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Menzer & Nelson

Chapter 25

WATER AND SOIL POLLUTANTS

Robert E. Menzer and Judd O. Nelson

INTRODUCTION

The ultimate sinks for most chemicals produced and used by man are water and soil. Three-quarters of the earth's surface is covered by water, and the remainder that is not covered by asphalt or concrete is covered by soil. Although water and soil are usually considered as separate ecologic systems, one needs to realize that suspended soil particles in water represent an interface between the two systems and serve as a mechanism for contamination of the one by the other. In reality it is impossible to consider any component of the real world in isolation from any other, as illustrated in Figure 25-1. For our purposes, however, we shall consider the presence, fate, and effects of chemicals in water and in soil as separate systems, as far as that is possible.

Systems of water may be compartmentalized based on their natural occurrence and the use made of them. One may consider separately the naturally occurring bodies of water: marine systems, fresh water systems, and the interface between them, the estuarine systems. One may also consider these systems on the basis of the use made of water removed from them for drinking purposes or other domestic consumption. Water systems are also the recipients of the products of domestic and industrial sewage systems. Bodies of water, including rivers, lakes, ponds, and the ground water, are also the recipients of runoff from agricultural and urban areas, which greatly modifies their capability to support life and their usefulness for other purposes.

Although water can be ultimately purified to a specific, definite chemical entity, soil has no commonly accepted compositional definition. Soils are composed of inorganic and organic constituents. The inorganic are silt, sand, and clay in varying ratios. These inorganic particles are coated and admixed with organic constituents, living and dead. The behavior of soil to a major degree is determined by the size and shape of the particles of which it is composed. Soil particles range in size from less than 0.002 mm to about

2.0 mm in diameter. Soils are classified according to particle size ranges as follows: clay, <0.002 mm; silt, 0.002 to 0.02 mm; fine sand, 0.02 to 0.20 mm; and coarse sand, 0.2 to 2.0 mm. The most important use of soil is for agriculture. Soil is the ultimate support of man's sources of most food and much fiber. In addition, the soil has been the final disposal site for much of the industrial and urban waste generated by man's societies.

The interface between soil and water is an intimate one. Virtually all water systems contain suspended soil particles, and virtually all soil contains at least a small amount of water. The sediment that is the end product of soil erosion is by volume the greatest single pollutant of surface waters and is the principal carrier of most pollutants found in water. In a joint study the United States Department of Agriculture and the Environmental Protection Agency have estimated that potential annual water erosion losses range from negligible to more than 100 tons of soil per acre. About 20 percent of the 438 million acres of crop land in the United States averages more than 8 tons of soil loss per acre per year; 30 percent averages less than 3 tons; and the other 50 percent between 3 and 8 tons (Stewart *et al.*, 1975). In fact, the sedimentary materials in water resulting from soil erosion accumulate more than 700 times more than those derived from sewage discharges (Weber, 1972). Thus, any treatment of the environmental toxicology of soil and water must consider each as a two-phase system, each containing the other and interacting through the water-sediment system.

Sources of Chemicals in the Environment

Chemicals in the environment may be classified in a variety of ways. In this chapter we have chosen to consider chemicals primarily according to their use; secondarily, by chemical properties. Thus, we will consider chemicals by their source as follows: (1) industrial, (2) agricultural, (3) domestic and urban, and (4) naturally occurring. No matter what use is made of chemicals, contamination of the environment may be either

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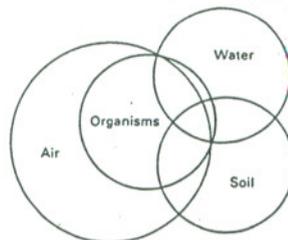


Figure 25-1. Overlapping relationships of environmental compartments.

from point sources or from nonpoint sources. The results of point source pollution are generally easy to identify and the remedies are frequently more attainable. Nonpoint source pollution, on the other hand, is generally less dramatic in its initial effects, but is more difficult to contain or correct.

The production, use, and disposal of industrial chemicals all lead to contamination of soil and water. Production activities lead to soil and water contamination when by-product chemicals are not properly conserved during manufacturing processes. For example, in various smelting operations toxic chemicals present in ores may not be properly controlled. Naturally occurring arsenic in copper ores, for example, frequently finds its way into soil and water. Accidental spillage of industrial chemicals may also result in contamination, sometimes dramatically, of soil and water. Careless manufacturing practices in a small chemical firm in Hopewell, Virginia, led to serious contamination of the James River and Chesapeake Bay by the pesticide Kepone. Even though these practices have now ceased, the contamination of the estuarine system will be present for many decades. Another example is the contamination of the Ohio River with carbon tetrachloride resulting from an accidental dumping of the material from a chemical plant. Such incidents of point source contamination of water can generally be prevented or controlled by the appropriate use of technology. The result, however, of not controlling such point source pollution is frequently a very high cost for decontamination, where that is even possible, and frequently both acute and chronic detrimental effects on organisms.

The use of chemicals for their intended purpose often leads to contamination, sometimes undesirably, of soil and water. Lead contamination of soils and occasionally water near highways results from the use of tetraethyl lead as an anti-

knock component of gasoline for automobiles. Although a commitment has been made to reduce the use of this compound in gasoline, the many years during which it was used and the nonpoint source nature of the contamination have resulted in concentrations of lead that will remain for many years in soils and water. A chemical that is intentionally added to water for therapeutic purposes is fluorine. The use of water fluoridation to prevent tooth decay is well known and has been practiced in the United States for many years. Excessive concentrations of fluorine, however, can result in undesirable effects in teeth, manifested primarily by their mottling and discoloration. Careful attention must be paid to the use of fluorine to prevent overfluoridation with its undesirable side effects.

The disposal of industrial chemicals following their use presents a major problem in several industries. Detergents used in clothes laundering are discharged into sewage systems and ultimately into rivers, lakes, and streams. Phosphate detergents then serve as nutrients for algae and other organisms that can cause major difficulties in these bodies of water. The green scum resulting from algal blooms is a familiar sight in some areas. The contamination of rivers resulting from discharge of water containing organic mercurials used in paper manufacturing presents a problem in some local situations. Other chemicals resulting from paper making can also present serious water pollution problems. Asbestos tailings resulting from mining operations have also contaminated water systems in some parts of the United States, and this has resulted in concern over the potential health effects of the material that then finds its way into drinking-water systems.

The use of chemicals in agriculture results in contamination of soil and water through the direct use of pesticides and fertilizers. Pesticides are, of course, applied directly to the soil in some cases to control insects, weeds, and plant diseases. Some of these chemicals can persist for many years and thereby cause concern about their potential movement from soil into water systems and from both soil and water into organisms that live in and on water and soil. The effects of pesticides in the food chain are now generally familiar. Likewise, fertilizers applied to the soil to promote plant growth and productivity can leach or run off from soil and find their way into natural water systems, causing an upset in the ecologic balance to the degree that organisms living in those systems can be either enhanced or otherwise affected.

The domestic and urban use and disposal of chemicals also result in the contamination of soil and water. Domestic wastes are concentrated in

sewage systems and landfill operations. Frequently, large buildups of heavy metals occur as a result. Pesticides and fertilizers used in suburban and some urban situations for lawn and home garden purposes or pest control in other situations also are serious problems when improperly used. Detergents may also cause difficulties as referred to above. Recently, the discovery that the process of purifying water can result in the chlorination of certain small organic chemicals to produce chlorinated hydrocarbons that are potential carcinogens has generated concern. In some parts of the country concentrations of such chemicals above levels considered to be safe have been found in drinking-water systems.

Finally, metals, minerals, and plant or animal toxins are found in the environment as natural components of water and soil systems. Although they have always been there and always will be, man's activities frequently result in excessive production or movement of such chemicals found naturally occurring in the environment and can result in concentrations detrimental to man or other organisms. Furthermore, the possibility of interaction of synthetic chemicals and pollutants with naturally occurring metals, minerals, and toxins must be considered.

Transport, Mobility, and Disposition

The fate and distribution of chemicals in the environment are determined by several variables that can interact in numerous ways. An analogy between pharmacodynamics and chemodynamics can be drawn to illustrate some basic similarities in each approach. First, one must appreciate the physicochemical properties of a chemical, such as water solubility, lipid solubility, partitioning behavior, vapor pressure, pKa

for ionic species, chemical stability, etc., if one is to predict the behavior of a chemical in a system—be it man or an ecosystem. Second, the processes that act within the system must be considered. Transport, via serum proteins versus suspended sediments; circulation, via the circulatory system versus the hydrologic cycle; degradation, in liver versus soil microorganisms; and excretion, via urine, feces, and expired air versus dilution in water and air to nondetectable levels or deposition in ultimate sinks such as deep ocean sediments, are all processes that act on chemicals to determine the mobility and final disposition of a chemical in a system. The analogy can be carried one step further to include target organs or tissues affected by the chemical in comparison with the susceptible species of an ecosystem. The fundamental difference in this consideration is one of scale, in both time and dimension, which then requires models of varying scale. Mathematical transport models for predicting the fate of chemicals remain primitive and approximate at best; the reader is referred to a National Academy of Sciences (1975) report on the subject for further information and references.

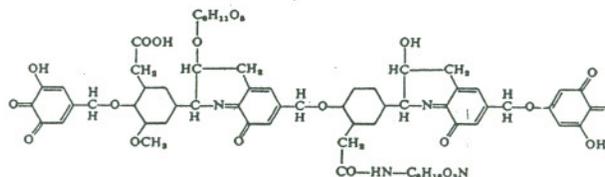
Water Solubility. The water solubility and latent heat of solution are critical properties of a chemical that affect its environmental fate. Many environmental toxicants are hydrophobic, having solubilities in the parts-per-million (ppm, mg/l) to parts-per-billion (ppb, $\mu\text{g/l}$) range. Reported solubility values vary with the method used for determination (Gunther *et al.*, 1968). Water solubilities are affected by pH (for ionizable chemicals), presence of dissolved salts and organics, and temperature.

Soil Adsorption. Adsorption to particulate matter is a major mechanism by which chemicals

are removed from solution. Adsorbent materials in soils and sediments can be divided into clay minerals and soil organic matter. Clay minerals include various hydrous silicates, oxides, and layer silicates. The clay minerals have been extensively studied and are characterized by physical structure or layering type, either 1:1 or 2:1, swelling ability, cation-exchange capacity, and specific surface (m^2/g) (Weber, 1972). These parameters are important considerations in the behavior of organic cations, polar organic molecules, and metal ions in soils. High specific surface is associated with small particle size; therefore, the colloidal fraction of the soil is a dominant factor in chemical-soil interactions. Cation exchange capacity of the inorganic fraction is a function of the magnitude and distribution of the structural charge. Exchangeability is dependent on the adsorbed cations, usually sodium, potassium, or calcium, and the nature of the replacing cations.

The water associated with clay plays an important role in defining its characteristics. Adsorbed water on clay surfaces is more ordered than free water. Water on the clay surface may also be more ionized than otherwise. Thus, the hydrogen ion concentration of the clay surface is high. The effect of pH on the adsorption of classes

pletely decomposed plant and animal material, and (2) humic substances, which are more or less completely altered or resynthesized materials. The former serve as a source for the latter.¹ Non-humic materials include well-known organic chemical groups with definite characteristics: proteins, carbohydrates, organic acids, sugars, fats, waxes, resins, lignins, pigments, and low-molecular-weight compounds. These materials comprise 10 to 15 percent of the soil organic matter. Their composition and residence times are quite variable. Humic substances account for 85 to 90 percent of soil organic matter and their nature is not well understood. Humic substances are fractionated to give fulvic acid, which is soluble in both alkali and acid; humic acid, which is soluble in alkali but not in acid; and the humin fraction, which cannot be readily extracted with cold alkali. Humic acid and fulvic acid are aromatic polymers with molecular weights that range from 5,000 to 100,000 and from 2,000 to 9,000, respectively. Functional groups that have been identified on humic substances are carboxyl, phenolic hydroxyl, alcoholic hydroxyl, carbonyl, and methoxy. Heterocyclic rings with oxygen and nitrogen atoms are also present. A hypothetical structure for humic acid has been proposed by Kononova (1966) as follows:



of chemicals has been summarized by Hamaker and Thompson (1972) (Table 25-1).

Adsorption data for chemicals in soils is usually expressed by the Freundlich isotherm, $x/m = KC^n$; x/m is the amount of chemical sorbed per weight of the adsorbent, C is the equilibrium concentration of the chemical, and K and n are constants. The constant K represents the extent of adsorption while the value n sheds light on the nature of the adsorption mechanism and the role of the solvent, water.

Soil organic matter usually ranges from 0.1 to 7.0 percent and serves as the most important sorptive surface for nonionic chemicals. Above a few percent organic matter, all the soil mineral surfaces are effectively blocked and thus no longer function as adsorbents. Soil organic matter can be divided into two main groups: (1) non-humic substances, which are fresh or incom-

Table 25-1. CLASSES OF MATERIALS RELATED TO THE EFFECT OF pH ON ADSORPTION*

CLASS	EXAMPLE	pK _a	MOLECULAR FORM		pH Effect
			Low pH	High pH	
Strong acid	Linear alkylsulfonates	3.7	Anion	Anion	Small
Weak acid	Picloram		Free acid	Anion	
Strong base	Diquat		Cation	Cation	Decrease at very low pH (18 N H ₂ SO ₄)
Weak base	Ametryne		Cation	Free base	Increasing adsorption to pH approx. pK _a and then decrease
Polar molecules	Diuron		Nonionized	Un-ionized	Small
Neutral molecules	DDT	Nil	Nonionized	Un-ionized	Probably none

* From Hamaker, J. W., and Thompson, J. M.: Adsorption. In Goring, C. A. I., and Hamaker, J. W. (eds.): *Organic Chemicals in the Soil Environment*, Vol. 1. Marcel Dekker, Inc., New York, 1972. Reprinted by courtesy of Marcel Dekker, Inc.

lates with pesticide volatilization, but is due to desorption of chemicals from soil adsorption sites by water molecules and the mass flow of chemical to the soil surface by the "wick effect." This phenomenon has been noted with chemicals such as 2,4-D esters, thiocarbamates, triazines, organochlorine insecticides, and *N*-methyl-carbamates. Volatility of organic chemicals from water increases with decreasing water solubility. As a result, a chemical with both low vapor pressure in the solid phase and very low water solubility would be much more volatile from aqueous solution than might be expected. DDT is again the example.

Partitioning. Many chemicals have low water solubility but high solubility in nonpolar solvents (lipophilicity). The partition coefficient as a measure of these properties is often determined in a system of *n*-octanol/water. The relationship between water solubility and partition coefficient is illustrated in Figure 25-2. The importance of partitioning behavior of chemicals lies primarily in the phenomenon of bioaccumulation (bio-magnification or bioconcentration). Organisms in contact with a solution of chemical that has a high partition coefficient will act as the nonpolar phase of the binary system and accumulate it through a partitioning process.

Bioaccumulation. Bioaccumulation is different from other environmental transport processes

because it concentrates rather than diffuses the chemical in question. This concentration effect is expressed as the ratio of the concentration of a chemical in the organism to that in the medium (usually water). The two properties of a chemical that are responsible for high bioaccumulation ratio values are (1) high partition coefficient, i.e., lipophilic, and (2) recalcitrance toward all types of degradation. Bioaccumulation ratios have been determined for a variety of environmental chemicals in laboratory model ecosystems and correlate well with the *n*-octanol/water partition coefficients (Fig. 25-2).

Degradation. Transformations of chemicals in soil and water occur by chemical, photochemical, and biochemical reactions. Degradation results in the true "disappearance" of a chemical's molecular form, as opposed to transport processes, which merely move chemicals from one environmental compartment to another. However, it must be recognized that transport processes that move chemicals to ultimate sinks, such as deep ocean sediments, for all practical purposes do remove chemicals from the environment.

Chemical transformations are classified as hydrolyses, oxidations, reductions, nucleophilic substitutions involving water, and free radical reactions. These reactions may be catalyzed by the presence of metal ions, metal oxides, clay

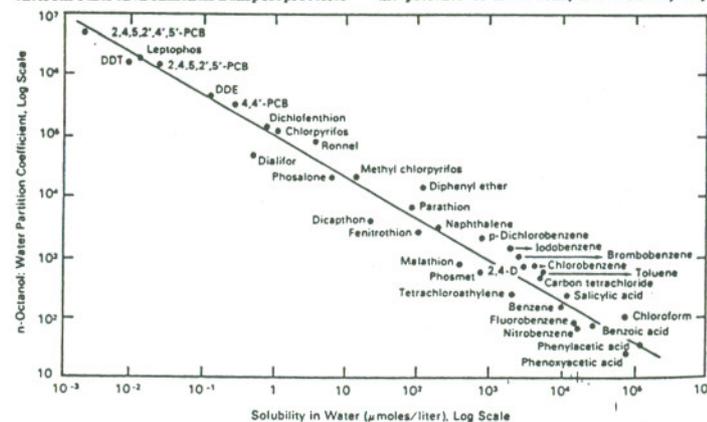


Figure 25-2. Relationship between water solubility and *n*-octanol/water partition coefficient. (From Freed, V. H.; Chiou, C. T.; and Hague, R.: Chemodynamics: transport and behavior of chemicals in the environment—a problem in environmental health. *Environ. Health Perspect.*, 20:55-70, 1977.)

surfaces, organic compounds, and organic surfaces. The pH of solutions and the effective pH of clay surfaces, which may be quite different from the surrounding aqueous environment, can significantly influence rates of degradation. Other obvious conditions that affect degradation rates are temperature, moisture content in soils, and other environmental processes that alter chemical concentrations. The kinetics of degradation rates are dependent on the mechanism of degradation. Some degradative processes follow first-order kinetics, while others are best described by a "hyperbolic rate model" (Hamaker, 1972).

Photochemical reactions of chemicals occur in air and water but are probably of little or no significance in soils. For a chemical to undergo a photochemical reaction, it must absorb light energy from an appropriate portion of the spectrum or have the light energy transferred through an intermediate substance known as a sensitizer. Ultraviolet light (4- to 400-nm wavelengths) has sufficient energy to break existing chemical bonds, but light above 450 nm, which represents an energy of 65 kcal/mole, is usually not sufficient to initiate reactions. Light of wavelengths shorter than 295 nm does not reach the earth's surface in appreciable amounts. The principal reactions are photo-oxidations and photoreductions which proceed through light-formed free radicals and which then react with molecular oxygen or abstract hydrogen from organic compounds, respectively.

Biologic reactions of chemicals in soil and water are mediated primarily by microorganisms. Microorganisms are quite versatile when confronted with foreign chemicals. The major reactions involved are dehalogenation, hydrolysis, oxidations, reductions, conjugations, and methylations. They are also very important in the natural cycles of many elements, such as mercury and arsenic. These natural cycles can be disturbed by introduction of various forms of metals and can increase formation of toxic species, e.g., methylmercury. The types and rates of microbiologic reactions are determined by the microbial ecology of any given system. Thus, pH, temperature, redox potential, nutrient availability and microbial interactions will affect the microbial degradation of a chemical.

Chemodynamics. As we have seen above, there are numerous routes by which chemicals enter the environment and many factors to consider in understanding their behavior once they are there. Much of what is known about chemodynamics is derived from studies of pesticides and, to a lesser extent, industrial chemicals and heavy metals. Certainly, pesticide applications, sewage sludge disposal, and industrial waste effluents each present different starting points for

a consideration of chemodynamics. We shall deal with environmental processes in the following sections and attempt to relate the (1) physicochemical properties of a chemical and (2) the environmental conditions that serve as modifiers of the processes. Each process has a rate that describes the transport from one component to the next and a rate that describes the degradation of the chemical in question. A complete analysis of all of the rates for entry, transport, and degradation of a chemical will describe its ultimate fate in the water and soil.

PESTICIDES

The major classes of pesticides have been grouped as "nonpersistent" or "slightly residual," "moderately persistent" or "moderately residual," or "persistent" or "highly residual" (Harris, 1969; Kearney *et al.*, 1969). Persistence times reflect the time required for 75 to 100 percent disappearance of pesticide residues from the site of application. Nonpersistent pesticides have persistence values of 1 to 12 weeks; moderately persistent pesticides, 1 to 18 months; and persistent pesticides, 2 to five years. Persistence times vary with environmental conditions and the generalizations about the classes are subject to several exceptions by individual pesticides within the class (Fig. 25-3).

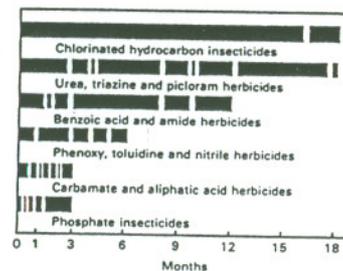


Figure 25-3. Persistence in soils of several classes of insecticides and herbicides. (From Kearney, P. C.; Nash, R. G.; and Isensee, A. R.: Persistence of pesticide residues in soils. In Miller, M. W., and Berg, G. G. [eds.]: *Chemical Fallow*. Charles C Thomas Publisher, Springfield, IL, 1969.)

Persistent Pesticides

Chlorinated Hydrocarbon Insecticides. This group of chemicals includes DDT, TDE (a major metabolite of DDT), methoxychlor, and related chemicals; the cyclodiene insecticides,

for inorganic mercury to methyl mercury under ideal conditions is less than 1.5 percent per month (Jensen and Jernelov, 1969).

Little or no methyl mercury is found in sediments. Conversion of inorganic mercury to methyl mercury results in its desorption from sediment particles at a relatively fast rate. Demethylation by sediment microorganisms also occurs at a rapid rate when compared to methylation. Methyl mercury released in surface waters can undergo photodecomposition to inorganic mercury. However, methyl mercury can also be bioaccumulated by plankton algae and fish. In fish, the rate of absorption of methyl mercury is faster than that for inorganic mercury, and the clearance rate is slower with a net result of high methyl mercury concentrations in the muscle tissue. Selenium, which is present in seawater and seafood, readily complexes with methyl mercury and is believed to have an important protective action against the toxic effects of methyl mercury. In summary, the danger of methyl mercury poisoning, as occurred in Minimata, arises from direct methyl mercury contamination rather than methylation of environmental sources of inorganic mercury.

Cadmium. Cadmium has long been recognized as a toxic element. Its importance as an environmental contaminant was demonstrated in the outbreak of *itai-itai* disease caused by smelter wastes that contaminate rice paddies (see Chap. 17). Cadmium deposits are found as sulfides with zinc, copper, and lead deposits, and cadmium is recovered as a by-product of smelting processes for those metals. A major environmental source of cadmium is vapor emissions that contaminate surrounding soil and water through fallout during smelting. Natural soil concentrations of cadmium are less than 1 ppm and average about 0.4 ppm. Sewage sludge is often contaminated with cadmium, which can then concentrate in plants grown on contaminated soils. The problem of heavy metal contamination, especially cadmium, has been one of the most serious concerns impeding the use and disposal of domestic sewage sludge on agricultural lands. Cadmium also enters agricultural soils as a contaminant of phosphate fertilizers. There is some evidence for the leaching of cadmium in soils.

Cadmium concentrations in fresh waters are usually less than 1 ppb while sea water ranges from 0.05 to 0.2 ppb and averages about 0.15 ppb (Fleischer *et al.*, 1974). Higher concentrations of cadmium in surface water are usually due to metallurgical plants, plating operations, cadmium pigments, batteries, plastics manufacture, or from sewage effluent. Mine drainage and mineralized areas also contribute significantly to

cadmium fluxes in the Mississippi River in the Missouri-Tennessee-Kentucky area.

Drinking water in soft water areas can serve as a source of cadmium through corrosion of plumbing. However, this source is estimated to be small in relation to food intake. As in the association of selenium and mercury, there appears to be a protective effect with zinc and calcium against cadmium toxicity.

Lead. The use of lead, its mining, and its processing date back several centuries. Changing usage patterns rather than increased consumption determine present environmental inputs from man's use of lead. Batteries, gasoline additives, and paint pigments are major uses, but combustion of gasoline additives is the major source of environmental pollution by lead. This source is primarily an atmospheric pollutant that enters soil and water as fallout, a process determined by physical form and particle size. The net result is a buildup of lead near heavily traveled roads.

Lead enters aquatic systems from runoff or as fallout of insoluble precipitates and is found in sediments. Typical fresh water concentrations lie between 1 and 10 $\mu\text{g/l}$ while natural lead concentration in soil range from 2 to 200 ppm and average 10 to 15 ppm. Deep ocean waters, below 1,000 m, contain lead at 0.02- to 0.04- $\mu\text{g/kg}$ concentrations, but surface waters of the Mediterranean Sea and Pacific Ocean contain 0.20- and 0.35- $\mu\text{g/kg}$ levels (National Academy of Sciences, 1972). Drinking water concentrations of lead may be greatly increased in soft water areas through corrosion of lead-lined piping and connections. However, average drinking water intake is considerably less than food sources.

The biologic methylation of inorganic lead to tetramethyl lead by lake sediment microorganisms has been demonstrated (Wong *et al.*, 1975). However, the fate of this volatile, water-insoluble form of lead is unknown.

Arsenic. Arsenic is widely distributed in the environment. Man's input of arsenic into the global cycle occurs through smelting, coal burning, and the use of arsenical pesticides. Speciation of arsenic is an important consideration in the fate, movement, and action of this element. The chemical and biochemical transformations of arsenic include oxidation, reduction, and methylation, which affect the volatilization, adsorption, dissolution, and biologic disposition of the arsenic species involved.

Arsenic contamination of soils from point sources such as copper smelters or coal-burning power plants is easier to control than the dispersive use of arsenical pesticides, resulting in nonpoint source pollution. Various forms of

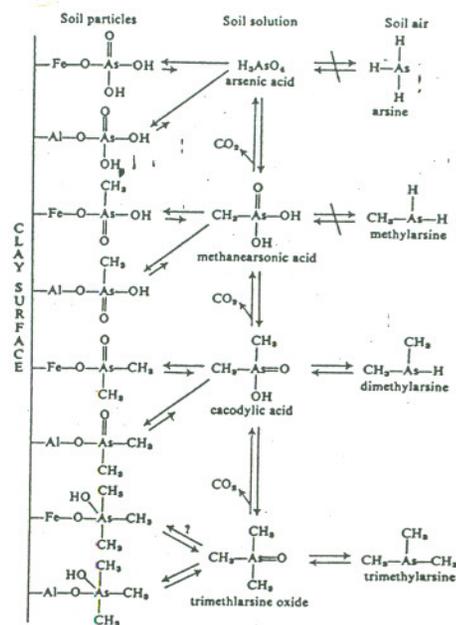


Figure 25-6. Dissolution and reactions of arsenicals within the soil environment. (From Woolson, E. A.: Fate of arsenicals in different environmental substrates. *Environ. Health Perspect.*, 19:73-81, 1977.)

arsenic are used as pesticides. Arsenic acid (H_3AsO_4) is a leaf desiccant used in cotton production, lead and calcium arsenates are insecticides, and organic arsenicals, which include methanearsonic acid and its sodium salts as well as dimethylarsinic acid (cacodylic acid), are used as postemergence herbicides. The transport of arsenic in the environment is largely controlled by adsorption/desorption processes in soil and sediments. Therefore, sediment movement is responsible for transfer of arsenic soil residues to their ultimate sinks in deep ocean sediments. The clay fraction, plus ferrous and aluminum oxides that coat clay particles, adsorbs arsenicals as depicted in Figure 25-6. The reactions of arsenicals in soil include oxidation, reduction, methylation, and demethylation. Conversion of arsenic to volatile alkylarsines leads to air transport loss from soils. The transformation processes of arsenic and its transport processes are intimately linked.

Arsenic concentrations in water are generally

much lower than in sediments. In Lake Michigan, the concentrations in water range from 0.5 to 2.3 $\mu\text{g/l}$ while sediment concentrations range from 7.2 to 28.8 mg/kg (Seydel, 1972). Inorganic arsenic exists in water in different oxidation states, depending on the pH and E_h of the water. Arsenate is apparently reduced by bacteria to arsenite in marine environments since the ratio of arsenite to total arsenic is much lower than is predicted thermodynamically. Methylation of arsenic occurs in both freshwater and marine systems and where arsenic is detected as arsenate, arsenite, methanearsonic acid, and dimethylarsinic acid (Braman and Foreback, 1973).

Bioaccumulation of arsenic species occurs readily in some aquatic organisms. Some seaweeds, fresh water algae, and crustaceans accumulate significant amounts of arsenic. Some arsenic in *Daphnia magna* and algae occurs as arseno analogs of phospholipids, indicating the mistaken accumulation and utilization of arsenate in place of phosphate. Crabs, lobsters, and

other marine organisms accumulate organo-arsenicals along the food chain.

Selenium. Selenium concentrations in natural waters depend largely on the occurrence of seleniferous soils. Average concentrations for selenium in natural waters are less than 10 µg/l, but can reach several hundred micrograms per liter in certain areas of some Western states. Dietary sources of selenium are usually more important than drinking-water sources.

Environmental redistribution of selenium through man's activities is due to copper smelting; lead, zinc, phosphate, and uranium mining and processing; manufacturing of glass ceramics and pigments; and burning of fuels.

Selenium can be methylated as also demonstrated for mercury, arsenic, lead, and tin. Sediment microorganisms are responsible for the production of dimethyl selenide and dimethyl diselenide from both inorganic and organic selenium compounds (Chau, 1976). The importance of volatile methyl selenide compounds in the biogeochemical cycling of this element is still uncertain.

INORGANIC IONS

Nitrate, phosphate, and fluoride are inorganic ions that have caused considerable concern over their environmental effects. With nitrates and fluorides the concern is principally human health, but nitrates and particularly phosphates also cause eutrophication of lakes and ponds, a process that is considered environmentally undesirable. Midsummer algal blooms are familiar sights in some parts of the United States.

Nitrates. Man has altered the nitrogen cycle through his agricultural and technologic practices; changing patterns in agriculture, food processing, urbanization, and industrialization have had an impact on the accumulation of nitrate in the environment. Intensive agricultural production has consumed an increasing amount of nitrogen-based fertilizers, particularly with corn, vegetables, other row crops, and forages. Nitrogenous wastes from livestock and poultry production as well as urban sewage treatment have contributed nitrogenous wastes to the soil and water environments. Nitrate and nitrite are used extensively for color enhancement and preservation of processed meat products. These practices inevitably lead to increased exposure of man and animals to significant nitrate levels in food, feed, and water (National Academy of Sciences, 1972).

The nitrate form of nitrogen is of concern because of the high water solubility of this ion and consequent leaching, diffusion, and environmental mobility in soil and water. Nitrate can contaminate ground water to unacceptable levels.

The current recommended limit for nitrate nitrogen in drinking water is 10 mg/l (45 ppm nitrate). In the Community Water Supply survey of the Bureau of Water Hygiene in 1969, the range of nitrate concentrations found was 0 to 127 mg/l. Nineteen systems, about 3 percent of those examined for nitrate, had concentrations in excess of the recommended limit (National Research Council, 1977). Nitrite is formed from nitrate or ammonium ion by certain microorganisms in soil, water, sewage, and the alimentary tract. Thus, the concern with nitrate in the environment relates to its conversion by biologic systems to nitrite.

Methemoglobinemia is caused by high levels of nitrite or indirectly from nitrate in humans. It results in difficulties in the oxygen transport system of the blood. Poisoning of infants from nitrate in well water was first reported in the United States in 1944. Cases numbering in the thousands have now been reported, mostly in rural areas, mostly involving poisonings in infants.

Of more recent concern is the production of nitrosamines in food by the reaction of nitrite with secondary amines. Other nitroso compounds can result from the analogous reactions of nitrites with amides, ureas, carbamates, and other nitrogenous compounds. Various dialkyl and related nitrosamines have been shown to produce liver damage, hemorrhagic lung lesions, and convulsions and coma in rats (Heath and McGee, 1962). *N*-Nitroso compounds represent a major class of important chemical carcinogens and mutagens. The various forms of cancer for which the environmental *N*-nitroso compounds are suspected to play a causative role occur after long latency periods and at relatively low absolute frequency in the general population. These factors make it difficult to establish cause-and-effect relationships between specific carcinogens and disease incidence (Wogan and Tannenbaum, 1975).

Phosphates. Although the principal problem of phosphates in the environment is not directly related to human health, there is considerable concern about the effects of phosphorus from various sources on water quality. There remains considerable disagreement and controversy about the principal source of phosphate found in water ecosystems. Some maintain that phosphate fertilizers are a major contribution to the levels of phosphates found in water while others claim that phosphate detergents are the major contribution (Griffith, 1973).

Phosphorus applied to the soil as fertilizer moves primarily by erosion because phosphate adsorbs strongly on soil particles. However, some soluble phosphorus compounds do move in

runoff water. The total phosphorus content of soils ranges from 0.01 to 0.13 percent (Stewart *et al.*, 1975). The phosphorus fertilizers applied as soluble orthophosphate soon revert to insoluble forms in soil. This conversion limits leaching and leads to a higher phosphorus concentration in sediments than in the original soil since phosphorus seems to be associated with finer particles. Control of phosphate pollution from agriculture will result from efforts to reduce erosion and sediment loss by modified agricultural practices.

The contribution of phosphorus to water from detergents is likely to be associated with the degree of urbanization. Efforts to control phosphates in water have concentrated on the detergent problem. Some states and local areas have restricted or banned the use of phosphate detergents completely. In some areas secondary treatment of sewage waste results in the precipitation and removal of phosphates from the effluent before discharge.

Phosphate is a major contributor to the eutrophication process in lakes and ponds (Thomas, 1973). The observer of a lake undergoing eutrophication notices first an extraordinarily rapid growth of algae in the surface water. Planktonic algae cause turbidity and flotation films. Shore algae cause ugly muddying, films, and damage to reeds. Decay of these algae causes oxygen depletion in the deep water and in shallow water near the shore. This rapid growth of algae gives rise to a number of undesirable effects on treatment of the water for consumption, on fisheries, and on the use of lakes for recreational purposes.

Fluorides. The beneficial effect of low levels of fluorides in preventing dental caries has led to the extensive use of fluoride in drinking water. The Safe Drinking Water Committee of the National Academy of Sciences has evaluated this practice as follows:*

Fluoride is found widely in water supplies, but the concentration is usually not great enough to be undesirable. The maximum concentration found for the 969 supplies studied in the 1969 Community Water Supply Survey was 4.4 mg/liter. Most supplies that were not intentionally fluoridated had fluoride concentrations less than 0.3 mg/liter.

A more extensive survey by the Dental Health Division of the U.S. Public Health Service showed more than 2,600 communities with a population of 8 million people had water supplies with more than 0.7 mg/liter of naturally occurring fluoride. Most of these communities are in Arizona, Colorado, Illinois, Iowa, New Mexico, Ohio, Oklahoma, South Dakota, and Texas. Of these, 524

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communities representing 1 million people had supplies with fluoride concentrations greater than 2 mg/liter.

Small amounts of fluoride, on the order of 1 mg/liter, depending on the environmental temperature, in ingested water and beverages, are generally conceded to have a beneficial effect on the rate of occurrence of dental caries, particularly among children.

Two forms of chronic toxic effects are recognized generally as being caused by excess in intake of fluoride over long periods of time. These are mottling of teeth enamel or dental fluorosis, and skeletal fluorosis. In both cases, it is necessary to consider the severity since the very mild forms are considered beneficial by some. The most sensitive of these effects is the mottling of tooth enamel, which, depending on the temperature, may occur to an objectionable degree with fluoride concentrations in drinking water of only 0.8-1.6 mg/liter. (These observations were made a number of years ago and there have been no recent studies to determine if these levels still cause mottling.) Apparently there has been little systematic investigation of the degree to which consumers of drinking water with several mg/liter of fluoride regard the resultant mottling as an adverse health effect.

Skeletal fluorosis has been observed with use of water containing more than 3 mg/liter. It now appears that there is some probability that objectionable dental mottling and increased bone density may occur in those with long-standing renal disease or polydipsia who consume water containing more than 1 mg/liter of fluoride for long periods of time. Increased bone density, however, has often been regarded as a beneficial rather than an adverse effect. (This therefore makes the implications of such changes unclear.) Intake of fluoride for long periods in amounts greater than 20-40 mg/day may result in crippling skeletal fluorosis.

Epidemiological studies where water is naturally high in fluoride have shown no adverse effects other than dental mottling except in rare cases. Controlled studies with fluoridation at the 1 mg/liter level have reported no instances of adverse effects. Available evidence does not suggest that fluoridation has increased or decreased cancer mortality rates.

ASBESTOS

Asbestos is a general term applied to a family of silicate minerals that have a number of properties in common that render them useful for several commercial purposes. These minerals are fibrous in structure and have electrical and thermal insulating properties as well as being sufficiently flexible that they can be woven into fabrics. The production and use of such materials has been described by Rosato (1959). Approximately 8% percent of asbestos use is in the construction industry, including cement products, floor tile, paper products, and paint and caulking,

with the remainder being used in transportation, textiles, and plastics industries (May and Lewis, 1970).

The definition of asbestos listed in the Glossary of Geology is as follows:^a

(a) a commercial term applied to a group of highly fibrous silicate minerals that readily separate into long, thin, strong fibers of sufficient flexibility to be woven, are heat resistant and chemically inert, and possess a high electric insulation, and therefore are suitable for uses (as in yarn, cloth, paper, paint, brake linings, tiles, insulation cement, fillers, and filters), where incandescent, nonconducting, or chemically resistant material is required.

(b) a mineral of the asbestos group, principally chrysotile (best adapted for spinning) and certain fibrous varieties of amphibole (example: tremolite, actinolite, and crocidolite).

The mineral fibers that comprise the asbestos group are the serpentine: chrysotile; and the amphiboles: actinolite, amosite (a cunningtonite-grunerite mineral), anthophyllite, crocidolite, and tremolite. Asbestos minerals are mined in Canada and the United States, where chrysotile accounts for about 95 percent of the production. Amosite and crocidolite make up most of the remainder. The largest chrysotile deposit in the world is found between Danville and Chaudiere, Quebec, Canada. Other deposits are found in northern Ontario, northern British Columbia, and Newfoundland in Canada, and in California, Vermont, Arizona, and North Carolina in the United States.

Asbestos is made up of fibrils of individual tubes of single crystals that bind together to produce a fiber. The size of the individual fibers varies greatly for the various minerals making up the asbestos group. Minimum fiber widths range between 0.06 μm for crocidolite to 0.25 μm for anthophyllite. Fiber lengths in general range between 0.2 and 2.0 μm . Occasional longer fibers up to 100 μm are found, although these are much rarer in the general environment than in occupational situations (Rendall, 1970).

Solubility is an important consideration in assessing the presence and impact of chemicals in soil and water. Asbestos minerals are soluble in acid solution to varying degrees (Choi and Smith, 1971). The isoelectric point of the various minerals differs widely; chrysotile has an isoelectric point of 11.8 while the amosite isoelectric point falls between 5.2 and 6.0 (Parks, 1967). As the pH of an aqueous medium falls below the isoelectric point, the charge of suspended asbestos particles will become more positive, thereby

^a From American Geological Institute: *Glossary of Geology*. The Institute, Washington, D.C., p. 41, 1972.

attracting other dissolved minerals that can interact with them. Therefore, the mobility, transport, disposition, and biologic properties of asbestos will vary widely depending on the mineral involved, the pH of the medium, and the presence of other materials with which the asbestos may interact.

A major difficulty in assessing the environmental impact of asbestos is the difficulty in detecting and analyzing it. Since asbestos is a very heterogeneous material, its detection is also difficult. A number of methods have been proposed for the identification and quantitation of asbestos in air, water, and biologic materials. Optical and electron microscopy, x-ray diffraction, and differential thermal analysis have all been proposed. Analytic problems are complicated by the difficulty of distinguishing between asbestos fibers and other fibers and particles of minerals that may be present in the same sample with them. The quantities present in environmental samples, furthermore, are generally quite small, and the particles present may exist in a wide range of sizes, making identification difficult and greatly complicating the quantitation of the mineral present. It is generally felt that transmission electron microscopy is the most satisfactory method for the detection of asbestos. A useful summary of the advantages, disadvantages, possibilities, and difficulties of various analytic techniques that have been investigated is given by Langer (1974) and Langer *et al.* (1974).

Asbestos is found ubiquitously in the environment. Chrysotile asbestos is a common air pollutant in most large urban areas in the United States (Selikoff *et al.*, 1972). In fact, because of the industrial use of asbestos, the highest concentrations found in air and water are generally in metropolitan areas (Cunningham and Pontefract, 1971; Kay, 1973). Asbestos fibers have been detected as contaminants of domestic water supplies derived from Lake Superior, generally thought to result from mine waste discharges.

An example of the contamination of a domestic water supply by asbestos minerals is illustrated by the case of Duluth, Minnesota. An iron ore mining company located at Silver Bay, Minnesota, discharges tailings into Lake Superior to the extent of approximately 70,000 tons per day. These tailings are the residue from the processing of taconite ore into pellets and are predominantly of the amosite type of asbestos. Bottom cummings in Lake Superior carry some of this discharged tailing material to Duluth, approximately 70 miles southwest. Duluth draws its water directly from Lake Superior and distributes and uses it unfiltered. The water in the Duluth domestic supply had been shown to contain numerous amphibole fibers and pieces as well as other crystalline material. The concentration of verified asbestos mineral fibers in the Duluth water

supply ranges from approximately 20×10^6 to 75×10^6 fibers per liter of water. These concentrations correspond to approximately 5 to 30 μg of asbestos fibers per liter of water (Nicholson, 1974). An analysis of the water system of Superior, Wisconsin, the neighbor city of Duluth, which draws only a portion of its water from Lake Superior, shows considerably fewer fibers. An analysis of the water from Grand Marais, Minnesota, which is upstream from Silver Bay, detected no asbestos fibers.

The health effects of asbestos in water have so far been incompletely ascertained. Asbestos is known to lead to asbestosis characterized primarily by pulmonary fibrosis, the formation of plural plaques, a greatly increased risk of bronchogenic carcinoma, plural mesothelioma, and peritoneal mesothelioma after occupational exposure to inhaled asbestos dust, as discussed elsewhere in this book. It is not clear, however, whether the ingestion of asbestos-contaminated water will lead to the same or similar diseases in man. Epidemiologic studies of cancer death rates in Duluth, Minnesota, have not yet revealed any increase in such conditions as compared with other areas in relation to the contamination of the water with mineral fibers. However, the contamination of the Duluth water supply began about 20 years ago, and it is not certain whether such conditions might show an increase within the next 5 to 15 years because of characteristic long latency periods. The assessment of the carcinogenicity of inhaled asbestos is complicated by the fact that synergism has been demonstrated by cigarette smoking. Whether some sort of synergistic effect may also occur with asbestos in drinking water is entirely unknown.

IMPACT OF CHEMICALS ON SOIL AND WATER SYSTEMS

The traditional view of the environment embodied in the phrase "balance of nature" represents an outmoded conceptualization of the forces that control environmental processes. There is, in fact, no simple balance of nature. The environment is composed of many systems and subsystems, each internally balanced in a dynamic way and influenced by many external processes that tend to interact and influence the structure and function of the whole system. The thrust of nature's "balance" is an evolutionary movement toward greater diversity, greater speciation, and more complex structure.

Man has been altering the course of evolution through technologic advances in agricultural and industrial practices. A side effect of a number of these advances is the introduction of chemicals resulting from agricultural and industrial practices to the soil and water ecosystems and the resulting impact of these chemicals on organisms

residing there. The effects of chemical pollution are threefold (Woodwell, 1970; Stickel, 1974): (1) a tendency toward simplification of communities through the elimination of more sensitive species and their replacement by larger populations of tolerant species, (2) the change in species relationships within communities, whereby the species that earlier might have enjoyed only a minor niche dominated by other species are allowed to expand into a dominant role in the ecosystem by the disappearance of the control species, and (3) alterations in nutrient cycles, which may have a long-lasting effect on the basic composition of the ecosystem. Alteration of nutrient cycles may lead in turn to permanent changes in an ecosystem through erosion and leaching, which in turn change the basic physical structure.

Effects of pollutants are seen primarily at the tops of food chains and are observed by man usually as changes in population levels of predator species. The chlorinated hydrocarbon pesticides and industrial chemicals, for example, may cause reproductive difficulties in birds, such as the peregrine falcon. Mink are highly sensitive to methyl mercury, while apparently other mammals are not so sensitive. Contamination with methyl mercury can thus alter the diversity and dominance characteristics of the ecosystem. Disturbances in the ecosystem can be detected in nutrient cycling even though no effects are measured in the diversity or population of the community. Several studies have now shown that changes in nutrients, such as nitrates, are more sensitive than biologic parameters to chemical stress (O'Neill *et al.*, 1977; Jackson *et al.*, 1977). This results from the fact that changes in nutrient pools must eventually directly affect the productivity of the entire ecosystem, even though the effects may not be measurable in biologic terms until a number of years later.

The net effect of decreased diversity in an ecosystem is a more unstable system. Such communities are subject to wide fluctuations in populations of organisms and are more easily influenced by outside pressures such as chemical pollutants. This leads in turn to the necessity for man's further intervention in an attempt to stabilize the system, a process that historically has sometimes been self-defeating.

In terms of human ecology we are just beginning our efforts to understand the impact of chemicals in the environment. The full range of effects of the loss of species diversity in the ecosystem on man is yet to be understood. Changes in the dominance characteristics of ecosystems will have a major effect on man's activities as they cause him to change strategies of pest control, alter his use of water systems for consumption

and recreational purposes, and change his perceptions of the aesthetic quality of the environment. Changes in nutrient cycling lead to the expenditure of energy and resources to correct resulting imbalances and to manage resource commitments and waste effluents. As man changes the agricultural ecosystem to his advantage, it is necessary to add nutrients in the form of phosphate and nitrate fertilizers, frequently leading to additional imbalances and problems in managing the contamination of water systems by these nutrients that result.

The effect of chemicals on man is known in many instances only indirectly through laboratory experimentation with test organisms, such as laboratory animals, at high doses. The same chemicals in the environment will not necessarily affect man in the same direct ways since they are always found in the presence of other chemicals with which they may interact. Interactions in the environment may alter mobility, transport, availability, disposition, and toxicologic effect, thus completely altering the properties of a chemical in its interactions with biologic systems.

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