

Sequestration of Organic Pollutants in the Environments: Implications on Bioavailability and Bioremediation

Kyoungphile Nam

*School of Civil, Urban & Geosystem Engineering
Seoul National University
(e-mail: kpnam@gong.snu.ac.kr)*

ABSTRACT

For the last several decades, the fate of organic pollutants has been extensively studied in natural environments with emphasis on sorption and desorption phenomena. Although the mechanisms involved are not clear yet there is a consensus about the existence of hysteresis in the sorption and desorption of organic pollutants. Furthermore, it is found that hysteresis is the outcome of slow nonequilibrium sorption of organic pollutants, which results in the formation of desorption-resistant fractions of the pollutants. Desorption-resistant fractions may increase as a function of the residence time of the pollutants in the environments. Field monitoring data show a slow but continuous decline of chemicals applied to soil, followed by little or no subsequent disappearance. One plausible explanation for such resistance to biodegradation, desorption, or extraction can be attributed the gradual movement of organic pollutants to less accessible remote sites inside the matrix with time. This phenomenon has been termed sequestration or aging. The fact that some pollutants are sequestered in soil with time may have a great impact on bioremediation and risk assessment. Some portion of the resistant pollutants may still be present in the environments after bioremediation. It requires vigorous means to completely remove the aged portion that may not be further bioavailable. However, precaution should be taken since aging is not always evident. Aging seems to be soil and chemical specific.

Key words: sequestration, aging, desorption-resistant fraction, bioavailability

1. Bioavailability of Organic Pollutants in the Environments

Bioavailability of organic compounds depends on both biotic and abiotic factors including the physical state (1), water solubility (2), or chemical structure (3), sorption/desorption (4) of substrates, size of soil aggregates (5,6), soil moisture (7), and types of microorganisms (8). The physico-chemical properties of organic compounds play a role in determining its bioavailability. The fact that a compound is readily utilized by bacteria in aqueous phase does not guarantee that the compound will be similarly biodegraded by the same bacteria in the natural environment. The most important factor is water solubility or hydrophobicity of a chemical of interest. Hydrophobicity is often expressed as octanol-water partition coefficient (K_{ow}), which indicates the tendency for a compound to partition into organic matter. Organic compounds, when introduced into natural environments, tend to sorb to clay minerals, organic matters (e.g., humic substances), or solid materials present. Sorption can be defined as any accumulation of organic compounds on or below the surface. A lot of studies have been performed to elucidate the mechanisms of sorption, and two proposed mechanisms are now available—hydrophobic sorption and partitioning (9,10). Hydrophobic sorption refers to the accumulation of hydrophobic organic compounds on hydrophobic surfaces. Partitioning is a continuous process describing that hydrophobic compounds enter into three dimensional structure of sorbents (e.g. organic matter) gradually. However, the two processes may not be separated and work simultaneously in the natural environment (12). Organic compounds accumulate on the hydrophobic surfaces of sorbents by hydrophobic sorption, and where available, the sorbed compounds may partition into the matrix. Details about the mechanisms are beyond the scope of this chapter. No matter which mechanism happens, it is clear that sorption of organic compounds has a great impact on their bioavailability to microorganisms.

Organic compounds introduced into soil are likely to be less bioavailable than the same compounds in solution, presumably due to the sorption of the chemicals. Since one of the most important sorbents of hydrophobic compounds in the nature is organic matter (10), the reduced bioavailability of hydrophobic compounds seems to be mainly related to organic matter. This reduced bioavailability often results in declined toxicity (12,13). Peterson et al. (14)

measured LD₅₀ to study soil properties influencing the toxicity activity of DDT to *Drosophila melanogaster*, and suggested that DDT may present little biological hazard in soils rich in organic matter. An inverse relationship between toxicity or biodegradation and degree of sorption of organic compounds (i.e., chlorinated insecticides and polycyclic aromatic hydrocarbons) was also reported (15,16).

Although not extensively studied, quality of organic matter may also influence bioavailability by affecting the partitioning process of organic compounds (17,18). A study (19) with chlorinated pesticides (e.g., alachlor, metolachlor, and propachlor) suggests that K_{OC} values decrease as the ratio of oxygen and nitrogen to carbon (O+N/C) of a sorbent increases.

2. Formation of Irreversible and Desorption-Resistant Fractions

Although biphasic sorption of organic compounds has long been known for pesticides including 2,4-D and picloram (20), tests of sorption of organic compounds before the 1980s were performed for less than 24-72 h because sorption was considered a fast process. However, Karickhoff (21) presented evidence that sorption may be a slow process extending from days to weeks. Later, a two-compartment model was proposed (22), which consisted of two sorption domains—a rapid component (S1) and a much slower component (S2). Organic compounds sorbed in the S1 state are easily extracted by solvent and readily bioavailable whereas compounds in the S2 state are resistant to solvent-extraction and bacterial utilization. This biphasic sorption behavior, often called nonequilibrium sorption, may result in the formation of desorption-resistant fraction, which probably is the reason for the persistence of some organic compounds in the nature.

Laboratory studies with historically contaminated soils and with environmental samples to which organic compounds have been intentionally added suggest the presence of irreversible sorption that results in desorption-resistant fractions. A number of studies have shown that a fraction of sorbed organic compounds is difficult to remove, and this fraction has been labeled the irreversible or resistant fraction (23). DiToro and Horzempa (24) suggested that hexachlorobiphenyl sorbed in sediment may have both reversible and irreversible components, and a similar observation was also made with polychlorinated

biphenyls (PCBs) congeners (25) and PAHs (26,27). Studies suggest that part of the desorption-resistant fraction is available to microorganisms, but another significant part is not utilized in reasonable time periods (28,29).

It is likely that not only hydrophobic compounds but also polar compounds show irreversible sorption and thus form desorption-resistant fractions. Ahlert and Uchirin (30) reported that benzene and toluene could form slowly reversible fractions in aquifer solids. In a study with picloram (31), the amount of the compound readily released from soil decreased appreciably with time for up to 300 days. The formation of slowly reversible sorbed fractions in soil has been observed with halogenated and nonhalogenated alkanes as well as trichloroethene (TCE), tetrachloroethene (PCE), and 1,2-dibromoethane (EDB) (32). These compounds are volatile, have weak to moderate equilibrium sorption tendencies, and do not contain strongly interacting functional groups that could form strong chemical bonds with soil. This suggests that strong chemical reactivity is not required for the formation of slowly reversible and desorption-resistant fractions. Pavlostathis and Jaglal (33) observed an initially fast rate and a subsequent slower rate of desorption with soil samples from a TCE-contaminated site. Moreover, the extent of TCE desorption decreased with increasing residence time of the compound in soil (34). Connaughton et al. (35) studies the rates of release of freshly added and aged (approximately 30 years) naphthalene and found that increased incubation time allowed the compound to be sorbed to compartments in soil that exhibited slow desorption kinetics. Similar observation was reported by Pignatello and Huang (36), who studied the reversibility of sorption of atrazine and metolachlor in a field soil. Their results suggest that the soil may contain a large fraction of slowly reversible contaminant, and that the size of this fraction increases with time.

3. Aging as an Explanation for Persistence and Declined Bioavailability

Based on field data reported and laboratory experiments, Alexander (37) proposed a phenomenon about the fates of organic compounds in solid matrices including soil, sediment, and aquifer. He suggests the presence of persistence of organic compounds, and the persistency increases as the residence of the compounds increases in soil. Long-term field monitoring provides evidence for persistence of

organic compounds, mainly pesticides, in soils. DDT applied to soil disappeared during the first 10 years after application, but little change was observed in subsequent years, resulting in a hockey stick-shaped curve (38). This curve of disappearance was also observed with many pesticides such as aldrin, dieldrin, lindane (38-40).

In recent years, a growing body of evidence has demonstrated that the availability of some organic compounds to extraction, living organisms or both diminished as the residence time of the compounds increases in soil. This phenomenon has been termed aging or sequestration (37). Aging does not include reactions that alter the structure of parent molecules such as polymerization and covalent bonding. Therefore, aged compounds should be readily biodegraded if the refractory fractions are extracted from a soil and added back to the soil. That this does occur was experimentally shown by Weissenfels et al. (12). In fact, decreased bioavailability is not entirely a new observation. It has been observed that the LD₅₀ of DDT of fruit flies increases as the compound resides in soil for increasing periods of time (41). Chiba and Morley (42) also showed that some pesticides become more difficult to extract as they reside in soil. A study with field soil contaminated with EDB showed that aging alters bioavailability of the compound to indigenous microorganisms (43). Whereas freshly added EDB was almost totally destroyed in several weeks, little EDB, which had resided in the soil for at least 19 years, was destroyed in 30 days. Similar observation was reported with PAHs (44,45).

The diminished bioavailability is observed with microorganisms and higher organisms as well. Scribner et al. (46) showed aged simazine residues are less bioavailable to sugarbeet (*Beta vulgarize* L.) compared to unaged simazine and desorb slowly into soil solution. Bioavailability of PAHs in sediment to the amphipod *Diporeia* sp. and to the oligochaete *Lumbriculus variegatus* also decreased with increases in the length of contact time between the sediment and the contaminant (47,48). Similar findings were obtained with earthworms (49) and plants (50). However, an aging effect and thus a declined availability may not occur or may not be appreciable in some environments or with some compounds. For instance, both freshly added and aged PCDDs (polychlorinated dibenzo-*p*-dioxins) were available for microbial reductive dechlorination (51).

4. Proposed Mechanisms of Aging

Since aging is thought to be the outcome of slow and irreversible sorption within the matrix of sorbents, aging mechanisms consequently are likely to be closely related with nonequilibrium sorption process. Organic compounds taken up rapidly by sorption from aqueous phase to external sorption sites can move slowly into internal remote sites or sites less accessible with time to extraction or microorganisms, or both. This physical sequestration of organic compounds may occur by association with the polymeric structure of soil organic matter (i.e., intraorganic matter diffusion) or by diffusion into tortuous pores of microporous particles (i.e., retarded intraparticle diffusion). Brusseau and Rao (52) reviewed literatures and suggested intraorganic matter diffusion as a possible mechanism for the nonequilibrium sorption of hydrophobic organic compounds. This hypothesis is consistent with the idea of partitioning of organic compounds into organic matter (53,54). For this model valid, the structure of organic matter should be three-dimensional. Evidence indicates that organic matter in soil and sediment has a three-dimensional network of polymeric chains with a relatively open, flexible structure perforated with voids (20,55-57). Another proposed mechanism, retarded intraparticle diffusion model, involves aqueous-phase diffusion of a compound within micropores of sorbents and the diffusion of the compound in pore water is retarded by sorption on pore walls (58). The finding that bioavailability or desorption of persistent compounds including aliphatic halocarbons, 1,2,4,5-tetrachlorobenzene, PCE, and EDB was enhanced by pulverization supports the hypothesis of intraparticle diffusion (43,59,60). However, either mechanism can not adequately describe the irreversible sorption of hydrophobic organic compounds. It is likely that both mechanisms may operate simultaneously, and their relative significance depends on the characteristics of sorbates and sorbents. It is also possible that sorbed compounds may diffuse into organic matter-coated micropores, where the two mechanisms work together. In this instance, sorbed compounds may undergo extensive sorption/desorption processes inside micropores. Indeed, a sorption model having a fast component governed by partitioning and a slow component controlled by micropore diffusion gave good fits to the elution of freshly added and aged atrazine and metolachlor from a fine sandy loam (61). This might happen if micropore are coated with organic matter, and evidence exists

that a significant amount of organic matter resides inside pores less than 10-nm diameter in soils and sediments (62,63). In model systems using synthetic beads, microporous sorbents having hydrophobic surfaces showed a significant decrease in the bioavailability of the test compound phenanthrene to bacteria compared to nonporous hydrophobic beads and microporous hydrophilic beads (64).

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