Transport and Transportation Pathways of Hazardous Chemicals from Solid Waste Disposal
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To evaluate the impact of hazardous chemicals in solid wastes on man and other organisms, it is necessary to have information about amounts of chemical present, extent of exposure, and chemical toxicity. This paper addresses the question of organism exposure by considering the major physical and biological transport pathways and the physicochemical and biochemical transformations that may occur in sediments, soils, and water. Disposal of solid wastes in both terrestrial and oceanic environments is considered. Atmospheric transport is considered for emissions from incineration of solid wastes and for wind resuspension of particulates from surface waste deposits.

Solid wastes deposited in terrestrial environments are subject to leaching by surface and ground waters. Leachates may then be transported to other surface waters and drinking water aquifers through hydrologic transport. Leachates also interact with natural organic matter, clays, and microorganisms in soils and sediments. These interactions may render chemical constituents in leachates more or less mobile, possibly change chemical and physical forms, and alter their biological activity. Oceanic waste disposal practices result in migration through diffusion and ocean currents. Surface area-to-volume ratios play a major role in the initial distributions of chemicals in the aquatic environment. Sediments serve as major sources and sinks of chemical contaminants. Food chain transport in both aquatic and terrestrial environments results in the movement of hazardous chemicals from lower to higher positions in the food web. Bioconcentration is observed in both terrestrial and aquatic food chains with certain elements and synthetic organics. Bioconcentration factors tend to be higher for synthetic organics, and higher in aquatic than in terrestrial systems. Biodilution is not atypical in terrestrial environments. Synergistic and antagonistic actions are common occurrences among chemical contaminants and can be particularly important toxicity considerations in aquatic environments receiving runoff from several terrestrial sources.

Introduction

Solid waste disposal in the U. S. amounts to roughly $170 \times 10^6$ tons ($154 \text{ Tg}$) annually (1-3). Of this, $44 \times 10^6$ tons ($40 \text{ Tg}$) are disposed of in the ocean (3) and $126 \times 10^6$ tons ($114 \text{ Tg}$) are placed in land disposal sites (2). Dredging spoils dominate ocean disposal [$39 \times 10^6$ tons ($35 \text{ Tg}$)] leaving $4.5 \times 10^6$ tons ($4 \text{ Tg}$) of sewage sludge and $0.5 \times 10^6$ tons ($0.4 \text{ Tg}$) of construction and demolition debris, garbage, and explosives. The sewage sludge, garbage, and explosives, along with some $4.7 \times 10^6$ tons ($4.3 \text{ Tg}$) of industrial wastes (acids, pesticide manufacturing wastes, etc.), make up a total of some $10 \times 10^6$ tons ($9 \text{ Tg}$) of hazardous wastes annually deposited in the ocean. It is estimated that the $126 \times 10^6$ tons ($114 \text{ Tg}$) of solid wastes in land disposal sites contain by current definition, about $5 \times 10^6$ tons ($4.5 \text{ Tg}$) of hazardous materials. This quantity could increase if the current definition of hazardous waste is redefined under the Resource Conservation and Recovery Act of 1976. Radioactive waste disposal in the U. S., aside from uranium mill tailings, amounts to 24,000 tons ($0.2 \text{ Tg}$) annually,—all of which is disposed of terrestrially (1). Uranium mill tailings represent a special case similar in magnitude to disposal of all industrial wastes. Estimated resource recovery from solid wastes was 5.9% in 1977 (1). This percentage has decreased from 6.5% in 1973 along with a decrease of $6 \times 10^6$ tons ($5.4 \text{ Tg}$) in total waste generation (2). The hazardous wastes generated in the U. S. each year are deposited on the land surface, in slurry ponds, in landfills, on the ocean floor, and reduced in volume through incineration. Each of

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these disposal techniques has potential adverse environmental consequences, including contamination of surface and ground waters leading to either immediate toxic effects on aquatic and terrestrial organisms or accumulation of levels of contaminants toxic to higher food chain organisms including man. To evaluate the possible occurrence and magnitude of adverse environmental effects of hazardous wastes, it is necessary to have information about exposure of plants and animals to these materials. Exposure results from movement of materials from disposal sites through pathways in air, water, and food. These pathways may be categorized as abiotic (atmospheric and hydrologic transport) and biotic (plant uptake and exudation and food chain transport and transformation) and generally result in exposure from some combination of inhalation, immersion and ingestion. Materials of concern include trace elements, synthetic organics, and radionuclides.

There are significant differences in the ways in which synthetic organic and trace or radioactive elements enter the environment and affect man. Elements occurring naturally in the environment are mined, processed, used, and disposed of with resulting dusts, gases, salts, and solids returned to the environment. Thus, the hazardous nature of elemental contaminants comes mainly from their redistribution in the environment, resulting in exposure of organisms to unnatural concentrations. Synthetic organics on the other hand are produced almost entirely from crude petroleum, natural gas, and coal; they are not natural constituents of the environment. Organisms have not been exposed to these materials over millions of years as they have to elements, and they have not developed biochemical mechanisms to immobilize or detoxify these materials. The synthetic organic compounds are often the most toxic environmental pollutants and the ones we know least about in terms of fate and effects in the environment.

After substances enter the environment, they may be diluted, concentrated, or transformed by chemical, physical, and biological processes. These processes may be categorized into three groupings (4): physical transport and spatial dispersion, interfacial processes including those which change the chemical and physical structure of compounds (e.g., sediment, water, air, soil, biota, water), and noninterfacial chemical transformations exogenous to biota. Specific physical, chemical, and biological parameters associated with interfacial processes may vary among terrestrial, fresh water and marine ecosystems, but the basic features of the interfaces are similar. Interactions occurring at interfaces mediate the ability of ecosystems to absorb contaminants, and simultaneously control their biological availability.

In this paper, the major transport pathways of hazardous materials from solid waste disposal (Fig. 1) will be discussed and evaluated in terms of their relative importance. The discussion will consider terrestrial, fresh water, and marine physical pathways of synthetic organics, trace elements, and radionuclides, followed by considerations of their biological transport through plant uptake and food chains. The phenomena of biological magnification and transformations, physicochemical sorption-desorption in soils and sediments, and synergisms among chemicals will be discussed in relation to their influence on availability and ultimate toxicity.

![Diagram of physical and biological transport pathways of hazardous chemicals from solid waste disposal.](image)

**Physical Pathways: Terrestrial Surface Disposal**

Hazardous materials disposed of on and in the land are ultimately exposed to surface and ground waters. Materials stored above the ground surface (e.g., fly ash, flue gas desulfurization (FGD) sludges, chemical process sludges) are subject to leaching by precipitation resulting in chemicals reaching surface waters (streams, rivers, lakes) through runoff. Particulate material may also be moved through erosion and become suspended sediments or bottom sediments of waterways. Materials disposed of on land surfaces are subject to resuspension in air and transport over fairly long
distances depending on material properties, wind vectors, and land features (5). Leached materials from aboveground disposal can percolate through soil horizons and into ground water. These materials as well as chemicals leached from subsurface burial can lead to possible contamination of drinking water aquifers or, through lateral movement of ground water, to contamination of surface waters.

Surface storage of slurries (fly ash, FGD sludge, chemical process sludges) depends upon evaporation or skimmer walls for water removal. Typically, these slurry ponds are surrounded by man-made dikes with clay cores covered by more permeable material which in many instances is fly ash, the solid waste itself. Fly ash disposal ponds can contribute major and minor elements, alter pH of surface waters, and can introduce elevated levels of trace elements to groundwater (6, 7). There are insufficient studies to date on the magnitude of possible future ground water contamination problems from leaching of the large quantities of FGD scrubber sludges which are expected to occur. However, results from some 8 years of monitoring the disposal of untreated scrubber sludge in unlined ponds have revealed no apparent adverse effect on surface or ground water quality (8).

Solid waste deposits at an abandoned chlor-alkali plant in the southeastern U.S. serve as an interesting example of several pathways of release of a hazardous chemical (mercury) to the surrounding environment (9, 10). This facility produced chlorine and caustic soda by the Hg-cell process from 1952 until 1972, when the facility closed because of an inability to meet newly imposed state and federal water quality standards. Waste products were disposed of in a 44 ha (44 dam²) sludge basin adjacent to a river. Results of several years of monitoring at this site indicate an annual release of 39 kg of Hg through leaching into the river, matched by an unexpected atmospheric release of 36 kg of volatile Hg from the surface of the basin. Surface temperature (which affects volatilization) and precipitation patterns (which affect leaching) for the region resulted in a uniform release of this 75 kg Hg over the entire year. Analysis of biota in the river at distances up to 100 mi (160 km) downstream indicated concentrations of Hg greater than 1.0 ppm in fish, of which > 80% was methylmercury. The authors conclude that this source of Hg will exist for roughly 100 years unless some abatement is attempted, and that these types of residual wastes will continue to grow in relative importance as sources of environmental contaminants (9).

**Subsurface Disposal**

Disposal of hazardous wastes below the soil surface in burial grounds and landfills eliminates the runoff pathway, but it puts wastes in close proximity to ground water, which can result in leachate production. Once materials are released from their disposal container or matrix into ground water, a host of factors governs their movement through the soil horizons both vertically and laterally. The transport of contaminants within the soil hinges on water movement associated with particular geologies and on chemical reactions within the soil profile. Water movement depends on horizontal gradients in the water table head and hydraulic conductivity. The chemical and physical reactions which occur simultaneously with ground water movement will affect the transport and retention of trace contaminants through the soil. Sorption and desorption processes between the trace contaminants and the organic and mineral phases of the soil are usually strong and can prevent, or at least retard, movement of contaminants by ground waters. On the other hand, some chemical forms of trace substances are repelled from the soil phases and may move readily with water. For example, at some valence states, some trace metals react with oxygen and become highly soluble, but at other valence states they form slightly soluble or nearly insoluble crystalline salts. Many reactions in the soil are pH- and Eh-dependent. In fact, several investigators suggest pH and redox potential (Eh) as the controlling factors of trace element mobility in soils and groundwater (11, 12). Some contaminants present in wastes may interact with the soil exchange complex and become more or less soluble than one would expect. Cobalt and lead complexation with organic materials in the soil solution are recently reported examples of increased solubility through chemical interaction (13, 14). Other contaminants, however, may become very insoluble following these interactions and may precipitate in the soil matrix. In this latter case, the retention of contaminants is greatly increased and the potential for reaching surface waters and aquifers is greatly reduced. A further consideration for evaluating transport of contaminants through soil profiles is that of microbial transformation and degradation which will be discussed in a later section. Finally, surface condition at the disposal site will influence subsurface transport through phenomena such as perched water tables, which are isolated zones of saturated soil above the continuous groundwater, causing infiltration of surface water into a landfill when the underlying soil is impermeable (15).

Movement of water and trace contaminants in leachate through solid waste disposal sites and into groundwater and river systems has received considerable attention over the past few years (16–18). Severe economic damage has been reported for a
Delaware community where leachate from a landfill polluted the drinking water aquifer (19). In another instance, selenium contamination of ground water from a dump in Long Island was observed 2 miles from the dump site (20). Results from surveying leachate of 20 municipal disposal sites (16) indicated the presence of relatively high levels of organic matter, N, P, K, and heavy metals. The presence of heavy metals and toxic organics in these leachates poses a potentially severe problem, because of long-term accumulation in soils with subsequent uptake by plant roots leading to introduction into food chains as well as potential aquifer contamination.

Several recent investigations have addressed attenuation of pollutants in landfills and assessment of health and environmental impacts of solid waste disposal (21–23). Griffin et al. (21, 22) have evaluated clay minerals in attenuating various chemicals in leachate from a 15-year-old landfill. They found in laboratory column studies that Cl, Na, and water-soluble organic compounds were unattenuated by clays; K, NH₃, Mg, Si, and Fe were moderately attenuated; and Pb, Cd, Hg, and Zn were strongly attenuated through precipitation at pH values of 5 and above. Adsorption of Cr (VI), As, and Se decreased with increasing pH. Their results suggest that overall pollution from landfill leachate would be reduced if landfill liners of clay materials were designed for higher hydraulic conductivity. Liners could be designed to selectively attenuate toxic pollutants in leachate and allow groundwater to dilute non-toxic components to lower concentrations.

Barnthouse et al. (24) have evaluated the potential impact on aquatic organisms of trace metals from coal conversion solid wastes disposal in landfills. Their analysis was based on consideration of abundance of trace metals in the wastes, mobility of trace elements in the wastes and in ground water, and toxicity of trace elements to aquatic biota. Since currently there are no operating full-scale coal conversion facilities in the U. S., several assumptions were necessary: solid wastes would consist mainly of ash, slag, and char containing trace elements in a reduced state in a slag-matrix; wastes would be buried, packed, and capped to reduce infiltration; conditions in the landfill would initially be aerobic but would eventually become anaerobic; Eh and pH would govern ion mobility; and both acidic and basic landfill environments would exist due to variations in feed-coal and processes. The results based on results of their analysis indicate Fe, Zn, Cr, Mn, and Ni as elements with high potential for adversely impacting aquatic organisms; Be, Mo, Sb, Se, Sr, and U are of low potential; and Al, As, B, Ba, Cu, Cd, Co, Hg, Mg, Pb, V, Tl, Ti, and Zn are of variable or uncertain concern.

Braunstein et al. (23) have recently assembled the available literature on transport and fate of organic contaminants from solid waste disposal in the coal conversion processes. They found little information about transport but did summarize available data on persistence and degradation in landfills and marine sediments. From their survey, they concluded that chemical and microbial interactions in sewage treatment plants and landfills were insufficient to prevent significant accumulation of PAH’s (polycyclic aromatic hydrocarbons) in rivers and reservoirs.

There is currently no U. S. policy on radioactive waste disposal, although we did cease ocean disposal in the early 1960’s (25). Solid radiological wastes are either combustible or noncombustible, and the factors governing their movement in the environment (both atmospheric and hydrologic) are quite similar to those of nonradioactive wastes. Because of the added dimension of radiation hazard to the basic elemental toxicity of some radioactive elements, their disposal or storage is more stringently controlled. Still, gases and particulates may escape during incineration, and incineration waste products (solids) plus other solid wastes may leach into surface and ground waters. Certain radioactive wastes, particularly the transuranic, present special problems because of their very long radiological half-lives, their high chemical toxicity (26), and their unusual environmental chemistry (27). Uranium mill tailings also represent a special case of solid radioactive wastes because of the large mass of material involved, the presence of most of the natural radioactive daughter products originally in the uranium ore, and the practice of relatively unprotected surface disposal. These tailings are subject to both leaching and atmospheric transport through resuspension (5), which can result in both ingestion and inhalation by man and other animals.

Incineration

Incineration of solid wastes, predominantly municipal garbage, produces two classes of pollutants which move through two separate pathways ultimately leading to surface waters and sediments. The first of these classes includes the ash and slag from incineration as well as any wastes produced from air pollution control devices associated with incineration. These materials are disposed of in landfills, ash ponds, and the like, and are subject to the physical transport considerations discussed in earlier sections. Incineration also produces gaseous and particulate pollutants including NOₓ, organics,
and trace elements that are released to the atmosphere. These pollutants are dispersed in the atmospheric environment as functions of wind speed, stack height, atmospheric stability, diffusion coefficients, as well as chemical interactions including photolysis, hydrolysis, and sorption and desorption phenomena (28). These materials may be deposited on land and water surfaces through wet deposition and dry fall. Man, plants, and other animals are exposed to incineration-produced contaminants through inhalation, immersion, and ingestion (foliar assimilation in the case of plants). Typically, particulates of the plume generated by incineration are depleted with distance from the source, depending on particle size distributions, while the gaseous forms may be transported over greater distances. It is not now possible to evaluate the regional impact of incineration in relation to other sources of atmospheric pollutants (i.e., fossil fuel steam stations, automobiles, industrial stacks, etc.) but incineration could be an important potential hazard in very localized situations, depending upon the composition of the wastes.

**Physical Pathways: Fresh Water**

Typically, hazardous wastes are not deposited directly into fresh water environments. Disposal of mine tailings such as the taconite disposal in Lake Superior (29, 30) represent a major exception. Additionally, in the Southeast, fly ash is pumped to holding basins adjacent to major waterways with skimmer wall outlets allowing both dissolved and particulate materials to flow directly into aquatic environments. Trace contaminants from solid waste disposal on land generally enter the aquatic environment in dissolved and suspended form in runoff, in dissolved form in ground water, and in wet- and dryfall from the air (incineration products). Trace contaminants that enter the aquatic environment are usually rapidly taken up through adsorption by components having the highest surface-to-volume ratios, primarily the small suspended solids and sediments, and absorption by similar sized microbiota. The largest reservoir of trace contaminants is the bottom sediment. Here a complex association of inorganic and organic components similar to those found in soil form a system which governs the availability of contaminants to the rest of the ecosystem. The physical factors, pH, Eh, pore space, and chemical transformations influence the retention and/or mobility of contaminants in aquatic systems. Similarly, biological transformations play a key role in aquatic transport and distribution. In streams, contaminants may be transported downstream in dissolved form or in association with suspended sediments ultimately to be deposited into lake sediments or taken up in food chains and cycled among various biological components.

Aquatic ecosystems are generally the environments most impacted by releases of hazardous materials from waste disposal. Aquatic plants and animals have the capability of accumulating much higher levels of contaminants than the concentrations found in water. Distributions of hazardous materials in fresh water systems can be widespread from localized sources—Hg from chlor-alkali industry (9, 31), PCBs in river-estuary systems (32). Many U. S. cities draw their drinking water supplies from surface waters. Contamination of these waters can lead to human health hazards and considerable expense, as has occurred with Kepone (25) and asbestos (29).

**Physical Pathways: Marine**

Solid wastes deposited in the ocean (i.e., sewage sludge, dredging spoil, industrial wastes) are subject to chemical, physical, and biological factors similar to those in fresh waters. Added factors in ocean environments include surface and deep water currents, salinity, and tidal actions. Wastes are generally released into oceans from barges over areas of minimum sediment migration. Turbidity caused by dumping dredge spoils generally clears within a day (33) although in some cases, light penetration may be continuously reduced by ocean disposal (34). Most wastes, but certainly not all, settle to the bottom. Others containing oil, garbage and other materials float and may be transported considerable distances by wind and ocean currents. Suspended materials are also transported over great distances. Horizontal currents in the New York Bight flush this 500 square mile (1.3 km²) area is less than one week (35). Vertical movement may be considerably slower. Gradual sediment migration can also carry along deposited contaminants. As in fresh water systems, solid wastes exposed to water may release hazardous materials which are sorbed to components with highest surface-to-volume ratios (i.e., suspended sediments, plankton). Contaminants enter food chains through animals grazing on plankton and directly from the water medium as has been demonstrated for Hg in fish (36). In the absence of water currents, diffusion from high to low concentration areas serves as a major mechanism in the mobility of dissolved contaminants in the water column. Escape from the ocean surface to the atmosphere will be an important route for volatile contaminants including those converted to volatile forms following chemical and biological interactions in sediments.
Most reports on effects of solid waste disposal on marine systems have dealt with the New York Bight area where about $4.5 \times 10^6$ tons (4.1 Tg) of sewage sludge are dumped each year. Abnormally high concentrations of C, Cu, Ag, and Pb have been reported (37). Copper was observed in concentrations toxic to clams, worms, and vegetation (35). Due to elevated levels of coliform bacteria in waters 6 miles (9.6 km) from the dump site, FDA closed an area 12 miles (19 km) in diameter to shellfishing (38). In 1961, an outbreak of infectious hepatitis was traced to raw shellfish taken from Raritan Bay, New Jersey (39). There have also been reports of higher than normal incidences of fin-rot on certain fish and exoskeleton erosion and gill clogging of crabs and lobsters (40).

**Biological Transport and Transformation**

At nearly every point along the physical transport pathways in both aquatic and terrestrial environments, opportunities exist for interactions with the biotic components. Organisms can absorb hazardous chemicals from their physical environment and dilute, concentrate, transform, and immobilize these materials, which may or may not affect ultimate toxicity. The biological pathways of concern here include microbial interactions in soil, plant uptake from the soil–soil water continuum, translocation in plant tissues, and food chain transmission to primary and secondary consumers in terrestrial ecosystems. Aquatic environment pathways include microbial-sediment interactions, absorption and adsorption from water by plankton, food chain transmission by consumers, and an added dimension of direct uptake from water by consumers. Direct uptake from air through inhalation by animals can occur in terrestrial environments—but probably does not represent a major pathway relative to solid waste disposal (exceptions: uranium mill tailings, other mining tailings, and incinerator emissions). Biological transport plays a major role in determining exposure of organisms to contaminants, but only a minor role in material transport through the environment with little or no effect on contaminant inventory.

**Generalized Food Chain**

Before considering specific food webs in aquatic and terrestrial ecosystems, it would be informative to look at a generalized food chain which includes the major mechanisms governing the flow of materials through biological systems (Fig. 2). A food chain is made up of trophic levels beginning with organisms that fix solar energy into chemical energy (primary producers) and continuing through various levels of organisms that feed upon this fixed solar energy (primary consumers, secondary consumers, decomposers, etc.). Primary producers generally serve as the base of food chains and may accumulate chemicals through roots (plant uptake), leaves (foliar absorption), absorption through cell walls in aquatic plants, and through adsorption on external surfaces. Chemicals physiologically fixed in plant tissues as opposed to those on plant surfaces or in intracellular water streams may have different properties and behave differently when ingested by consumers (41). Fixation may be in vacuoles with organic and inorganic chelating agents, in structural molecules, and in cellular waters. Chemicals may return to the physical environment from plants through death, exudation, and leaching, or they may enter food chains through ingestion by consumers. Following ingestion, chemicals may pass through the digestive tract or they may be assimilated. Assimilation rates may vary from < 1% per day for certain chemicals up to 100% per day for others depending upon both animal and chemical species in question (42). Following assimilation, chemicals are distributed in various tissues at various rates in the consumer’s body. Cadmium for example tends to accumulate in renal tissues, methylmercury in the central nervous system, and chlorinated hydrocarbons in adipose tissue. Other chemicals, particularly some heavy metals and

![Figure 2](image_url)

**Figure 2**. Schematic representation of a generalized food chain illustrating material flows within and among three trophic levels made up of producers, primary (1°) consumers, and secondary (2°) consumers.
Terrestrial Food Web

Soils tend to be the sink for most chemical contaminants released to terrestrial environments (Fig. 3). In addition to water relations and sorption-desorption phenomena discussed earlier, microbial interactions and root uptake play major roles in transport and distribution of chemicals in terrestrial systems. Microbes can operate in both aerobic and anaerobic environments and have profound effects on chemical mobility. From the soil-soil water continuum plants may accumulate chemicals through root uptake, a process of both active and passive nature. Root uptake of solutes from soil appears to be governed by solute demand of vegetation, root permeability to solutes, and supply of solutes in the soil (43). Plants show preferential uptake of particular elements and can exclude others at membrane boundaries. Heavy metals entering plant roots are believed to be chelated prior to their movement in xylem and phloem streams (12). Decomposer organisms may also accumulate chemical contaminants from soil water and soil organic matter. Both plants and decomposers may be eaten by consumers with accompanying transfer of chemicals. Man occupies the positions of both primary and secondary consumers. Ultimately, all organisms die, thus returning chemicals to the soil.

As an example of biological transport of chemicals through a terrestrial system, Figure 4 illustrates several major pathways in a forested landscape. Chemical contaminants in the soil are accumulated through root uptake from several soil horizons and may be translocated throughout the plant. Consumers may accumulate these chemicals through ingestion of plant parts. Dead vegetation and animals fall to the forest floor and through decomposition release chemical contaminants that may be leached into the soil. The death of plant roots also serves as a source of materials back to the soil. Forest floor litter may accumulate contaminants, particularly trace elements, through interaction with organic acids produced during decomposition (44, 45). As discussed earlier, materials in litter and soil may be physically transported to aquatic systems through runoff and ground water movement.

Aquatic Food Web

Typically, aquatic food webs are more complex than those found in terrestrial systems (Fig. 5). Adsorption-desorption of chemicals on suspended sediments and direct absorption by organisms from

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**Figure 3.** Schematic representation of a terrestrial food web illustrating different physical and biological components and directions of material flows among these components.

**Figure 4.** Pathways of chemical transport during plant uptake from soils and subsequent translocation within the plant in a forested environment.
water are added parameters in aquatic systems. Chemical contaminants generally reach aquatic environments by direct deposition (disposal), runoff from land surfaces, and leachates in ground water. Chemical and physical reactions among sediments, interstitial water, the water column, and decomposers can affect the routes and rates of transfer as well as the chemical and biological properties of contaminants. Aquatic plants obtain chemical compounds from the water column through absorption although surface adsorption is important because of high surface-to-volume ratios found in algae and other phytoplankton. Animals feeding upon these primary producers are exposed to both adsorbed and absorbed chemicals which may differ in mobility and availability. Decomposers may act upon organic matter in anaerobic sediments resulting in release of heavy metals to interstitial water and their subsequent diffusion into the overlying water mass. Because of the chemical and biological activity present, sediments may act as sources and sinks of chemical contaminants in the aquatic environments. Although man may represent a primary consumer of aquatic primary producers in some countries, typically he is a secondary consumer feeding on fish, shellfish, and mussels that are exposed to contaminants from water and from the food chain.

A common aquatic food chain in fresh waters of the southern United States is illustrated in Figure 6. Arrows indicate the directions of major material flows. In this particular example, taken from a study of methylmercury cycling in a pond (46), phytoplankton in the seston make up the primary producers. The zooplankton component of the seston is the primary consumer trophic level. *Gambusia* represent the secondary consumers; blue gill and carp represent omnivores; macrobenthos represent both primary and secondary consumers; and large mouth bass represent tertiary consumers or predators. Transport pathways not illustrated in this example are those occurring in bottom sediments and return of contaminant from consumers to water. Numerous other examples of chemical contaminant transport and distribution in aquatic environments exist for trace elements and synthetic organics. DDT, for example, has been observed in almost all major aquatic environments on earth. Waterfowl also should be mentioned in considering food chain transport of contaminants from aquatic environments because of their feeding and migratory habits, and their role as food items for man (47).

**Biological Concentration**

The ability of animals and plants to accumulate chemical contaminants to levels above those of their food source or substrate is a common biological phenomenon. Accumulation of pesticides by target and nontarget biota is particularly well documented (48–50). Trace elements, including heavy metals and radionuclides are also accumulated to varying degrees (31, 51, 52). The terms "biomagnification" and "bioaccumulation" have come into vogue in describing accumulation of contaminants by organisms, but these terms can be misleading, since biodilution can occur in successive steps of a food chain. In this paper biological concentration is defined as the amount of a chemical accumulated by an organism by adsorption and absorption resulting in an increased concentration.

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**Figure 5.** Schematic representation of an aquatic food web illustrating different physical and biological components and directions of material flows among these components.

**Figure 6.** Transport pathways among the major components of a fresh water pond ecosystem following chemical addition to the water.
in the organism. The biological concentration factor is defined as the ratio of the concentration in the organism to the concentration in the surrounding air, water, or soil, and/or the food consumed. In aquatic systems, water is typically the reference point, while soil serves a similar role in terrestrial systems. Biomagnification, therefore, is a phenomenon occurring when the biological concentration factor is greater than unity.

Biological concentration of chemicals is governed by the amount of chemical present in the diet or surrounding environment, the chemical and physical form of the chemical which determine its biological availability, the quantity of contaminated food which is consumed, the degree of assimilation of the chemical through cellular barriers (i.e., cuticle, lung, digestive tract, gills), and the extent of retention in the organisms' tissues. Contaminants are bioconcentrated when they are selectively moved toward specific surfaces or cells and are accumulated faster than they are released. This accumulation occurs with natural chemicals for cellular maintenance and growth. It can also occur with natural hazardous elements or with synthetic organics when there is a strong chemical or physical resemblance to a common element or molecule which is necessary for everyday life processes.

Due to the variations that exist in the factors governing biological concentration among different environments and species as well as within one species in a particular environment, it is not true that because biomagnification occurs at one step in a food chain, it will also occur in subsequent steps. Following an analysis of the extensive pesticide literature, Kenaga (53) concluded that there were no consistent patterns of maximum bioconcentration factors of pesticide residues in the various plant and animal species considered. Pesticides and other contaminants may reach maximum biomagnification in algae or other first link organisms in food chains followed by little or no increase in concentration in subsequent links.

Biological concentration factors for hazardous elements (Table 1) may vary over many orders of magnitude (10^{-3} to 10^{9}) in aquatic and terrestrial environments (51, 52, 55). Typically, biomagnification is greatest in aquatic environments where surface-to-volume ratios are greatest (i.e., plankton) and where adsorption may overshadow absorption in relative importance. Bioconcentration factors for trace elements in terrestrial environments are generally less than unity with some exceptions. Similar values for radionuclides in terrestrial environments also less than unity (52), indicating a reduction in concentration (i.e., biodilution) as one proceeds through subsequent steps in the food chain.

Organic contaminants including pesticides and industrial chemicals (Table 2) tend to exhibit higher biomagnification in aquatic environments than do trace elements. The chlorinated hydrocarbons (all the compounds in Table 2) are biologically concentrated to higher values than most other synthetic organics because of their fat solubility and resulting potential for storage in adipose tissue (53). The data shown in Table 2 include information from Metcalf (56) on the pesticides DDT, DDE, aldrin, dieldrin, hexachlorobenzene (HCB); from Laska et al. (57) on hexachlorobutadiene (HCBD); from Metcalf (58) on the plasticizer di-2-ethylhexyl phthalate (DEHP); and from Jernelov (59) on EDC-tar, a by-product of vinyl chloride manufacturing. Bioconcentration factors for synthetic organics varied less among plant and animal species than did those for trace elements. Data from several literature sources were summarized by Herbes et al. (60) for polycyclic aromatic hydrocarbons (PAH) resulting in an expression of bioconcentration factors as a function of molecular weight. The wide spread of bioconcentration factor values they observed at different molecular weights was apparently due to differ-

| Table 1. Biological concentration factors in aquatic and terrestrial environments for trace elements that may occur in hazardous wastes. |
|---------------------------------------------------------------|
| **Biological concentration factor** | **As** | **Cd** | **Hg** | **Pb** | **Zn** |
|-----------------------------------|-------|-------|-------|-------|-------|
| **Aquatic**                       |       |       |       |       |       |
| Water                             | 1     | 1     | 1     | 1     | 1     |
| Plants                            | 170   | 1000  | 1000  | 200   | 1000  |
| Invertebrates                     | 330   | 2000  | 100,000 | 100 | 10,000 |
| Fish                              | 330   | 200   | 1000  | 300   | 1000  |
| **Terrestrial**                   |       |       |       |       |       |
| Soil                              | 1     | 1     | 1     | 1     | 1     |
| Plants                            | 0.01  | 0.3   | 0.4   | 0.07  | 0.4   |
| Invertebrates                     | 0.01  | 17    | 17    | 0.02  | 8     |
| Mammals                           | 0.001 | 0.008 | 5     | 0.001 | 0.6   |
| Birds                             | 0.001 |       | 50    | 0.001 |       |

* Ratio of concentration in organism to concentration in substrate.
ences in lipid content and PAH excretion rate.

Biocenentrations factors for organics in terrestrial environments are more difficult to obtain because of uncertainties in food source or substrate concentrations. One of the classic examples is that of DDT in the soil-earthworm-robin food chain. Beginning with a DDT concentration of 9 ppm in soil, it reached 140 in earthworms and 440 in robins; this represented a concentration factor of 50 for robins relative to soil (49). Typically, biocenentrations factors for pesticides in terrestrial invertebrates (earthworms) relative to soil average 9 (61), and a recent thorough review of organochlorine pesticide residues in birds and mammals (62) indicates biocenentrations factors of 3–15 for birds and 10–30 for small mammals relative to concentrations in their food source.

**Biological Transformations**

Inorganic and organic chemical contaminants introduced into the environment are subject to biochemical interactions typically with microorganisms in soils and sediments although there are some biochemical transformations of hazardous chemicals in higher organisms. Microorganisms are very versatile in their ability to chemically interact with natural and synthetic chemicals (63, 64). Reactions include: release of ions and other products during decomposition of organic materials; immobilization of chemicals by incorporation into microbial tissues; reduction of oxidized states under anaerobic conditions; and indirect transformation through microbial influence on soil or sediment pH and Eh. *Thiobacillus* spp. bacteria have the capacity to oxidize elemental sulfur to form sulfuric acid (63) and this may be an important factor in dissolution of mine tailings. Soil microbes can reduce selenate, selenite, molybdate, and arsenate (65). Simple aliphatic acids and amino acids are continuously produced in soil by microbes (66), and some such as citric and oxalic acids act as strong chelating agents (67). Synthetic organics, particularly the PAH’s, are very resistant to microbial degradation in soils and sediments (68, 69). Several microbial species, including *Pseudomonas* and *Mycobacterium*, have utilized various synthetic organic contaminants (e.g., benzo(a)pyrene) as sole carbon sources, but only in laboratory studies (70).

The biochemical process of methylation of heavy metals and metaloids has received considerable attention in recent years, although the reaction was first observed with arsenic in the late 1930’s (71). Methylation is believed to be a detoxification mechanism for converting toxic ions to a more volatile form that will be released to the atmosphere (72). Several microbial species are capable of performing this transformation in soils and sediments under both aerobic and anaerobic conditions. Methylated forms of trace metals are frequently more toxic and are more readily absorbed by higher organisms than are inorganic forms. Methylation of mercury by microbes in marine and freshwater sediments is the best documented case of this type of biological transformation (31). Microbes have also been shown to demethylate mercury in sediments (73), which only serves to further confuse the issue of the source of elevated methylmercury in fish tissues. Arsenic, selenium, lead, and tin are examples of other toxic elements that undergo methylation (74).

Higher organisms, including man, are capable of effecting biotransformations of hazardous chemicals. Reactions of Cd and metallothionein during retention of this element in renal tissues are well documented by Friberg et al. (75). Stickel (62), in her review of pesticide residues in birds and mammals, stated “chemical changes of organochlorine insecticides within the animal body are inherent and critical parts of the kinetic process. These changes may drastically alter the toxicity, solubility, storage potential, and other characteristics of the parent compound. An evaluation of the effects of a chemical cannot be complete without an evaluation of the effects of its metabolites.” She also pointed out the dangers of “lethal mobilization” of chlorinated hydrocarbons stored in fatty tissues which can occur when these chemicals are suddenly released to the blood stream by some external stress.

Biotransformations of hazardous chemicals in the

### Table 2. Biological concentration factors for selected synthetic chlorinated hydrocarbons in aquatic environments.

| Aquatic | Biological concentration factor<sup>a</sup> |
|---------|------------------------------------------|
|         | DDT | DDE | Aldrin | Endrin | HCB | HCBD | DEHP | EDC-Tar |
| Plants  | 180,000 | 39,000 | 4,500 | 520 | 1 | 1 | 54,000 | 1 |
| Invertebrates | 8,000–35,000 | 20,000–46,000 | 45,000 | 50,000 | 1,250 | 22–500 | 21,000–107,000 | 30–3000 |
| Fish    | 85,000 | 27,000 | 31,000 | 1,300 | 290 | 440 | 130 | 13 |

<sup>a</sup> Ratio of concentration in organism to concentration in substrate.
environment are particularly important in determining effects on man and other organisms because it is the molecular form and biochemistry of these transformed chemicals that determine their persistence, bioaccumulation, and toxicity.

**Synergisms and Antagonisms**

A discussion of physical and biological transport pathways would not be complete without including consideration of synergism and antagonism that may occur among chemical contaminants. The combined action of two different chemicals may be greater than the same as, or less than the sum of the independent actions of both materials. If the combined action is the same as the sum of the two, the chemical effects are said to be additive, and the increase is a simple algebraic addition. In the case of potentiation (synergistic action) the effect is greater than a simple algebraic addition. In the case of additive effects, the two compounds usually have the same points of attack. In potentiation, one compound usually acts on the metabolism of the second compound. The concept of synergism or potentiation covers both increases in usual effects of toxic compounds and production of lesions not observed by the action of either toxic compound alone (76). Similar considerations apply to antagonism. There are numerous examples of synergism and antagonism among organic and inorganic contaminants in the environment (76, 77). The protective nature of arsenic to selenium poisoning and vice versa is well documented (78). Because of the high probability of concurrent exposure of aquatic organisms to multiple chemicals from landscape runoff and waste disposal practices, considerable attention has been devoted to possible synergistic actions that might occur in this environment (79, 80). Synergistic and antagonistic actions simply add to the complexities of evaluating environmental transport and effects of hazardous chemicals.

**Conclusions**

Solid waste disposal in terrestrial environments can result in hazardous chemical release to surface and groundwater through leachate production and movement. Additionally, terrestrial disposal sites may contribute to air pollution through resuspension of materials such as mine tailings and through stack gas and particulate release during incineration. Constituents of solid waste, including solid residues from incineration and FGD scrubber systems, once entering groundwater, can percolate through soils and contaminate surface streams and drinking water aquifers. Dominant physical factors governing leachate movement in soils include water movement, solubility, pH, Eh, and clay content. Each of these factors can also influence chemical and physical states of chemicals in groundwater. Increased clay content decreases contaminant mobility through attenuation and can significantly affect biological availability. Organic acids in soils also affect mobility of contaminants in groundwater. Soils serve as a major reservoir of hazardous chemicals in terrestrial environments.

Freshwater environments receive hazardous waste directly through intentional disposal, and indirectly through runoff and groundwater. Contaminants are transported in both dissolved and suspended form. Adsorption generally occurs rapidly on the suspended sediment and plankton, which have high surface-to-volume ratios. Material transport is subject to stream and lake currents while diffusion is important in still waters. Marine environments receive hazardous waste from intentional dumping of sewage and industrial chemicals as well as in runoff from terrestrial and freshwater environments. Sediment migration is an important consideration in contaminant transport in this environment. As in freshwater systems, adsorption plays a major role in initial distribution of hazardous chemical inputs. Sediments act as the major sink and secondary source of trace contaminants in both freshwater and marine environments.

Biological components interact with physical transport pathways at numerous points in the environment. Organisms may absorb and/or adsorb chemical contaminants from their surrounding air and water medium or through the food chain. Assimilation of chemicals from food sources varies according to both animal and chemical species in question. Direct accumulation of contaminants occurs in higher organisms through inhalation in terrestrial environments, and epidermal absorption (gills) in aquatic systems. Biological concentration occurs when organisms accumulate chemicals in their tissues to levels higher than those in their food sources or substrates. Organics tend to bioconcentrate to higher extents than trace elements, and aquatic species tend to bioconcentrate chemical contaminants to higher extents than do terrestrial species. Biological dilution is not unusual in terrestrial environments. Biological transformations occur, mainly in microorganisms, and change the chemical and physical nature of contaminants, thereby altering their mobility and biological availability. Higher organisms are also capable of biologically transforming contaminants, with resulting change of mobility in their tissues. Synergism and antagonism among chemical contaminants are important considerations, particularly in aquatic envi-
environments which receive inputs from numerous atmospheric and terrestrial sources.

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