however, that the release of solids-associated contaminants when exposed to water, or the impact of the contaminants on water quality, cannot be predicted based on the total concentration of the contaminants in the solid (Refs. 17-3, 17-4). In order to develop technically valid, cost-effective, environmentally protective solid waste disposal regulations, an "environmental hazard assessment approach" must be used to classify solid wastes on a site-specific basis. This chapter describes the elements of such a hazard assessment approach.

17-2 THE ENVIRONMENTAL RISK ASSESSMENT APPROACH — AN OVERVIEW

The environmental hazard assessment approach is an outgrowth of the work that has been done by the chemical industry and more recently by governmental agencies such as the U.S. EPA Office of Toxic Substances, in prescreening new chemicals for their potential environmental hazard prior to their large-scale manufacture. There are two basic factors motivating work in this area. One is the series of chemically-caused environmental crises that have resulted in wide-spread environmental contamination by potentially highly toxic, persistent contaminants such as PCBs, DDT, mercury, and, most recently, kepone. There is no doubt that it is necessary to prescreen all chemicals in order to try to prevent chemical crises of this type. The other factor is the need to establish technically valid chemical screening requirements so that environmental protection can be ensured and thus governmental agencies can be prevented from making the kinds of arbitrary decisions with respect to the chemical safety as occurred with nitrilotriacetic acid (NTA), a replacement for phosphate in household laundry detergent formulations. It is now well known that large amounts of money were lost by the chemical industry and, hence, consumers because the U.S. Department of Health, Education, and Welfare (HEW) at the last minute prevented the use of NTA, based on controversial studies conducted by HEW staff. A comprehensive review of the suitability of the use of NTA as a replacement for phosphate in detergents has since been conducted by an International Joint Commission for Great Lakes Water Quality task force that has recommended its use in the Great Lakes Basin. The development of an appropriate hazard assessment would, if properly conducted, prevent the next PCB-type crisis and protect the chemical industry and consumers from inappropriate governmental decisions with respect to new chemical - new product development.

While there is general agreement concerning the need for an environmental hazard assessment approach, there is some controversy regarding the detailed procedures to be included in it. It is generally agreed, however, that the over-all approach that is being formulated by the American Society for Testing and Materials (ASTM) Subcommittee E-35.21 "Safety to Man and the Environment," is a technically valid, cost-effective, environmentally protective approach that should be followed for prescreening new chemicals for their potential environmental impact. A discussion of the principles of a hazard assessment for pre-screening new chemicals is presented in the ASTM publication edited by Cairns *et al.* (Ref. 17-5) and, for existing chemicals, in a publication by Lee *et al.* (Ref. 17-6).

As designed for aquatic systems, hazard assessment is developed from two types of information: aquatic toxicology and environmental chemistry-fate. Aquatic toxicology defines the response of selected aquatic organisms to given concentrations of particular forms of contaminants or given dilutions of a particular effluent, when exposed for a given duration. Environmental chemistry-fate defines the transport and transformation of the chemical or effluent and defines the expected concentration of the chemical and its potentially significant transformation products in the aquatic compartments of concern, the water, the sediment, and so on. An assessment of aquatic environmental hazard is then made by comparing the expected concentrations to those that have been found to be harmful to aquatic organisms, to man when he eats the aquatic organisms, or to other beneficial uses of the water. As discussed by Cairns *et al.* (Ref. 17-5) and Lee *et al.* (Ref. 17-6), a hazard assessment should be conducted in a series of levels or tiers of increasing sophistication so that highly innocuous and highly hazardous materials can be readily identified with limited testing and so that it is possible to make situation-specific judgments regarding necessary testing.

The basic philosophy that the authors feel should apply to any situation of potentially hazardous chemical use or discharge is to allow the source of the contaminant of concern (the municipality, industry, operator of a disposal site, and so on) the option of conducting a detailed evaluation to determine the potential environmental hazard associated with the manufacture and use and/or disposal in the desired manner. If the source is unwilling to make such an evaluation, then worst-case assumptions should be made to ensure that unacceptable environmental degradation does not result from these activities.

17-3 HAZARD ASSESSMENT APPROACH FOR SOLID WASTES

A key component in defining the fate and behavior of contaminants associated with solid wastes is a leaching procedure, since it is this process that mobilizes the solids-associated contaminants in disposal sites so that they may affect water quality. As discussed previously, however, this leaching should not be mechanically performed by a single rigid procedure, but should be conducted to take into consideration the characteristics of the material and the disposal site. While there does not yet exist sufficient information to develop a detailed hazard assessment program or a widely applicable leaching test to evaluate the solid waste-associated contaminants, the RCRA guidelines should describe a general leaching procedure to be used, indicating the factors to be considered in developing site-specific leaching tests, and giving guidance on how these factors are to be incorporated into such leaching tests.

The authors have conducted a comprehensive study of the U.S. EPA and Corps of Engineers' elutriate test, a leaching test designed to evaluate the release of dredged sediment-associated contaminants upon their open water disposal. This test was developed because the previously used bulk sediment criteria lacked validity; but when the elutriate test was developed, essentially nothing was known about appropriateness of the test conditions specified (although they were chosen on the basis of what was believed appropriate for hydraulic dredging-hopper disposal operations) or its predictive capabilities. The Lee *et al.* (Ref. 17-3) and Jones and Lee (Ref. 17-4) studies, undertaken to resolve these questions, included the evaluation of over 50 sediments from about 20 river and harbor areas in the United States and *in situ* monitoring of about 20 disposal operations. Their studies provide insight into the factors that should be considered in developing a leaching test for assessing the hazard associated with solid-waste-associated contaminants. The following section is based largely on the findings of these studies. It is important, as discussed above, that each of these parameters be carefully evaluated for solid waste disposal sites.

17-3.1 Factors to be Considered in Designing Leaching Test for Solid Waste

The first important factor to be considered in developing a leaching test for solid waste is the leaching solution to be used. For some situations, the only liquid with which the solids will come in contact at the disposal site is water. In other instances, liquid wastes may be disposed of at the same site. There is no point in leaching solid wastes with acetic acid — "garbage juice" — such as is proposed by the U.S. EPA, if these wastes will not be in contact with a dilute acetic acid solution or its equivalent at the disposal site. The leaching solution used in the testing must bear some relationship to that actually encountered at the disposal site, because markedly different chemical release from solids can be promoted by different leaching solutions.

Another important factor that must be considered in establishing chemical leaching tests for solid wastes is the control of the oxidation-reduction conditions present during leaching. If the solid waste disposal site is likely to be anoxic (i.e., no oxygen present), then the leaching test should be conducted under an anoxic condition. Lee *et al.* (Ref. 17-3) and Jones and Lee (Ref. 17-4) evaluated the effects of redox conditions of elutriate test results and found that, for some contaminants, markedly different release occurred under oxic as opposed to anoxic conditions, with generally greater release occurring under anoxic conditions. They found that, unless this parameter is controlled (i.e., assuring oxic or anoxic conditions as desired), the results were variable and largely uninterpretable because the oxygen demand of some sediments was sufficient to deplete the oxygen in the test vessel if no supplemental oxygen was provided, a depletion that would not be encountered at most dredged sediment disposal sites. For most dredging cases, unless the disposal site or chemical characteristics dictate otherwise, the elutriate test should be run under oxic conditions, as the sediment is generally dumped into oxic waters. The redox conditions must be examined for each solid waste disposal site and appropriate conditions incorporated into the leaching test for solid wastes.

Specification of leaching test parameters also should consider the importance of the liquid-to-solid ratio, i.e., the ratio of the leaching solution to the solid waste, in the disposal area. The elutriate test liquid-to-solid ratio is usually 80% by volume, based on the optimum dredge pumping ratio. It was found, in evaluating the impact of this factor on elutriate test results, that the liquid-to-solid ratio affected the amount of release of some contaminants (Ref. 17-4, 17-3). This effect was, however, highly sediment- and contaminant-specific and was not predictable. It underlines the importance of mimicking the liquid-to-solid ratio appropriate for the system under investigation. Because it is difficult to define the actual liquid-to-solid ratio at each particular solid waste disposal site, the leaching test procedure should be conducted with several liquid-to-solid ratios that cover the range likely to be encountered and define the sensitivity of the contaminant release to this condition. In general the liquid-to-solid ratio associated with water percolating through the pores of the solid material is a more appropriate guide to the leaching test ratio than an arbitrarily selected value. Studies need to be conducted on a variety of solid wastes and at a variety of solid waste disposal areas in order to determine what range of liquid-to-solid ratios should be used and to determine the influence this parameter will have on the release of contaminants in question.

Another factor that needs more detailed investigation before a general procedure can be developed for formulating site-specific leaching tests is the contact time between the leaching solution and the solid waste sample. Lee *et al.* (Ref. 17-3) and Jones and Lee (Ref. 17-4) found that, for some contaminants, the sediment-water contact time could have a marked effect on the release of the contaminant in the elutriate test, depending on sediment characteristics. Because the retention time in solid waste disposal sites may be highly variable, it is necessary to choose this condition on a site-specific basis, at least until its impact on leaching test results has been defined. Similarly the degree and method of agitation used during the leaching procedure must be chosen so that leaching test results properly simulate environmental conditions. Alternatively, a completely mixed system could be used, which would likely represent worst-case release; data interpretation would then have to take that into account.

Other factors that will need to be evaluated in establishing a widely applicable leaching test are the impact of leaching solution pH, temperature, and the organic content of the solids. The method of separation of the leachate from the solid must also be evaluated for each contaminant of interest. For some contaminants, there can be considerable sorption on membrane filters typically used for this purpose. Centrifugation can become quite cumbersome if a large number of different analyses need to be run, and may result in more of the contaminant being separated out than would be retained by the disposal area. Settling alone does not generally adequately separate contaminant forms of interest from the solids which would be retained within the disposal area. As a practical consideration, studies should be conducted to determine the length of time that samples may be stored prior to leaching and the storage conditions. It has been found that freezing or drying of solids can alter their tendency to release or sorb contaminants. Lee *et al.* (Ref. 17-3) found it satisfactory to store their sediments in the dark at 4°C for a maximum period of about two weeks. They felt that longer storage periods would have resulted in sediments and associated contaminants' being sufficiently changed to substantially alter test results.

It is likely that as the various factors discussed above are evaluated for their impact on leaching test results and are defined for a variety of solid waste disposal sites and materials, other factors will be identified as important, constraints will be placed on use of the test procedure, and some factors will be found to be unimportant in affecting results. However, until sufficient field studies are conducted to do this sorting, each of these factors must be carefully evaluated for its appropriateness for the disposal site of concern and the material of concern.

Ham *et al.* (Ref. 17-7) and Thompson (Ref. 17-8) conducted laboratory studies of leaching tests for industrial wastes. Ham *et al.* evaluated three different batch test procedures (as opposed to column leaching tests) in an effort to define which would most closely represent an appropriate "standard" test, both from practical and technical points of view. They stressed the importance of proper interpretation of the results of any leaching test based on contaminant, landfill, and organism characteristics, and pointed out that "... a certain concentration of a given parameter in the test leachate should not be taken to indicate that the waste is hazardous in the landfill." Ham *et al.* provided a discussion of merits and drawbacks of each of the three tests evaluated in terms of properly mimicking solid **536** waste disposal sites, interpretability, and the ease of conducting the procedure. They indicated that because landfills (municipal) produce acidic leachates comparable in pH and buffering capacity to the synthetic leachate leaching solution used in one type of test, it would be more appropriate to use such a solution than deionized water or acetate buffer (pH 4.5) also evaluated. As pointed out by Ham *et al.*, while the liquid-to-solid ratio is important, it is generally arbitrarily assigned; they suggested that ratios of 1:10 to 1:4 are reasonable. While tests were run for 24 or 48 hr periods, they pointed out that these leachings may simulate years of *in situ* leaching, during which time the chemical may be substantially altered. The number of elutions and agitation techniques were also evaluated by Ham *et al*; they indicated that, although they are also ultimately rather arbitrarily assigned, they should be based on chemical characteristics. While stressing the importance of proper interpretation of leaching test results, Ham *et al.* provided little explicit guidance and had conducted no field work to attempt to correlate the results of their work with actual leachate generation in the field. They suggested, however, that this type of leaching test would likely represent worst-case conditions.

Thompson (Ref. 17-8) used a modified elutriate test, similar to the one developed by the U.S. EPA and Corps of Engineers for evaluating contaminant release from dredged sediment, to compare chemical (mostly heavy metals) leaching from industrial sludges both raw and chemically stabilized by a variety of techniques. As part of his modifications to the dredged sediment elutriate test, he apparently conducted some studies on the effects of various test conditions to optimize the release of contaminants in his test. He indicated that a 1:8 solid-to-liquid ratio (on a weight basis) appeared to be appropriate, and that a contact time of 30 min provided as much contaminant release as "longer" periods. He did not apparently evaluate the effect of not controlling redox conditions. As Thompson indicated, there are a number of problems in using this test in its current form to say anything about the hazard associated with solid wastes disposed of on land. The field verification portion of Thompson's overall study has apparently (according to Thompson) been recently completed but no comments were made about those results. It should be noted, as indicated previously, that the elutriate test for dredged sediments has been extensively evaluated by Lee *et al.* (Ref. 17-3) in the laboratory and in the field for its ability to properly assess potential contaminant release during open water dredged sediment disposal. These studies indicated that the dredged sediment elutriate test adequately predicts sediment-associated contaminant release during open water dredged sediment disposal.

The leaching procedure, as indicated above, is a technique of imitating, in the laboratory, the mobilization of solids-associated contaminants within a solid waste disposal site. Once an estimation is made of the forms and concentrations of the contaminants that are likely to migrate out of a particular disposal site, it is possible to assess what concentrations and forms of a contaminant may enter an aquatic system.

17-3.2 Transport and Transformation from Disposal Site to Aquatic System

Lee and Jones (Ref. 17-9) and Lee *et al.* (Ref. 17-6) have presented detailed guidance on the factors to be evaluated in determining the environmental chemistry-fate of a material upon entry into an aquatic system and on developing a tiered hazard assessment approach for estimating the potential impact of a contaminant or discharge on an aquatic system. Before that hazard assessment approach can be applied for solid wastes, an evaluation must be made of the transport and transformation of the contaminants in the solid waste leachate *en route* to an aquatic system, in order to derive the expected concentrations and forms of the contaminants of interest entering the aquatic system. Figure 17-1 is a generalized, schematic contaminant chemistry-fate model alluding to many of the reactions into which a contaminant in a solid waste leachate could enter, all of which must be considered. The major types of reactions that can occur in such a system are acid-base, precipitation, complexation, oxidation-reduction, hydrolysis, photolysis, gas transfer, biochemically mediated reactions — biotransformation, and sorption. Movement over the surface, through the unsaturated soil, in groundwater, into roots of vegetation, as well as volatilization followed by atmospheric transport are the major modes of transport of dissolved and particulate forms of contaminants.

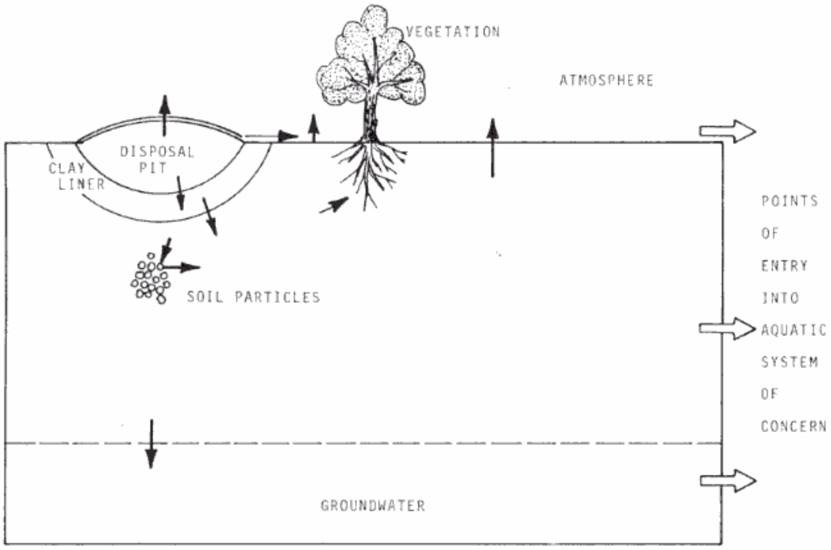


Fig. 17-1. Transport and transformation of solid waste-associated contaminants en route to aquatic systems.

The models to describe the transport and trans-formation processes must be formulated on a site-specific basis. Of particular importance in model development are reactions with solid phases, such as sorption on soil particles. It has been repeatedly demonstrated that sorption tends to greatly detoxify contaminants or render them unavailable to aquatic organisms.

Another potentially important reaction is the sorption of contaminants on hydrous metal oxides, such as aluminum hydrous oxide and especially iron hydrous oxide. Many solid waste disposal site leachates are anoxic and therefore are likely to contain high concentrations of ferrous iron. Upon contact with oxygen, the iron will be oxidized and will precipitate as ferric hydroxide. Ferric hydroxide is an efficient scavenger for many trace contaminants, which tends to reduce the availability of many contaminants to aquatic organisms.

One of the potentially most important aspects of a contaminant chemistry-fate model for the system described in Fig. 17-1 is the interaction between the contaminant leached from the solid waste and the disposal pit liner and/or the soils of the area. It has been found by Green *et al.* (Ref. 17-1) that a number of organic solvents can affect the characteristics (most notably, permeability) of clay liners frequently used in industrial and some municipal disposal pits. Some solvents, such as carbon tetrachloride and xylene, caused clays to shrink, allowing the fluid to run through the liner in channels. However, when these solvents were mixed with others, such as water or acetone, the clays did not crack. It is important to evaluate this situation at each disposal site and for each of the wastes being disposed of, as the presence of certain organic solvents could markedly affect the transport of these and other contaminants present with them.

It is important to emphasize that one should not assume that the concentrations and forms of a contaminant in a leachate of a laboratory leaching test, such as those proposed by the U.S. EPA or ASTM Committee D-19.12, will be the concentrations and forms of the contaminants that enter a water body near a land disposal site. There is a wide variety of physical, chemical, and biological reactions, and dilution that tend to greatly reduce the concentrations of available forms of contaminants that would enter a waterbody compared to what would be found in the disposal site leachate. It is evident that the initial proposal of the U.S. EPA that is, to apply a factor of 0.1 for dilution and other reactions to the laboratory leachate contaminant concentration and then judge the "hazard" by comparing this number with the U.S. EPA Red Book criterion, is inappropriate. It may overestimate or underestimate the hazard to aquatic systems of the solid waste; in the experience of the authors, it is more likely that it will greatly overestimate the potential hazard.

The following discussion of how this information is used in an aquatic hazard assessment was adapted largely from Lee and Jones (Ref. 17-9) and Lee *et al.* (Ref. 17-6).

17-3.3 Characteristics of Aquatic Hazard Assessment

As indicated previously, an environmental hazard assessment for chemicals entering aquatic systems is built upon two basic components: aquatic toxicology and environmental chemistry-fate of the chemical in the aquatic system. The characteristics of each are discussed below.

Aquatic Toxicology. The aquatic toxicology portion of hazard assessment provides information on the response of aquatic organisms to concentrations and forms of chemicals and durations of exposure that may be encountered in the environment. The objective is to produce a concentration of available forms (or dilution)-duration of exposure-"no effect" relationship, such as the general case shown in Fig. 17-2. All chemicals affect aquatic organisms in accord with relationships of this type, in which the concentration of available forms of the contaminant can be increased significantly without harming the organisms, provided that the duration of the exposure of the organisms to the chemical is sufficiently short. Further, for all chemicals, there is a chronic exposure safe concentration for available forms, below which no known impact of the chemical has been found. At concentrations of contaminants below the chronic safe concentrations, changing the duration of exposure has no effect on toxicity of the chemical to aquatic life. It is important to emphasize that the response of various organisms to various parts of the available form-duration of exposure- "no effect" relationship shown in Fig. 17-2 will vary. In the high concentration of available form-short duration

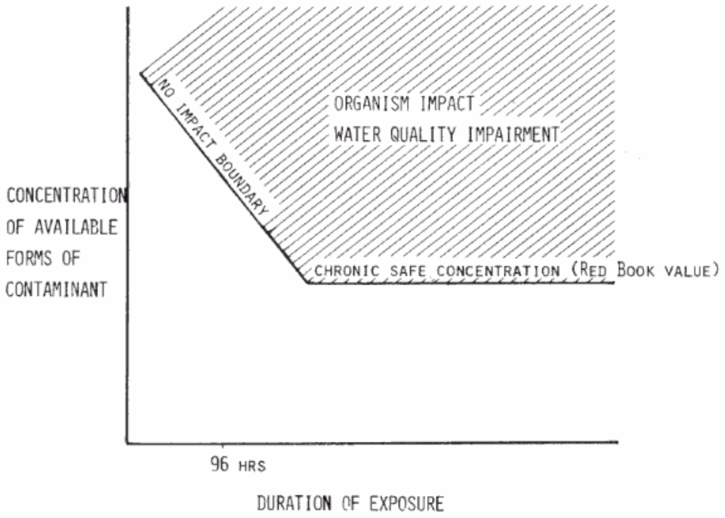


Fig. 17-2. Generalized relationship among concentration of available forms, duration of organism exposure, and no impact level. *Source*: Lee *et al*. (Ref. 17-6).

situation, such as on the left side of the diagram, the effects that are typically noted are those of acute lethality, while on the right side of the diagram, where the concentration of available forms has an impact on the aquatic organisms, the effects of the chemical on the organisms are primarily those associated with impairment of rates of growth or reproduction, alteration of behavioral patterns, etc. Every meaningful environmental hazard assessment should include the development, even in a rudimentary way, of a concentration-duration of exposure to available forms- "no effect" relationship shown in Fig. 17-2. It is evident that environmental chemistry will play a dominant role in developing this relationship because this is specific not only to a type of chemical, but also to each form of a chemical that exists within aquatic systems. A free "aquo" species of a chemical will show a different toxicological behavior in general, then a complexed, sorbed, or otherwise transformed species.

Although organism toxicity is often the focal point for impact of chemicals on aquatic systems, there is a variety of other concerns that must be considered in evaluating the environmental impact of a chemical. Among these is the bioconcentration of the chemical, that is, its effects on higher trophic levels, including man, that would use these organisms as a food source.

Other areas of concern for chemicals in aquatic systems that should be evaluated under the biological testing for hazard assessment include taste and odor production for domestic and industrial water supplies, stimulation of growth of excessive amounts of certain organisms such as algae by aquatic plant nutrients, as well as a whole host of aesthetic effects such as color, turbidity, and floating debris.

Environmental Chemistry-Fate in Aquatic Systems. Environmental chemistry-fate for aquatic systems considers for all modes of input, including solid waste disposal sites, the transport and transformation of the chemical of concern and its potentially significant transformation products, from its point of entry to the aquatic system to its final disposition in the water of concern or its exit from the system. Environmental chemistry-fate also considers the chemical processes that influence the form(s) (chemical and physical) of the contaminant and its transformation products in each of the major components of the environment. For example, for the aquatic environment, it is necessary to evaluate the forms and concentrations of each form in true solution (dissolved), associated with particulate matter (such as erosional materials and organic detritus that are suspended in the water column and deposited in the sediments), and contained upon or within aquatic organisms. There is also the potential for some highly volatile compounds to be transported to or from gas bubbles in the water column. Few chemicals are completely conservative (nonreactive) in the environment, i.e., whose concentrations in the environment change only as a result of physical processes of dilution and dispersion. Most chemicals undergo a variety of transformations, the majority of which can have a pronounced effect on the environmental concentrations of the toxic forms of the contaminant.

Major types of reactions that commonly occur in the aqueous environment were previously cited. Sorption reactions can be divided into several categories. One is biotic uptake of the chemical where associated transport and transformation within the aquatic organism must also be considered. Generally included within biotic uptake are those reactions that take place outside of the cell or organism involving extracellular enzymes. Another category of sorption is abiotic sorption, association of the contaminant with particulate matter present in aquatic systems such as clay particles, detrital minerals, organic detritus, and iron and aluminum hydrous oxides. A special case of absorption involves the uptake and release of contaminants from the aquatic system to the atmosphere.

One of the potentially important aspects of an environmental chemistry-fate model for aquatic systems is the interaction between the dissolved contaminant and suspended and deposited sediments. Many of the chemicals having the greatest potential hazard to the environment are highly hydrophobic and, therefore, tend to become strongly attached to particulate matter within the water column and within the sediments. Some of the most important forms of this particulate matter as discussed previously are the hydrous metal oxides of iron and aluminum. Lee (Ref. 17-10, 17-11) has discussed the role of iron hydroxide in influencing the behavior of chemical contaminants in aquatic systems.

Each of the above-mentioned transformations can be described by chemical thermodynamics and kinetics, whereby a position of equilibrium (thermodynamics) is obtained for a particular environmental system. The position of equilibrium is governed by the characteristics of the system, such as temperature, light, mixing-turbulence, suspended solids, and a variety of chemical properties, such as pH, gross and individual organic content, redox (oxidation-reduction) conditions, and, for air-water transfer, Henry's constant. The equilibrium positions are generally described by mass law relationships involving a thermodynamic or quasi thermodynamic equilibrium constant.

While many chemical reactions proceed rapidly, being essentially instantaneous from an environmental impact point of view, there are many reactions that are significant in aquatic and other environmental systems, for which the rates are sufficiently slow to require consideration of their chemical kinetic properties. For these types of reactions it is necessary to

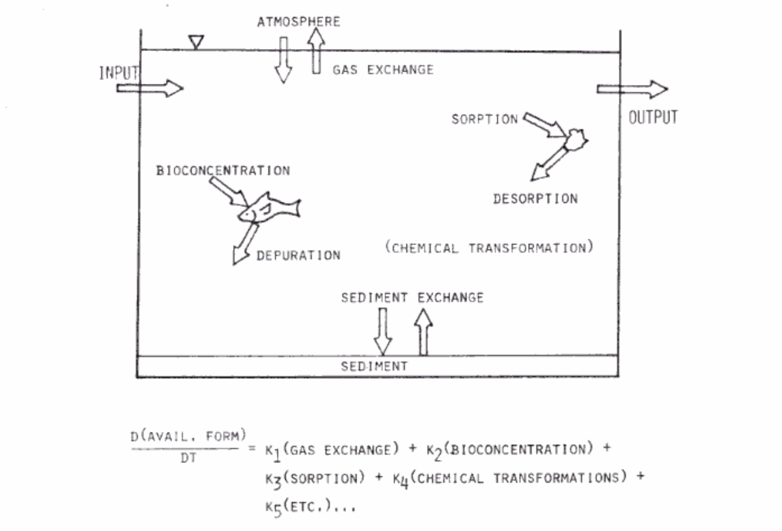


Fig. 17-3. Environmental chemistry-fate model. ***Source*****: Lee *et al.* (Ref. 17-6).**

Develop chemical kinetic-rate expression, a differential equation with a rate constant multiplied by the activities of the chemical species that are involved in limiting the rate of reaction.

Figure 17-3 presents a generalized model describing the environmental chemistry for a chemical contaminant in an aquatic system. To mathematically represent this model requires the development of a series of differential equations that, when solved simultaneously, provide a description of the distribution of the chemical in various forms and in the various parts of the environment that can interact with aquatic systems.

It should be emphasized that, for large aquatic systems, there exists, between the point of entry of the contaminant and its ultimate fate, a concentration gradient, that is governed by physical processes of advection and mixing. Therefore, Fig. 17-3 should be modified in general to show this component of the environmental chemistry-fate model that, as noted above, can be the most important component describing the behavior of many chemicals in aquatic systems.

The model described in Fig. 17-3 is generally termed a dynamic model in which there is an attempt to develop differential equations that describe the overall processes involved. The modeler must determine which pathways are significant in transporting and transforming a particular contaminant within the water body of concern such that it can cause degradation of the water quality (beneficial use) of the water. The prescribed model is based primarily on the characteristics of the chemical and how it interacts with environmental compartments rather than being based on a particular system. Other approaches taken for environmental chemistry-fate modeling and their shortcomings are discussed by Lee *et al.* (Ref. 17-6).

A key component of any environmental chemistry-fate modeling effort is the proper verification of the model. No model should be used to make management decisions unless it has been verified; that is, it must have been demonstrated to predict, with adequate reliability, the concentration of the contaminant of interest in various environmental compartments under altered load conditions, with-out having had the rate constants retuned.

The outcome of the environmental chemistry-fate modeling should be an estimate of the expected concentrations of the potentially hazardous forms of the contaminant of concern in the various aquatic environmental components. This, combined with information on the expected residence times of various types of organisms in the compartments, can be used to estimate the durations of exposure of organisms in each component to the available forms of the contaminant. During the process of making an assessment of the hazard associated with the in-put of solid waste disposal site-derived contaminants, the predicted concentration-duration of exposure coupling is compared with the "no effect concentration-duration of exposure" relationship developed for the chemical in question in the toxicological portion of the hazard assessment. Figure 17-4 shows schematically a variety of the possible couplings and their relationship to the area of "impact." The hatched area in this figure represents the area shown in Fig. 17-2 in which the combination of duration of exposure and concentrations of available forms of a contaminant is sufficient to have an adverse effect on aquatic organisms and/or water quality. The numbered curves (1-5) show results that could be obtained through environmental chemistry-fate modeling, where a combination of dilution and chemical reactivity bring about a certain concentration-duration of exposure relationship. Curve 1 represents that coupling typical of spill situations, where there is toxicity for a short time associated with the point of entry before any reactions or dilution takes place. This might also be the situation associated with the mixing zone for a particular discharge.

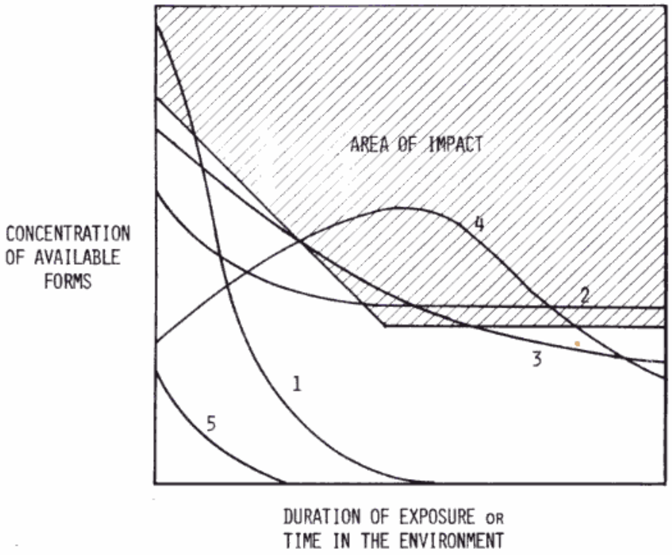


Fig. 17-4. Typical concentration of available forms–duration of exposure relationships in aquatic systems. *Source*: **Lee** ***et al.*** **(Ref. 17-6).**

Curve 2 in Fig. 17-4 is a case where the chemical does not show any acute toxicity at levels that are normally found in the environment but is chronically toxic either to the organism or to higher forms that may use the organism as food. PCBs, DDT, and mercury would all fall into this category. Because of the bioaccumulation of some of these types of chemicals within the higher trophic level fish, there is a potential for harm to man and other animals that use fish as a source of food.

Curve 3 represents the type of situation that might be associated with municipal wastewater discharges that contain ammonia, where for short durations of exposure there is no impact. However, for some receiving waters there is a sufficiently large intermediate zone at some distance from the point of discharge where there would be toxicity to fish that reside in the area. Eventually the ammonia would be oxidized or diluted to nontoxic levels farther down the stream from this zone.

Curve 4 is representative of the situation where there is a transformation of the chemical added to the system that causes it to be more toxic as it goes down-stream. Eventually it is either diluted or detoxified through other reactions. An example of this type of situation is one involving the addition of a complexed heavy metal to the environment where the complex is biodegradable, releasing the toxic form of the heavy metal at some distance downstream in sufficient concentrations to be toxic to aquatic life in that region.

Curve 5 is the case that exists for most chemicals for which there is sufficient treatment or controlled use so that there is no toxicity associated with it, either acute or chronic. It is important to emphasize that while the various conditions shown in Fig. 17-4 are represented by smooth curves, for any real systems there are fluctuations about the mean concentration that can be of significance in affecting water quality.

The contaminant input from solid waste disposal sites can follow any of the patterns shown in Fig. 17-4. It is expected that if there is toxicity from this source, it will be localized near the point of entry, since it is not likely that the rate of input and concentrations of contaminants would be sufficient to cause widespread contamination. An exception to this would be contaminants with high volatility, such as PCBs, which are transported in significant quantities from solid waste disposal sites to the atmosphere and then to aquatic systems through precipitation and dustfall. It is expected that solid waste disposal sites would contribute greater amounts of contaminants during wet periods than dry periods. These seasons would also in general be the periods in which the greatest amount of dilution would be available in receiving waters.

It is important in assessing the significance to water quality of contaminants associated with solid waste to focus on the amounts and forms of contaminants that enter the first water body in which there is an aquatic resource recognized to be of beneficial use to man, e.g., a fishable stream or lake, rather than on an intermittent flow system in which there is no significant resource for man. High concentrations of contaminants in soils, groundwater, or surface runoff immediately adjacent to the solid waste disposal contaminant input may not be of significant harm to aquatic life, especially fisheries in receiving waters where there is concern about fisheries or other aspects of water quality.

For existing solid waste disposal sites or where the same kinds of wastes will be placed in similar geological formations adjacent to existing sites, it may be most cost-effective and reliable to install a series of monitoring wells and sample them and surface runoff in order to assess the likelihood of environmental "contamination" and the impact on groundwater quality. This type of assessment should be conducted in accord with the hazard assessment approach outlined by Lee *et al.* (Ref. 17-6). While their approach specifically discusses application to surface waters, it can be adapted to assessing the hazards to municipal and agricultural users of groundwater supplies. In making this evaluation, it is important to consider the possible transformation and dilution between the point of sample collection and point of water quality concern. As discussed by Lee (Ref. 17-12), it is important to take a much more conservative approach toward groundwater contamination than generally needs to be taken for surface waters. Once ground-waters have been contaminated to the point at which their beneficial use in impaired, they are generally much more difficult to restore than surface waters.

17-3.4 Tiers of an Aquatic Hazard Assessment

A hazard assessment should be conducted in a series of levels or tiers of increasing sophistication and detail, with a decision point at the end of each tier. In each tier an estimate is made of some aspect of the aquatic toxicity of the chemical and also of the expected environmental concentrations (environmental chemistry-fate) of the chemical. These two components are compared to make a decision regarding the potential aquatic environmental impact. Decision choices at the end of each tier's testing could be (1) to not allow disposal of the particular solid waste in the place and manner evaluated because of excessive expected hazard, (2) to restrict such disposal or require treatment of waste to reduce expected environmental hazard to an acceptable level, (3) to proceed with disposal as evaluated, as the expected hazard is acceptable, or (4) to continue testing to better define the potential environmental impact. As the more sophisticated tests tend to be much more expensive, decision to conduct addition testing tiers must be weighed against (1) the cost of assuming a significant hazard does in fact exist and thus of providing the treatment or finding alternative disposal necessary to reduce the environmental hazard, and (2) against the costs, both social and economic, of not allowing production of certain materials.

As successive tiers of testing are conducted, precision and accuracy of the estimates of the contaminant's toxicology, and the environmental concentrations of the contaminant and its transformation products as well as the reliability of the decision made should be improving. Figure 17-5 illustrates this concept.

Because of the tiered structure of this hazard assessment approach, the testing done in the early tiers can detect both those contaminants that would be highly hazardous as a result of their estimated environmental concentration being considerably above the "no-effect" level estimated through the aquatic toxicology testing, as well as those contaminants for which the expected concentrations are well below "no-effect" levels. The situations of greatest concern are those in which there is some overlap in confidence levels (as shown in Fig. 17-5) or a relatively small difference between the estimated environmental concentration and the maximum "no-effect" concentration. Under these conditions continued testing is probably needed, as the reliability of the estimates of both the toxicological properties and environmental concentrations at the lower tiers are usually quite rough. However, as shown in Fig. 17-5, with more sophisticated testing in higher level tiers, it is possible to refine these error bars and thereby more clearly discern whether or not there is a potential impact in a particular system. While there may be considerable controversy regarding an appropriate magnitude of separation between the estimated environmental concentration of available forms and the "no-effect" level, this would typically be on the order of a factor of 10 to 100. There are some site-specific considerations that should be given in establishing the margin of safety that should be used in this type of evaluation.

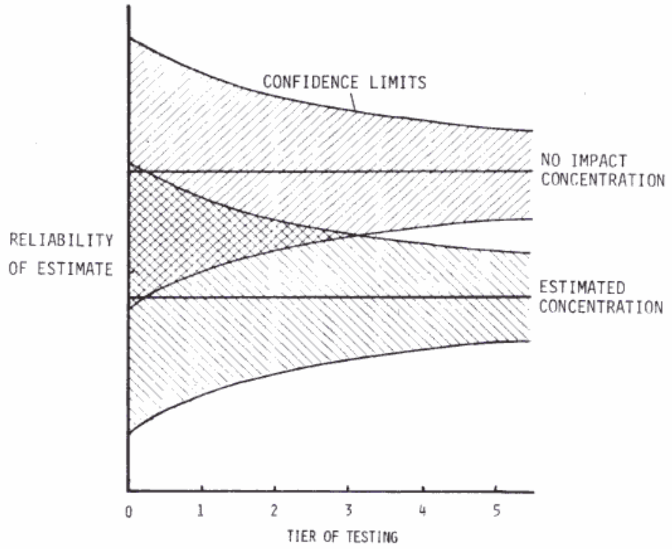
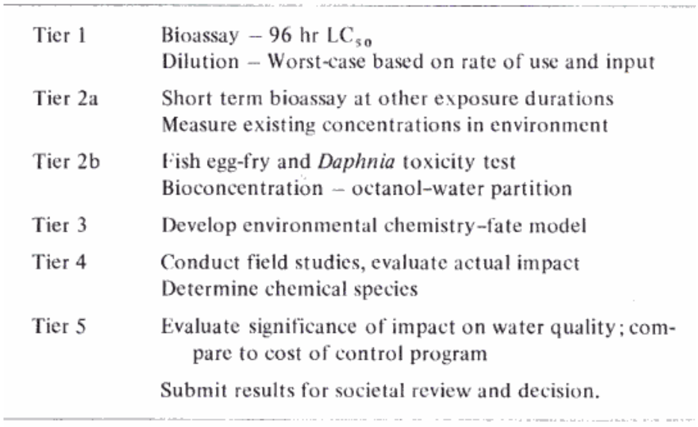


Fig. 17-5. Examples of increasing reliability with increasing testing. ***Source*****: Cairns** ***et al*****; (Ref. 17-5).**

The main reason for conducting a hazard assessment in tiers is that it is generally less expensive, more technically appropriate, and equally protective to evaluate the potential environmental impact to the degree necessary to make decisions on the degree of contaminant control required based on actual expected impact, rather than to treat routinely for worst case conditions in which it is assumed that the toxicity associated with a particular effluent or source extends for considerable time and distance from the point of discharge or that any concentration of contaminants above U.S. EPA water quality criteria or state water quality standards equivalent to these criteria represents a deterioration of water quality. This latter approach is the ultraconservative approach that, while providing environmental protection, will certainly result in the needless expenditure of large amounts of money for pollution control with little or no additional improvement in water quality beyond that provided using the hazard assessment approach. In the 1980s hundreds of millions to billions of dollars will be spent for pollution control in order to comply with the provisions of RCRA, Public Law 92-500, and the 1977 Amendments of this Clean Water Act. It is essential that all funds spent in the name of water pollution control be directed toward controlling water quality problems. The tiered hazard assessment approach provides a technically valid basis for ensuring that the expenditures made in this area provide the opportunity to result in the greatest possible improvement in water quality for funds expended.

Table 17-1 presents a summary of the types of toxicological and environmental chemistry-fate information that are needed for a generalized tiered hazard assessment program that could be used to assess the significance of the input of contaminants derived from solid waste disposal sites or any other source of contaminant for aquatic systems. Further information on testing requirements of each tier and the use of this information is provided by Lee *et al.* (Ref. 17-6).

TABLE 17-1. Environmental Hazard Assessment for Aquatic Systems



Tier 1	Bioassay – 96 hr LC_{50} Dilution – Worst-case based on rate of use and input
Tier 2a	Short term bioassay at other exposure durations Measure existing concentrations in environment
Tier 2b	Fish egg-fry and *Daphnia* toxicity test Bioconcentration – octanol–water partition
Tier 3	Develop environmental chemistry–fate model
Tier 4	Conduct field studies, evaluate actual impact Determine chemical species
Tier 5	Evaluate significance of impact on water quality; compare to cost of control program
	Submit results for societal review and decision.

Source: Lee *et al.* (Ref. 17-6)

17-4 CONCLUSIONS AND ACKNOWLEDGMENT

For a variety of reasons discussed in this chapter, the U.S. EPA's original approach for assessing the aquatic environmental hazard associated with solid wastes disposed of on land by conducting a single leaching test and comparing contaminant concentrations in the leachate multiplied by 0.1 to the U.S. EPA Red Book criteria, is not technically valid. The release of contaminants from solid wastes depends on many factors: characteristics of the chemical of concern, of other chemicals present, and of the particular disposal site. A site-specific leaching test must be conducted for each system of concern in order to estimate the concentrations and forms of contaminants likely to leave a waste disposal site. The studies conducted on the dredged sediment elutriate test can provide considerable insight into the test conditions that need to be evaluated for their appropriateness for representing solid waste disposal sites. Field studies must also be conducted in conjunction with the development of a laboratory leaching test, as was done for dredged sediment disposal, to verify its ability to predict contaminant leaching from solid wastes.

In interpreting the results of leaching tests, it is important that consideration be given to the behavior of the contaminants within the disposal site, as well as en route to a water body of concern. A contaminant can be greatly detoxified, or made less available to aquatic organisms, by many of the physical, chemical, and biological transformations that it undergoes in these systems.

Recently, a hazard assessment approach has been developed for aquatic systems that can be used in conjunction with the information on transport and transformation of the contaminant between the disposal site and a water body of concern, to assess the aquatic environmental hazard of contaminants associated with solid wastes disposed of on land. The investment of time and money in conducting a hazard assessment will be highly cost-effective in that it will provide a technically valid basis by which an environmentally protective solid waste contaminant management program can be designed, avoiding overdesign to cover worst-case conditions.

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