

Aging, Bioavailability, and Overestimation of Risk from Environmental Pollutants

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As they persist, or age, in soil, organic compounds become progressively less available for uptake by organisms, for exerting toxic effects, and for biodegradation and bioremediation by microorganisms. This declining bioavailability is not reflected by currently used methods for the chemical analysis of soils for determining concentrations of organic pollutants. As a result, such methods overestimate exposure, and thus risk, from toxic chemicals in contaminated sites.

The validity of current methods for analyzing soils to assess the risk from organic pollutants has been cast in doubt by recent research. The focus of much of the concern with analytical methods has been increasing the recovery and sensitivity of chemical procedures, and the relevancy of these procedures to living organisms has been largely ignored. However, a primary reason for performing these analyses is to provide information on the exposure of living organisms to, and hence the risk from, these pollutants. The underlying issue is one of bioavailability.

To environmental scientists, bioavailability represents the accessibility of a chemical for assimilation and possible toxicity. To mammalian toxicologists, the term represents the availability for crossing a cell membrane and entering a cell. The first usage is the one followed here.

In this review, information will be presented to show that the bioavailability of organic pollutants in soil declines with time and that current analytical methods, because they measure total and not bioavailable concentrations, may overestimate the magnitude of the environmental and societal problem from these pollutants. Both early and recent evidence for these changes in accessibility will be presented, and the toxicological significance of these observations will be considered. The relevance of current analytical methods will then be evaluated. Differences in bioavailability among species, environments, and compounds and the consequent need for new analytical methods will be reviewed. Finally, the mode of biological acquisition of these compounds and possible mechanisms for the time-dependent decline in bioavailability will be discussed.

Many of the organic pollutants in soil were introduced years or sometimes decades ago at a time when industry and the public were not adequately aware of the scope, magnitude, and importance of soil pollution. Even early research, which has largely been forgotten, provided evidence that the availability of certain chemicals that have been in soil for some time is less than freshly added compounds, and hence the term aging (or weathering) was applied to the phenom-

enon. Although the early findings and their importance have been obscured with the passage of time, awareness now is growing among environmental toxicologists, risk assessors, and regulatory agencies that the total concentration of a toxicant in a contaminated environment frequently overestimates the risk of pollutants to humans, animals, and plants.

Early Evidence

Data showing the time-dependence of changes in bioavailability are now compelling. The early information came from studies of concentrations of pesticides in the field measured for long periods of time and from measurements of toxicity of pesticides to invertebrates and plants. For example, long-term monitoring of soil revealed that DDT, aldrin and its epoxide (dieldrin), heptachlor and its epoxide, and chlordane disappeared slowly at first, but then the rate of loss fell to such an extent that further loss was either extremely slow or ceased (1). Although the initial disappearance might be partially the result of volatilization or abiotic degradation as well as biodegradation by soil microorganisms, the fact that the disappearance was almost imperceptibly slow after several years indicates that those insecticides had become poorly available to the indigenous microorganisms; otherwise, these biodegradable compounds should have continued to disappear. The results of several long- and short-term monitoring studies are presented in Figure 1, which shows that the period when little or none of the insecticides is available to soil microorganisms may occur either soon or long after the compounds were introduced into the soil. Such results also show that the percentage of the compound that is poorly or no longer bioavailable differs markedly among the several soils and sites that were examined. This failing on the part of the soil microflora cannot be attributed to low winter temperatures, periods of drought, or other adverse conditions because the monitoring often extended for several years and was done in fields or experimental plots where crops were growing.

Early toxicological studies also demonstrated the time-dependent diminution in bioavailability. For example, simultaneous biological assays of acute toxicity to the fruit fly, *Drosophila melanogaster*, and chemical determinations gave similar results shortly after lindane was applied to soil, but much of the insecticide remaining in the soil after 22 months did not detectably affect the fruit flies (2). A decline in toxicity to oats as napropamide persisted in soil is also suggested by observations that quantitative bioassays detected progressively less than chemical measurements of the herbicide with residence time (3).

Recent Evidence

Organic compounds that have aged in the field are less bioavailable, often appreciably so, than the same compounds

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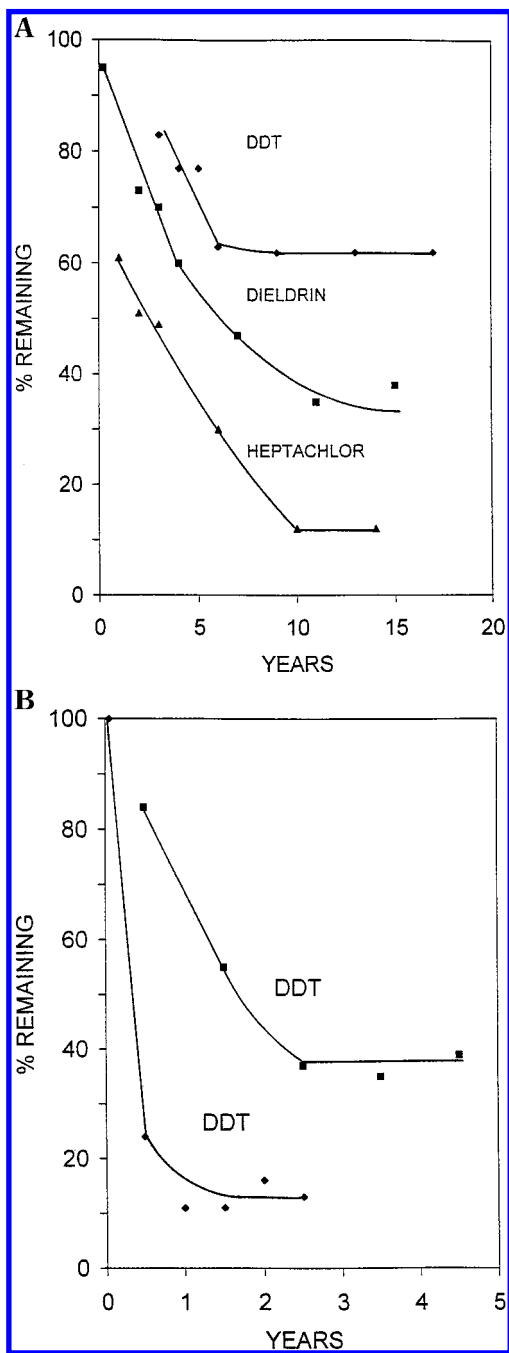


FIGURE 1. Changes in concentrations of three insecticides in long-term (A) and short-term (B) monitoring of several field sites. Calculated from data of Nash and Woolson and Lichtenstein et al. (7). In other field sites, the monitoring period was not sufficiently long to show the possible existence of a phase with little or no further disappearance of the insecticides.

freshly added to samples of the same soil. In a field treated with DDT 49 years earlier, approximately 30, 12, and 34% of DDT and the DDE and DDD formed from the added insecticide were available for uptake by the earthworm *Eisenia fetida* compared to newly added chemicals, and 28 or 43% of dieldrin applied at the same time was available based on concentration in the worms or percentages assimilated, respectively. Similar reduced bioavailabilities of DDT, DDE, and DDD but not dieldrin were observed in soil from a waste-disposal site in which the insecticides had aged for some 30 years (4). Field aging also diminishes the availability to microorganisms of 1,2-dibromoethane that persisted for 3 years (5), simazine applied for 20 consecutive years (6), and

TABLE 1. Compounds Shown To Become Less Available for Microbial Degradation as a Result of Aging

| compound | soil | aging period (d) | ref |
|---------------|------------------------|------------------|------|
| naphthalene | Colwood loam | 365 | (73) |
| naphthalene | Mt. Pleasant silt loam | 68 | (17) |
| phenanthrene | Mt. Pleasant silt loam | 110 | (74) |
| phenanthrene | 16 soils | 200 | (9) |
| anthracene | Lima loam | 203 | (18) |
| fluoranthene | Lima loam | 140 | (18) |
| pyrene | Lima loam | 133 | (18) |
| atrazine | Ravenna silt loam | 90 | (75) |
| atrazine | 16 soils | 200 | (9) |
| 4-nitrophenol | Lima loam | 103 | (10) |
| 4-nitrophenol | Edwards muck | 103 | (10) |

polycyclic aromatic hydrocarbons (PAHs) in soils from a closed coking plant (7) and manufactured-gas plant (8).

Laboratory tests confirm the lesser availability to microorganisms of aged than unaged compounds in highly dissimilar soils (Table 1). The bioavailability to microorganisms decreases with time but reaches a value below which a further decline is no longer detectable. How long it takes to reach that value and the final percentage availability vary among soils and compounds. The process may be complete in days or weeks or may take in excess of 200 days, and the loss in availability may be small or large (9, 10). Laboratory tests suffer from several problems associated with the interpretation of the data in terms of issues in the field because it is not yet clear how aging in nature should be simulated in the laboratory and because of the possibility that additions of pollutants in a convenient solvent may introduce artifacts.

These investigations with individual compounds probably explain why bioremediation by microorganisms often does not result in total elimination of target contaminants, as in tests with pentachlorophenol, DDT, and DDE in contaminated soils (11, 12). Typically, the bioremediation of soils containing PAHs, although reducing the concentration of many individual compounds, does not rid the treated site of PAHs that are known to be degraded in microbial cultures. The microorganisms are present, the environmental conditions are conducive to their activity, but somehow the compounds are inaccessible. The view that the contaminants became sequestered as they reside in the field gains credence in light of the finding that biodegradation of the seemingly resistant PAHs takes place if they are extracted and then added back to soil (7).

Toxicological Significance

Aging is toxicologically significant because the assimilation and acute and chronic toxicity of harmful compounds decline as they persist and become increasingly sequestered with time. Studies with mammals, for example, have shown that less 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) was absorbed after it had been in soil for 8 days than after a contact period of 10–15 h. The number of fruit flies (*D. melanogaster*), house flies (*Musca domestica*), and German cockroaches (*Blattella germanica*) killed by DDT and dieldrin declined markedly with increasing times of residence of these compounds in soil (13). Similar but largely forgotten data were obtained many years earlier by Peterson et al. (14), who found a marked and progressive reduction in toxicity to *D. melanogaster* as DDT persisted for 108 days in soil. An effect of aging on plants has also been noted with three herbicides: napropamide, simazine, and atrazine (3, 6, 15). In each instance, toxicity was less than that anticipated based on analysis by the usually used procedures of vigorous extraction of the soil followed by chromatography. Aging also reduces

the effectiveness of at least some genotoxic compounds in soil. Thus, by means of a solid-phase assay, it has been found that the genotoxicity of the carcinogens benzo(a)pyrene and 9,10-dimethyl-1,2-benzanthracene diminished rapidly and to a great extent within a 15-day period, although analysis following vigorous extraction showed only a slight decline in concentration after about 2 months (16).

Additional experimental evidence for the progressive decline in bioavailability with time has been obtained in tests with the earthworm *E. fetida*. With the progress of aging, decreasing quantities of naphthalene, phenanthrene, atrazine (17), anthracene, fluoranthene, and pyrene (18) were assimilated by the animals. The decline in availability of DDT and DDE to worms may even reach values of ca. 90% (4). Yet the types of chemical analysis used for assessing risk and making regulatory decisions fail to show the parallel diminution in bioavailability.

Although aging reduces exposure and thus toxicity and risk, it does not eliminate exposure and risk. For example, TCDD and polychlorinated and polybrominated biphenyls that have persisted for long periods still are available to mammals (19–22), field soils treated with DDT and chlordane 20 years earlier and dieldrin and heptachlor some 33 years earlier still were toxic to the termite *Coptotermes formosanus* (23), and some DDT, DDE, DDD, and dieldrin present in a soil treated 49 years earlier were available for uptake by *E. fetida* (4). Similarly, under experimental conditions, aged polychlorinated dibenzo-*p*-dioxins obtained from river sediments can be reductively dechlorinated by a microbial mixture (24), and part of the PAHs aged in soil in the laboratory can be taken up by earthworms (18).

Toxic substances that leach through soil may pose a risk to humans who obtain drinking water from groundwater sources. Because aging reduces the amounts of various compounds that are desorbed and may then pass through soil (25, 26), it also indirectly affects human exposure.

Nevertheless, a time-dependent decline in bioavailability does not always occur. This may be related to properties of the soil or of the compound. Instances in which bioavailability did not diminish include the biodegradability of simazine (6), the dermal and oral availability of TCDD and dieldrin to rodents (27, 28), and the uptake of DDE by earthworms in one soil (4). Only a small loss in bioavailability of certain compounds in sediments may occur with aging, witness that the rate of microbial dechlorination of polychlorinated biphenyls in Hudson River sediments contaminated for at least 15 years was only about 20% slower than compounds freshly added at 20 ppm (29). In addition, toxic compounds may exist in pockets or in nonaqueous-phase liquids within the soil, and after some physical disturbance, they may be released and become bioavailable. Although such compounds are aged in the sense of time, they have not been sequestered in a fashion to reduce their bioavailability to living organisms.

Incorrect Analytical Methodologies

The widely used protocols of federal and state regulatory agencies rely on analytical methods that entail vigorous extraction of soils and sediments with organic solvents. The aim is to remove all, or as much as possible, of the pollutant from the environmental sample. Each method is carefully evaluated to assess its accuracy, as well as its precision and sensitivity, but the accuracy is interpreted in purely chemical terms. The relevancy of such methods to the toxicity of the compound in the form in which it exists in nature is generally not considered in carrying out risk analyses, except that a default value is sometimes included to relate to the particular environmental matrix. The fact that the compound may become progressively less bioavailable as it persists, even in a single environmental matrix, is not considered in assessing risk. Thus, the regulator is not making use of information

that bioavailability may decline with little or no reduction in the concentration as determined by procedures that rely on initial vigorous extractions. Hence, such methods are often not relevant for prediction of potential exposures to, and thus risks from, contaminated soils or sediments.

The evidence is compelling that the quantities recovered by vigorous extraction fail to predict declining bioavailability as compounds persist in soil. For example, despite the marked diminution in effectiveness in killing three species of insects as dieldrin and DDT aged in soil, >90% of the dieldrin and ca. 85% of the DDT could still be recovered by vigorous extraction (13). Vigorous methods of extraction with organic solvents also did not reflect the decline in availability of atrazine and four PAHs for uptake by *E. fetida* (17, 18) as these compounds became increasingly sequestered with time in soil. The genotoxicity of benzo(a)pyrene and 9,10-dimethyl-1,2-benzanthracene (16) and the phytotoxicity of napropamide (3) and atrazine (15) also were not reflected by the chemical analyses following vigorous extraction of samples of the soil.

If the total concentration at a polluted site is greater than the regulatory level but the bioavailable concentration is below that value, a site that might be slated for expensive cleanup might, instead, be deemed to present an acceptable risk. The public concern about a contaminated location might be allayed by the more meaningful assessment. Moreover, a site that was bioremediated but still contained concentrations of one or more contaminants above the target levels may have indeed been successfully cleaned up, even though conventional analysis suggested that the remediation was inadequate. This is true both of engineered and intrinsic bioremediation, which frequently do not destroy all of the targeted compounds. Because such bioremediation treatments act on the fraction that is bioavailable, to microorganisms at least, the accessibility of the portion that remains may be so low that the site presents little or no risk to higher organisms.

Species, Environmental, and Chemical Differences

It is not presently known whether the percentages of a compound that are bioavailable are the same among different species. If the values are the same, the information obtained in measurements with one species could be used for predicting the extent of bioavailability for a second. If two species acquire an aged compound solely by spontaneous desorption and the rate of acquisition is limited by the desorption rate, the bioavailability of the aged substance will be the same for those organisms. On the other hand, if some species have mechanisms to facilitate desorption or to overcome the binding of sequestered molecules, the amount of the aged compound that will be available or the rate of its uptake will differ from organisms not having such mechanisms. Indeed, evidence exists that species differ in the extent to which sorbed, although not necessarily aged, chemicals are utilized or assimilated. For example, of two bacteria able to metabolize nonsorbed phenanthrene, only one used the sorbed hydrocarbon at a rapid and measurable rate (30); if that bacterium utilized the sorbed molecule only following its spontaneous (or abiotic) desorption, the other bacterium also should have done so. Clearly, a mechanism for facilitated desorption exists.

Other information exists suggesting that species differ in their use of aged compounds. For example, the rate and extent of loss of bioavailability resulting from aging of phenanthrene and atrazine were different when measured with earthworms and bacteria (31). Likewise, the assimilation of four aged PAHs by *E. fetida* after bacterial bioremediation suggests that the extent of availability is not the same for the earthworm and the bacteria (18). These experiments were not designed to determine whether accessibility was the same

for dissimilar species, but because the data are suggestive and the issue is of considerable importance, further evaluation is warranted. Should it be found that accessibility varies among species or even by route of exposure (e.g., dermal, intestinal, or respiratory in humans and animals), a single assay of bioavailability will not be sufficient.

Differences among soils also affect the aging-induced changes in biological accessibility. An effect of soil type was evident in the early work of Edwards et al. (2), who found that the decline in toxicity of lindane was marked in only one of the three soils tested. Appreciable differences among soils are also evident from the patterns of persistence of DDT, aldrin, and the dieldrin formed by the epoxidation of aldrin; i.e., if the marked decline in their rates of disappearance indicates sequestration in a form unavailable to indigenous microorganisms, differences among soils are indicated by (a) differences in the times at which the initial, more rapid phase of chemical disappearance ends and by (b) the dissimilarities in percentages of the originally applied insecticide that remain (1). Approximately 10–60% of the originally added chemical was present when the rates of disappearance fell to negligible values. However, definitive conclusions cannot be drawn from these data because not only were the soils different but so too were the temperature, rainfall, and vegetation. On the other hand, laboratory evaluations in which the only variable was soil type have shown clearly that the time-dependent diminution in bioavailability of lindane to *D. melanogaster* in three soils (2) or phenanthrene to *E. fetida* in seven soils (26) varies with soil type.

Regulatory decisions would be simplified if it was possible to predict the extent of decline in availability in different soils. Early studies with a few soils suggested that aging is more marked in soils with high than low organic matter content (2, 10). More recent investigations revealed that the bioavailability to microorganisms of aged phenanthrene was reduced in soils with >2.0% organic C but not in soils with lower percentages of organic C (32). The rate and extent of decline in availability of phenanthrene and atrazine for bacterial degradation were appreciably different among 16 soils deliberately chosen because of their dissimilar properties. Aging of atrazine was least in soils with <0.7% organic C, although no such effect was evident with phenanthrene (9). The extent of reduction in bioavailability to microorganisms was modestly correlated with organic C content and nanoporosity in the 7 nm–10 μ m diameter range (N. Chung and M. Alexander, unpublished data).

The initial rate of disappearance of a chemical in a given soil depends on temperature, moisture, and other environmental factors. Because of the resulting greater or lesser period of contact of the compound with the soil, it may be more or less sequestered. This view is supported by the observation that, in a single soil type supporting different rates of biodegradation, more phenanthrene became unavailable to bacteria if the initial rate of biodegradation was slow than if it was fast (K. Nam and M. Alexander, unpublished data). A reexamination of long-term field data on persistence of DDT and dieldrin also gives credence to the view that, in addition to soil properties directly influencing sequestration, the slower the initial rate of loss of a chemical, the more will become biologically unavailable (1).

An aging-related decline in bioavailability also is evident in other environments containing abundant particulate matter. For example, biota-sediment accumulation factors for 2,3,7,8-tetrachloro- and octachlorodibenzo-*p*-dioxin for the oligochaete *Lumbriculus variegatus* were 1.5- to 2-fold lower in sediments after 21 months of aging compared to the recently added dioxins (33). The rate of pyrene uptake from lake sediments by the amphipod *Diporeia* sp. also declined with aging (34). Naturally aged benzo(a)pyrene was less available to the amphipod *Eohaustorius washingtonianus*

and the clam *Macoma nasuta* in contaminated estuarine sediment than the newly added compound (35). Considerable portions of the PAHs and hexachlorobenzene in sediments are not available for utilization by indigenous microorganisms (36, 37), although several PAHs and hexachlorobenzene added to samples of the sediment are metabolized. Aging also appears to occur in aquifer sands, as is evident from the observation that aging rendered phenanthrene less readily decomposed by microorganisms (10).

Too few compounds have been tested to permit generalizations on the role of chemical properties on the occurrence, rate, or extent of aging-induced changes in bioavailability. Cationic and highly hydrophobic compounds are extensively sorbed, but it is not now known whether the lesser accessibility of organic molecules resulting from aging is related to this initial adsorption. Hydrophobicity, charge, molecular size or shape, or some other property may be correlated with rate or extent of aging, or both, but definitive answers must await additional experimentation.

Inorganic ions are also subject to aging. Aging has thus been shown to occur with Zn, As, Cd, Ni, Mn, Co, and other elements. These changes resulting from the aging often also affect the degree of exposure, as shown in measurements of the dermal bioavailability of Ni (38). Although the effects of aging of both organic compounds and inorganic ions reduce risk, the mechanisms probably are quite different.

New Assay Methods

The regulator is faced with a major dilemma because the magnitude of reduction in bioavailability resulting from aging is different for a single compound in different soils, for different compounds in the same soil, and for different periods of time that a compound has remained in soil. How does one predict the degree of exposure and risk from an aged compound? Bioassays are an obvious means of performing assessments, but biological measurements frequently do not have adequate precision for regulatory purposes, and they are time-consuming and expensive. An alternative is a chemical or physical assay, but the results of that assay must correlate well with the results of bioassays. If the degree of bioavailability is not the same for humans and different groups of animals, plants, and microorganisms—or by route of exposure—the chemical or physical assays would have to be correlated with the particular organism of concern or the likely route of exposure. Alternatively, a conservative course of action might be followed, and the species for which bioavailability is highest might be used in correlations with the nonbiological assays.

Several chemical and physical methods have been considered as ways to measure the bioavailability of organic compounds in soil. The results of analyses by such procedures have been correlated with bioavailability to earthworms, springtails, nematodes, and microorganisms (31, 39–43). The observation that the time-dependent decline in bioavailability is accompanied by a time-dependent decline in the quantity of compounds extracted from soil by a mild procedure (9, 10, 31, 44) suggests that a mild-extraction technique might serve as the basis for a surrogate assay for bioavailability.

Mode of Acquisition

Processes involved in sorption and desorption probably control the reduction in bioavailability, but few studies have been designed to relate the chemical and biological phenomena. Although the sorbed molecule must be desorbed to be biologically available, most studies of desorption have been conducted without consideration of the possibility of facilitated desorption associated with the excretions or surfaces of living organisms. The rates of utilization or uptake of sorbed (but not necessarily aged) organic compounds

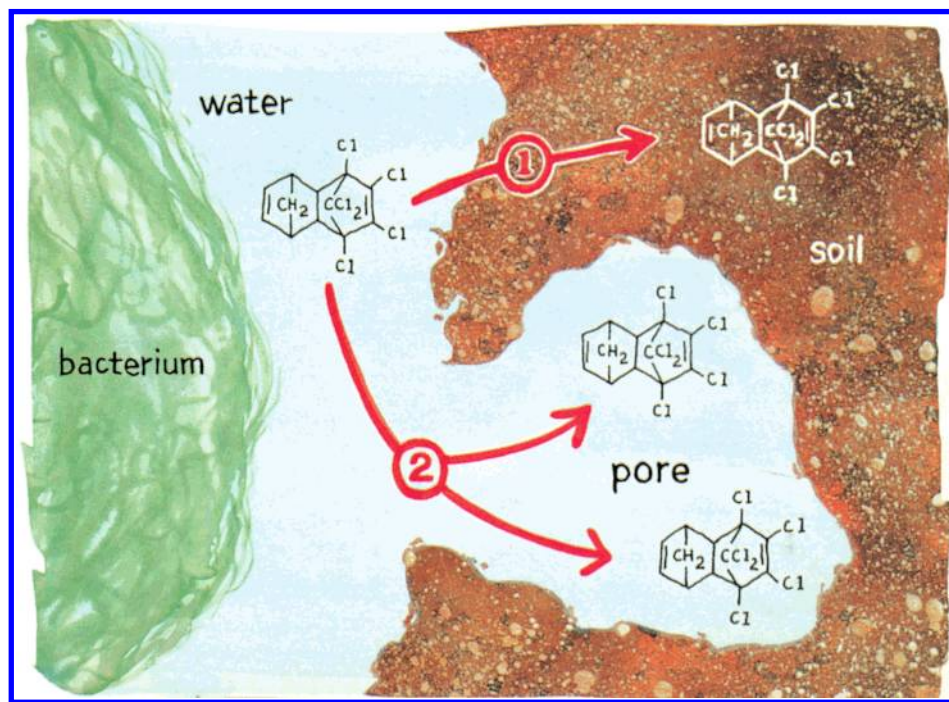


FIGURE 2. Sequestration of aldrin resulting from diffusion into the solid portion of soil or entry into nanopores. Reprinted with permission of T. Dunne from *American Scientist* (1997, 85, p 319, July/Aug).

frequently are limited by the rates of abiotic desorption (the rates measured in the absence of organisms), yet the rate at which animals and microorganisms acquire organic compounds for uptake, toxicity, or biodegradation is sometimes faster than the rate of mass transfer from the surface of a particle when measured in the absence of organisms. For example, although field evidence indicates that desorption and subsequent movement of TCDD is extremely slow, much of the compound may be fully bioavailable to mammals following ingestion or pulmonary exposure and to benthic invertebrates (45–48). In addition, only 3–4% of the fluoranthene absorbed by deposit-feeding invertebrates comes from abiotic desorption as sediment passes through their guts (49). These findings are consistent with the observation that the digestive fluids of marine deposit feeders solubilized 10 PAHs from contaminated harbor sediments, possibly because of surfactants in the digestive fluids (50).

Moreover, some bacteria utilize sorbed phenanthrene and biphenyl far more rapidly than the rate of their desorption from aquatic sediments or polyacrylic beads measured in the absence of bacteria (26, 51), and the rates of biodegradation of aged PAHs in a soil from a contaminated field site were sometimes faster than the rates of their abiotic desorption (52). Microorganisms produce surfactants or other emulsifiers that desorb organic compounds from soil (53), and several surfactants enhance microbial degradation of sorbed phenanthrene (54). It has been suggested that bacterial utilization of sorbed naphthalene is associated with their attachment to soil particles (55), a physical contact that may explain how some bacteria use sorbed biphenyl (51). That the mode of acquisition may entail attachment of cells to a surface is supported by investigations of bacterial degradation of hexadecane, di(2-ethylhexyl) phthalate, and pyrene dissolved in nonaqueous-phase liquids (56–58) and of the microbial utilization of hexadecane, which has low water solubility, by a bacterium that does not produce an extracellular surfactant or emulsifier but does adhere to the surface of this hydrocarbon (59). Therefore, although a molecule must be desorbed to become bioavailable, that desorption may require biological intervention, as by the release of a surfactant or other excretory product or by a physical contact

with hydrophobic constituents on the surface of an organism or exposed tissues.

Aging Mechanisms

Despite the reservations suggested by evidence of facilitated desorption, the literature on abiotic desorption has considerable relevancy to changes in bioavailability resulting from aging. It is believed that during aging, molecules slowly move into sites within the soil matrix that are not readily accessed by even the smallest of microorganisms, no less the tissues of higher organisms. The chief sorbent for hydrophobic molecules is the organic matter of soils, and this fraction is presumably where hydrophobic molecules become entrapped. A role for organic matter content of soil in reducing the bioavailability of aged phenanthrene for microbial degradation has been proposed (32), although organic matter may not be the only soil property that is important (9). If the molecules thus sequestered are inaccessible to organisms and even to extracellular enzymes of microorganisms and if diffusion out of these remote sites is extremely slow, the bioavailability of those compounds will be governed by the very slow rate of release to an accessible site. In a reasonably short time period, therefore, little would be available to an animal, plant, or microorganism.

Minute pores or voids may also be important in soils. Pores with diameters <100 nm are present in all soils and sediments examined (60–62), and pores or voids with diameters of 0.3–1.0 nm are also abundant (63), the latter being in the size ranges of the organic molecules of toxicological importance. Most of the surface area is associated with these pores so that their role in the sorption of toxic compounds is quite plausible. The organic fraction of soil contains an abundance of such nanopores (64, 65), and the sequestered compound may thus be localized in the minute pores of the organic matter. However, for a molecule to become poorly available, its desorption must be exceedingly slow. Tests with beads having pore diameters of 2.5–15 nm showed that phenanthrene was quickly desorbed and rapidly metabolized by microorganisms if the pores did not have hydrophobic surfaces, but desorption was slow and

biodegradability was enormously reduced if the pore surfaces were hydrophobic (66, 67).

Reduced bioavailability may also be associated with the entry of organic compounds into the solid phase of the organic matter. The molecules would partition into solid organic matter and, with time, move away from the outer surface to sites inaccessible to tissues, cells, or enzymes. Only with the exceedingly slow diffusion of a compound through the solid and to its outside would it then become available. Tests with solid alkanes, waxes, and low-molecular-weight synthetic polymers have shown that a PAH initially entrapped within such model solids is only very slowly degraded by bacteria (68). Nevertheless, soil organic matter is neither a simple polymer nor a homogeneous solid. It is highly heterogeneous and contains in its macromolecular structure, in addition to nanopores, regions that vary in polarity, density, and degree of coiling (69). This has led to the view that hydrophobic molecules that become resistant to desorption—and presumably are nonbioavailable—have become entrapped both within the solid phase of the organic matter and also in nanopores or voids existing at specific sites in that organic matrix. According to this hypothesis, the voids are present in the fraction of organic matter that behaves like a glassy or microcrystalline polymer in that it has an internal, quasi-permanent nanopore structure in which sorption can occur (70, 71). Two possible mechanisms of sequestration and loss of bioavailability of aldrin are illustrated in Figure 2. It has also been proposed that mineral precipitation may block the small pores (72), which could reduce bioavailability of entrapped molecules.

Relevance

Because exposure to persistent compounds is overestimated by currently used chemical methods, the risk is likewise being overestimated. Inasmuch as aging appears to occur in many and possibly most contaminated soils, the bioavailability of aged chemicals probably is being overestimated very frequently. As a consequence, current approaches to evaluating sites for cleanup sometimes may alarm people in localities where the risk is small. They probably lead to choosing some sites for remediation where little such need exists and thus delay the cleanup of polluted areas where the risk is greater. They also probably result in requirements for cleanup that are unnecessarily stringent and thus lead to expenditure of funds that could be better used to decontaminate additional areas. Therefore, a more widespread recognition of bioavailability of aged compounds is necessary—among scientists, environmental engineers, regulators, and the public at large.

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