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THE EFFECTS OF AGING ON THE SORPTION/DESORPTION BEHAVIOR OF ORGANIC CHEMICALS IN SOILS AND RELATION TO BIOAVAILABILITY

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ABSTRACT

EFFECTS OF AGING ON THE SORPTION/DESORPTION BEHAVIOR OF ORGANIC CHEMICALS IN SOILS AND RELATION TO BIOAVAILABILITY

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Observations on the behavior of pesticides in field-weathered soils have demonstrated that increased soil-chemical contact time (aging) may lead to increased persistence of contaminants in the environment. Aged chemicals can act as long-term sources of groundwater contamination, and aging may reduce the effectiveness of soil remediation technologies such as soil washing, pump and treat, and in-situ bioremediation. Environmental fate characterization based on laboratory studies of freshly added chemicals fail to consider the effects of aging and hence may underestimate the persistence of organic compounds in the environment. For example, although the soil fumigant ethylene dibromide (EDB) is readily biodegradable, relatively water soluble, and volatile, EDB residues have been found in field soils 20 years after its last known application. However, the causes of increased persistence due to aging are not well understood. One possible cause of increased persistence is a reduction in the bioavailability of contaminants to degrading microorganisms. This decrease in bioavailability is likely due to changes in the physical/chemical disposition of the contaminants due to aging. For example, an increase in sorption to soils due to aging can limit the extent of biodegradation of organic contaminants. Also, desorption from soils, which may decrease with aging, is thought to be the limiting factor controlling the rate of degradation of organic contaminants by degrading microorganisms.

This study describes three experiments designed to test the role of aging and its effect on the sorption/desorption dynamics and bioavailability of chemicals in soils. One experiment examined the sorption/desorption behavior of chlorobenzene on four soils (soil organic carbon content from 0.4 – 7.8 %) after soil-chemical contact times (aging) of 24 hours and 14 months. Another experiment examined the sorption/desorption behavior of four compounds (EDB, chlorobenzene, 2,4-D, and atrazine) on one soil type after aging times of 24 hours, 1 month, and 14 months. Lastly, the sorption/desorption behavior and bioavailability of biphenyl to *Pseudomonas putida* P106 was studied after aging times of 24 hours and 8 months.

Increases in sorption due to aging were found for some chemicals (2,4-D, EDB) but not others (chlorobenzene). Large differences in sorption/desorption behavior for similar compounds (EDB and chlorobenzene) were observed, indicating that generalizations about compound behavior in soils are inappropriate. Desorption profiles were consistent in that aged chemicals showed a much larger desorption resistant fraction after long aging periods and this was true for all soil types. Desorption rates were unaffected by aging time. Biodegradation of biphenyl decreased with increased aging time and the desorption resistant fraction (observed in the desorption profiles) appeared to be inaccessible to microbes.

I would like to dedicate this work to my mother and father.

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EFFECTS OF AGING ON THE SORPTION/DESORPTION BEHAVIOR OF ORGANIC CHEMICALS IN SOILS AND RELATION TO BIOAVAILABILITY

Introduction and Literature Review

An understanding of the sorption/desorption dynamics of organic contaminants in field-weathered soils is crucial to understanding contaminant fate and behavior in the environment. Sorption/desorption processes are known to affect biodegradation, which is one of the main routes for the dissipation of contaminants in the environment (*Alexander, 1994*). Sorption of contaminants to soils is known to limit the *extent* of biodegradation in the environment. Desorption may be the kinetically slow step controlling the *rate* of contaminant biodegradation in the environment (*Carmichael, et al., 1997*). Soil-chemical contact time (aging) has been shown to play a dominant role in the sorption/desorption dynamics of contaminants in soils. The effects of aging may reduce the effectiveness of soil remediation technologies (soil washing, pump and treat, and bioremediation) and aged chemicals can act as long term sources of groundwater contamination. The main purpose of this work is to determine the effects of aging on the sorption/desorption and biodegradation dynamics of contaminants in soils.

According to partition theory, sorption of organic contaminants in soil-water systems is due primarily to partitioning into bulk phase soil organic matter (SOM) (*Chiou, et al., 1979*). Partitioning of organic contaminants into SOM is analogous to the dissolution of an organic chemical in a bulk phase organic solvent. The extent of uptake depends on the SOM content and the relative solubility of the contaminant in water and

SOM. This process is distinct from adsorption, which refers to the condensation of a solute or vapor on the adsorbent surface. Partition theory predicts linear and singular isotherms whether approached from the sorptive or desorptive direction. Most laboratory studies dealing with sorption and desorption of organic contaminants and pesticides have assumed rapid (24 hours or less) and reversible equilibrium. There are numerous examples that demonstrate these assumptions may not be valid. Deviations from these assumptions could have major effects on predictions of contaminant transport and biodegradation. One study indicated that sorption was a slow process and could take hundreds of days to reach equilibrium and that sorption on aquifer material was an order of magnitude greater than that predicted by partition theory (*Ball and Roberts, 1991*). Another study found that the equilibrium sorption coefficient (K_p) may increase between 30 % and tenfold between short and long equilibration times (*Pignatello and Xing, 1996*). These investigators also observed that sorption isotherms might become increasingly non-linear with time (*Xing and Pignatello, 1996*). There are several recent examples in the literature that sorption and desorption isotherms are often not reversible. One study found that desorption was not complete and reversible even when the adsorption time scale was short (7 days) (*Pavlostathis and Jaglal, 1991*). Fu *et al.* (*1994*) found that sorption was rapid (equilibrium reached in 1-7 days) in a low organic carbon (OC) (0.157 %) sandy sediment but that a large fraction of naphthalene (over 40 %) was not removed by successive desorption steps. Desorption hysteresis and incomplete desorption have also been observed in long contaminated field soils (*Steinberg, et al., 1987; Scribner, et al., 1992; Connaughton, et al., 1993*).

Despite a great deal of empirical evidence that soil-chemical contact times (aging)

can affect the sorption/desorption process, there are relatively few long-term, laboratory controlled aging studies which explicitly measure sorption and desorption parameters. Most long-term aging studies have utilized field-contaminated soils. Steinberg *et al.* (1987) found that 1,2-dibromoethane (EDB) persisted in an agricultural field up to 19 years after its last known application. This is despite the fact that EDB is volatile (vapor pressure = 13.8 mm Hg), moderately water-soluble (water solubility = 4250 mg/L), has low affinity for soils, and is degraded rapidly by soils organisms under both aerobic (*Pignatello, J.J., 1986*) and anaerobic conditions (*Castro and Belser, 1968*). In the majority of these field studies, freshly added chemicals are "spiked" into clean soils and parameters such as extractability (*Hatzinger and Alexander, 1995*), biodegradability (*Steinberg, et al., 1987; Hatzinger and Alexander, et al., 1995*), bioavailability (*Scribner, et al., 1992*), or desorption rate (*Steinberg, et al., 1987; Scribner, et al., 1992; Pavlostathis and Mathavan, 1992; Pavlostathis and Jaglal, 1991*) are measured for both freshly added and field-aged chemicals. Conclusions in these types of studies have been consistent, demonstrating that field-aged chemicals all have reduced extractability, bioavailability, biodegradability, and a reduced extent of desorption. However, information in field studies can be limited because of uncertainty of the total chemical mass involved (Harmon and Roberts, 1994) and uncertainty (in some cases) about soil/chemical contact times.

Attempts to reproduce results from field studies in long term, laboratory controlled aging studies have been inconclusive. Furthermore, there are very few long term (> 3 month), laboratory controlled aging studies which explicitly measure sorption and desorption parameters. In a seven-day, laboratory aging study, Wu and Gschwend

(*1986*) found that sorption kinetics were controlled by an intraparticle diffusion mechanism. Their results indicated that sorption and desorption should be completely reversible given the appropriate time scale in accordance with a reversible diffusive exchange mechanism. Another study (*Connaughton, et al., 1993*) using aged (3 months) and relatively "unaged" (3 day) naphthalene in soil also suggested a completely reversible diffusion mechanism, although reversibility was not seen on the time scale of their experiment. The desorption of hexachlorobenzenes aged on sediments from days to weeks was found to be completely reversible (*Karickhoff and Morris, 1985*). There was no irreversible fraction observed even for samples aged for up to 28 days. Other studies have demonstrated that sorption is a slow process which may take hundreds of days to reach equilibrium (*Ball and Roberts, 1991; Pignatello and Xing, 1996*). The studies mentioned above would implicate a diffusive transport mechanism for the sorption/desorption behavior of organic chemicals in soils and tend to contradict observations from field studies.

Several other laboratory studies document the irreversibility of contaminant sorption by soils. Fu *et al.* (*1994*) found that sorption of PAH's (polynuclear-aromatic hydrocarbons) in low OC (0.157 %) surface sediments was rapid (reached in 1-7 days) and that desorption was not reversible even for samples that were aged for short time periods (1 or 7 days). They found that the irreversible (non-desorbable) fraction was 30-50 % of the adsorbed amount. According to calculations based on diffusion coefficients, sorption which takes place for days may take years for desorption to be completed (*Kan, et al., 1994*). Pavlostathis and Jaglal (*1991*) also observed that even short-term (7 days) sorption / desorption was not reversible. Numerous other investigators have found that

the irreversible fraction of a chemical increased with increased aging time (*Pavlostathis and Mathavan, 1992; McCall and Agin, 1985; Pignatello, 1990a*). Results from these studies are consistent with observations from field studies, but in contrast to results from studies demonstrating reversibility of the sorption/desorption process. Furthermore, another study found that aging had little effect on the desorption curves of tetrachloroethene and 1,2-dibromo-3-chloropropane from aquifer sediments (although aging was for only 5 and 30 days) (*Pignatello, 1991*). However, it is not possible to say whether aging affected the desorption *rate* or not, since this parameter was not measured. In contrast, it has also been observed that aging does effect the desorption rate of picloram in soil where aging was done for 0, 28, and 200 days (*McCall and Agin, 1985*). It is clear from the above examples that the observed effects of aging on contaminant dynamics in laboratory studies have been inconclusive. The studies conducted to this point in time have found no consistent effects of aging and have not identified a causative mechanism for the observed effects.

Results of the studies cited above have led to the formulation of conceptual models to aid in the understanding of the processes involved in the sorption/desorption behavior of organic chemicals in soils. There are several excellent reviews of these models available (*Pignatello and Xing, 1996; Pignatello, 1989; Hatzinger and Alexander, 1995*), so they will be discussed only briefly here. The first model, the sorption-retarded pore diffusion model (SRPD) (*Pignatello and Xing, 1996*), assumes complete sorptive and desorptive reversibility based on an intraparticle diffusion mechanism. Movement of a chemical into and out of an idealized, spherical sorbent (soil particle) is highly retarded due to microporosity and tortuosity of the sorbent (*Wu and*

Gschwend, 1986). Movement of the chemical may be slowed by partitioning into and out of organic matter on the pore walls. Another model, the organic matter diffusion (OMD) model assumes that the sorbate interacts mainly with the organic matter in the sorbent and it diffuses through the organic matter polymer, which is viewed as a lattice-like structure (*Brusseau and Rao, 1989a; Pignatello and Xing, 1996*). The organic polymer may be in a condensed (glassy) or relaxed (rubbery) polymeric state, with sorbate diffusion being faster in the relaxed state.

It is also possible that sorption and desorption behavior is the result of a surface adsorption process in which strong chemical or physical bonds may take place between the sorbate and the soil particle surface (*Hatzinger and Alexander, 1995)*. The soil surface may be the outer surfaces of clays, interlayer spaces of clays, or the surface of organic matter. Crucial to this model is a determination of the surface area of organic matter, but standard methods for this process have been questioned recently. Isaacson and Frink (*1984*) proposed that the irreversible fraction of phenols and some substituted phenols may be the result of hydrogen bonding of these compounds to humic material. Other researchers have also implicated specific adsorption interactions with soil materials, although these types of interactions are limited to ionic compounds and those with polar functional groups (*Nearpass, 1976; Hayes, 1970; Li and Felbeck, 1972; Boyd and Mikesell, 1987*). Recently, some experimental evidence has suggested that surface adsorption models may be able to explain sorption/desorption behavior in soils (*Kan, et al., 1994*). Since it has been demonstrated that surface adsorption can lead to hysteresis (*Adamson, 1990*) even on model sorbents, it seems reasonable to consider a surface adsorption model along with the SRPD and OMD conceptual models.

There is also some evidence that the sorption of organic contaminants may cause conformational changes in the structure of soil humic and fulvic acids. Evidence indicates that this psuedomicellar behavior of humic and fulvic acids has the ability to sequester hydrophobic species in the solution environment (*Engebretson, et al., 1996; Engebretson and von Wandruszka, 1994*). Physical entrapment due to structural changes would explain the existence of a desorption resistant fraction often observed in sorption/desorption studies. Computational molecular modeling approaches have demonstrated that organic contaminants such as atrazine can be trapped in structural voids of humic acids by means of H-bonding (*Schulten, 1995*). The importance of the physical structure of SOM and its constituents and its role in organic contaminant entrapment in the environment has not been studied in-depth and needs further analysis.

There are also several mathematical models, both mechanistically and non-mechanistically based, which have been used in an attempt to predict sorption and desorption behavior. The two most widely used mathematical models are the two-box model and the radial diffusion model. The two-box model (Cameron and Klute, 1977) assumes that sorption/desorption occurs on "fast" and "slow" sites in the soil (see Figure 1). The model describes two possible compartment configurations, a series version ($C_o \Leftrightarrow S_1 \Leftrightarrow S_2$) and a parallel version ($S_1 \Leftrightarrow C_o \Leftrightarrow S_2$). Although mathematically identical, the series version makes more physical sense because the S_1 compartment can be conceptualized as the exterior of the sorbent and the S_2 compartment as the interior of the sorbent. The rate constants describe fast sorption (K) or slow desorption (k_d) between the compartments. The variables S_1 and S_2 give the fraction of chemical in each compartment. This model makes no assumptions about the mechanisms of soil/chemical

interactions. The radial diffusion model (*Wu and Gschwend, 1986*) assumes the sorbent is a perfect sphere where movement of chemical into the sorbent is governed by retarded

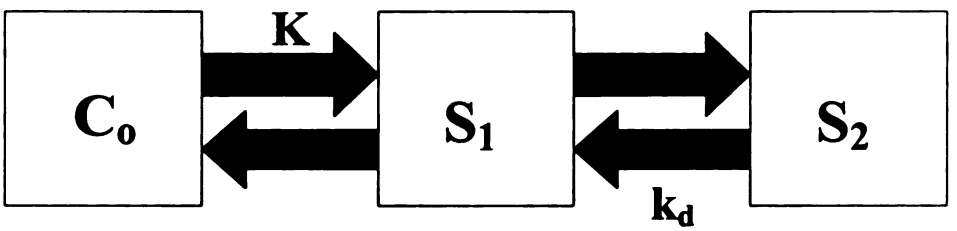

Figure 1.1. Schematic diagram of the Two-Box Model (from *Guerin and Boyd, 1993*).

diffusion. This retarded diffusion is due to movement of the sorbate through soil micropores and / or microscale partitioning of the sorbate into and out of organic matter on pore walls. This model uses only on fitting parameter, the effective diffusion coefficient (D_{eff}) where:

$$D_{eff} = D_m * n / ((1-n) * p_s * K_p)$$

D_m = pore fluid diffusivity of the sorbate, n = porosity of the sorbent, p_s = specific gravity of the sorbent, K_p = equilibrium sorption coefficient of the specific soil/solute pair, and (1-n) = the mass of the sorbent. This model assumes a mechanism of interaction between the soil and sorbate, and in order for the model to be correct, sorption and desorption should be completely reversible. Although other mathematical models have been employed to predict sorption/desorption behavior, most are variations of the ones discussed above.

There are very few studies that have explicitly analyzed the role of soil organic matter in the aging process. Given the dominant role of SOM with respect to organic

contaminant interactions with soil, it seems reasonable to expect that the effects of contaminant aging may be different in soils with different SOM content, especially if the OMD model is valid. Although no studies have examined the role of SOM and aging explicitly, scrutiny of the literature demonstrates that there may be a correlation between SOM content and the effects of aging. In a review paper on aging, Loehr and Webster (*1996*) thought that the effect of aging time on sorption and desorption may be more pronounced in soils with high organic carbon content.

With respect to the forward process, sorption, some investigators have found that equilibrium does not appear to be reached quickly (in 24 hours or less) while in other cases, equilibrium appears to be approximated within this time frame. Ball and Roberts (*1991*) investigated the long-term sorption of tetrachloroethene and tetrachlorobenzene on very low organic carbon (OC) (0.021 %) aquifer materials and found that equilibrium may take hundreds of days to be established. Another study looked at the sorption of PAH's on relatively low OC surface sediments (0.157 %) and found that sorption was complete in one day (*Fu, et al., 1994*). It is not clear whether the differences in OC content between sorbents in these studies were significant enough to account for the observed behavior. Pignatello and Xing (*1996*) reviewed slow sorption and desorption behavior and found that sorption increased between 1.3 and 10 times for long and short aging times, although there appeared to be little correlation to SOM content. The same two investigators found that sorption isotherms may become more non-linear with aging time (between 1 and 180 days) (*Xing and Pignatello, 1996*). They also found that for dichlorophenol (DCP) the largest relative increase in the sorption coefficient (K) between 1 and 180 days occurred in soil (1.74 % OC) rather than in peat (54.07 % OC) (*Xing and*

Pignatello, 1996).

For the reverse process, desorption, some investigators have noticed the relationship between a larger resistant (non-desorbable) fraction and increased SOM (*Pignatello, 1990b; Carroll, et al., 1994*) for chemicals aged in soils. At least one investigator found that the rate and extent (which determines the resistant fraction) of desorption of aged trichloroethylene, toluene, and xylene were not correlated to SOM content, nor to specific surface area or water solubility (*Pavlostathis and Mathavan, 1992*). In one of the most comprehensive studies done on aging (*McCall and Agin, 1985*), there appeared to be a greater effect on $K_d$app (the apparent equilibrium distribution coefficient) of picloram aged in low OC soils (0.45 %) than in high OC soils (2.9 %). The $K_d$app was measured by a 2 minute desorption protocol after aging picloram on these soils for 0 and 300 days. In the low OC soil the $K_d$app increased 5.4 times, but only 1.6 times in the high OC soil. Also measured were $K_d$app values after sorption for 100 days and for desorption (after 100 days of sorption), the difference in these values represents the degree of hysteresis between a single sorption and desorption equilibrium point after 100 days. The difference in the values for the high OC soil was only 1.08 times (effectively the same, no hysteresis) whereas in the low OC soil the difference was 11.25 times. These changes indicate that the effect of aging is greater in low OC soils than in high OC soils. This may be in contrast to what some researchers have expected, but it seems to agree with the results found by Xing and Pignatello (*1996*) and their study with DCP on peat and soil. Furthermore, assuming that the 7-8 fold difference in OC content was the reason for the discrepancy in the sorption results found by Ball and Roberts (*1991*) and Fu et al. (*1994*), the correlation between lower OC

content and larger aging effects would explain their results as well.

The study discussed in the following chapter was initiated because of the lack of long term, laboratory controlled aging studies explicitly measuring sorption and desorption parameters and because of the need to look at the role of SOM content in the aging process. In this study, the sorption isotherms of chlorobenzene (CB) on four soil types with a range of SOM content (from 0.69 to 13.42 %) were measured after 24 hours and 14 months of aging. Then, desorption kinetics were measured for chlorobenzene on each soil after the sorption times mentioned above, with desorption being followed for up to four months. This was done in an effort to examine the effect of aging on one compound in several soils to establish the role of SOM content in the aging process.

There has been very little work examining the role of sorbate properties in the aging process and how this may affect sorption/desorption behavior. Several researchers have observed that increasingly hydrophobic compounds (as measured by K_p, the equilibrium partition coefficient) exhibit slower sorption/desorption behavior in soils (*Karickhoff and Morris, 1985; Brusseau and Rao, 1989b*). In contrast, Oliver (*1985*) found that desorption behavior was largely independent of adsorbate properties even for a wide variety of aged non-polar organics in sediments. These compounds exhibited nearly a four order of magnitude range in hydrophobicity, as measured by K_{ow} (octanol-water partition coefficient). If hydrophobicity affects desorption as observed by Karickhoff and Morris (*1985*), it seems likely that these differences would have been observed in the aged sediments by Oliver (*1985*) given the range in hydrophobicity of the solutes. Another study (*Stauffer and MacIntyre, 1986*) tried unsuccessfully to correlate sorption coefficients to sorbate dipole moments. In their discussion, these investigators stated that

sorbate polarizability might be a better parameter with which to predict sorption behavior. They did find a positive correlation between sorbate molar volumes and sorption coefficients. The aforementioned studies only compared behavior of non-polar organics, which are largely unreactive with soil components. Their behavior in soil is expected to be governed by a single mechanism, solute partitioning into SOM (*Chiou, et al., 1979*).

Several other studies have examined the aging behavior of both polar (or compounds with polar functional groups) and non-polar organic compounds. Xing and Pignatello (*1996*) examined sorption isotherms of dichlorobenzene (non-polar) and dichlorophenol (polar) in soil after 0 and 30 days of aging and found that the K_p increased only 1.3 times for dichlorobenzene (DCB; log K_p = 3.38) but 2.7 times for dichlorophenol (DCP; log K_p = 2.75). This would suggest that the non-polar compound, although slightly more hydrophobic, had faster sorption kinetics than the polar compound and therefore approached equilibrium faster. These results are in agreement with the results of another study (*Brusseau and Rao, 1989a*) in which linear free energy relationships (LFER's) were observed between sorption rate coefficients (log k) and sorption equilibrium coefficients (log K_p) for both polar and non-polar compounds. For polar (Type II) and non-polar (Type I) compounds with similar partition coefficients, the polar compounds exhibited substantially slower sorption/desorption kinetics. They attributed this to the increased reactivity of polar compounds or compounds with polar functional groups. The polar compounds must diffuse through organic matrices (a physical non-equilibrium process or PNE) and are subject to specific chemical interactions due to their polar functional groups (a chemical non-equilibrium process or CNE), whereas the

relatively unreactive non-polar compounds are subject only to the former process. When the results of Xing and Pignatello (*1996*) are viewed in the context of these findings, it is reasonable to expect that DCP would exhibit a larger increase in K_p upon aging than DCB. Based upon the data of Brusseau and Rao, the relatively similar log K_p values for DCB and DCP would translate to a log k value for DCP that is two orders of magnitude slower that that for DCB. So it is apparent, from this data, that DCB would approach equilibrium much more rapidly than DCP.

Brusseau and Rao (*1989a*) presented evidence that polar compounds are rate-limited due to diffusion (PNE) and CNE whereas non-polar compounds are rate limited solely by diffusion. Polar compounds, such as atrazine, picloram, and chlorophenols, which have reactive functional groups, are known to form specific interactions with soil (*Hayes, 1970; Li and Felbeck, 1972; Nearpass, 1976*). Given the temporal nature of bond formation, polar compounds which interact by dual mechanisms (at least) may demonstrate dramatic sorption and desorption differences from non-polar organics, which have a single and general sorption mechanism, if enough aging time is allowed for these specific interactions to form. The literature indicates some evidence of this occurrence. Winkelman and Klaine (*1991*) found that bound residues of atrazine in soil microcosms increased with increased aging time. Ma and Selim (*1994*) also found that sorption and desorption behavior of atrazine was highly hysteretic and this hysteresis increased with aging time. They also found that atrazine had not reached sorption equilibrium even after 22 days. The same behavior was observed for alachlor (*Xue and Selim, 1995*). Alachlor was characterized in this study as a moderately non-polar compound, but they stated that sorption of alachlor occurred by at least two types of mechanisms: hydrophobic binding

to aliphatic parts of humic acid *(Senesi, et al., 1994)* and by coordination binding to clay and organic matter surfaces (*Bosetto, et al., 1993*). Alachlor has also been shown to penetrate the interlayer space of montmorillonite (*Bosetto, et al., 1993*).

In contrast, Boesten and van der Pas (*1988*) found no sorption/desorption hysteresis of cyanizine (a triazine herbicide similar to atrazine) and metribuzin, both polar compounds, in soil suspension. Interestingly, this study incorporated no long term aging component, as sorption and desorption were followed for only 24 hours. This may account for the lack of hysteresis observed in this study, in contrast to the two previously mentioned studies, in which aging was performed for up to 22 days (*Ma and Selim, 1994; Xue and Selim, 1995*). Another study on atrazine (*Moreau and Mouvet, 1997*) found that atrazine sorption in soil (0.65 % OC) was complete after 72 hours and that desorption was completely reversible. One possible reason for this conclusion was that sorption was not followed for longer than 96 hours, in which case slow approach to equilibrium would not have been observed. Furthermore, desorption may have appeared to be reversible if sufficient time (only 3-4 days in this case) was not allowed for bound residues to form, as may have occurred in the 22 day aging studies. Conclusions from these studies would suggest that aging time may have more of an effect on the dynamics of polar compounds, which interact with soils by two or more mechanisms, than for non-polar compounds.

In an attempt to better understand the effects of aging on the dynamics of polar and non-polar compounds in soils, the study in chapter 3 was undertaken to explicitly measure sorption and desorption parameters for chlorobenzene, EDB, atrazine, and 2,4-D on a Capac A soil. Sorption isotherms and desorption kinetics were measured after 24 hours, 1 month, and 14 months of aging for each compound, with desorption being

followed for up to four months. This study was initiated because of the lack of long term, laboratory controlled aging studies and because of the need to examine the role of sorbate properties in the aging process.

Sorption/desorption behavior of organic chemicals in soils may be the most important factor governing their bioavailability. Bioavailability of organic contaminants to bacteria is an important determinant of the contaminants' environmental persistence. Bioavailability also determines the toxicological and herbicidal activity of chemicals (i.e., pesticides) in the environment. Sorption to soils is known to play a role in bioavailability by limiting biodegradation of a chemical in the environment (*Wszolek and Alexander, 1979; Steen et al., 1980*). Most researchers have assumed that before a sorbed molecule can be taken up by a bacterium, it first has to diffuse to the solid-liquid interface, partition into the water, and then must diffuse to the bacterium through the aqueous phase (*Harms and Zehnder, 1995*). This assumption appears to be correct based on studies by Ogram, et al. (*1985*) and Steen et al. (*1980*), although a study by Guerin and Boyd (*1992*) concluded that generalizations regarding availability of sorbed contaminants are inappropriate. Guerin and Boyd (*1992*) demonstrated that different bacterial species have different abilities to use substrates and may, in fact, be able to use sorbed substrates. This may be due to organism specific properties such as attachment, motility, or affinity for the particular substrate.

If bacteria can only use dissolved substrates, sorption can limit bioavailability in two ways: 1) decreasing aqueous concentrations to low levels due to sorption or 2) limiting high theoretical biodegradation rates due to small desorption rates (a desorption limited process) (*Harms and Zehnder, 1995*). These factors will limit the initial

biodegradation rate but not the extent biodegraded, assuming bacteria are able to enhance desorption. Several studies have concluded that bacteria are able to enhance desorption, which means that desorption is slow relative to biodegradation and that biodegradation increases desorption. Harms and Zehnder (*1995*) found that 3-chlorodibenzofuran desorption was driven (enhanced) by cells attached to Teflon sorbents. They concluded that bioavailability was dependent on the specific affinity of a bacteria for a specific substrate and the tendency of that organism to adhere to a surface. Rijnaarts, et al., (*1990*) also found that microbes enhanced desorption and that initial rates of biodegradation were consistently higher than initial desorption rates. The study of Guerin and Boyd (*1992*) found that one bacterial species was able to enhance desorption whereas another species was not.

An area where more research is needed is studying the effect of aging (soil-chemical contact time) on the bioavailability of contaminants in soils. Since many field soils have been contaminated for periods of months to years, conclusions from short-term bioavailability studies may be inappropriate for long-term contaminated sites. Observations from field studies have demonstrated that aged chemicals are less bioavailable than freshly added ones (*Steinberg, et al., 1987; Weissenfels, et al., 1992; Scribner, et al., 1992*). The study by Weissenfels, et al. (*1992*) demonstrated that the strength of PAH sorption to soils, which may increase with aging, decreased the amount of PAH degraded and that freshly added chemicals do not accurately mimic the behavior of aged chemicals. They also found that the aged PAH's on a high OC soil (13.6 %) were less bioavailable than aged PAH's on a low OC soil (1.0 %). The extent of freshly added phenanthrene mineralized was found to be greater than the extent mineralized for aged

phenanthrene in a muck soil (11.22 % OC) (*Hatzinger and Alexander, 1995*). However, no difference was observed between the extent mineralized for freshly added (0 days) and aged (84 days) phenanthrene in a loamy soil (2.33 % OC). Rates of degradation were decreased for aged phenanthrene on both the loam and the muck. In a sandy soil (1.34 % OC), they found no difference in the rate or extent of degradation for aged versus freshly added chemical. 4-Nitrophenol was added to the loam and muck soils and mineralization was assessed at 0, 40, and 103 days. In both soil types, rates and extents of mineralization decreased with increased aging time. These results show the effect of aging on biodegradation and would seem to indicate that aging has more of an effect on bioavailability in high OC soils than in low OC soils, in agreement with the results found by Weissenfels (*1992*).

In a study by Guerin and Boyd (*1993*) on the bioavailability of naphthalene, increased aging time (up to 300 days) decreased initial mineralization rates. Although a portion of the sorbed naphthalene pool was initially available for mineralization, access to this material diminished as aging time increased. Guerin and Boyd (*1993*) also observed that sorbed naphthalene appeared to be more available to bacteria in low OC soils than in high OC soils. Using the two-box model, they attributed this to a larger fraction of the compound residing in a non-labile state in the high OC soil as compared to the low OC soil. Only one study has explicitly measured both desorption and biodegradation rates for freshly added and aged chemicals (*Carmichael, et al., 1997*). Desorption rates of chrysene and phenanthrene (both PAH's) were found to be much faster than observed mineralization rates for freshly added compounds. They also found that desorption rates for field-aged chemicals were equal to or slower than mineralization

rates, so it was concluded that desorption of aged PAH's may control their fate and availability. This may explain why the persistence of PAH's has been observed even in soils that have active populations of PAH-degrading organisms.

In order to better understand the effects of aging on bioavailability and on the fate of chemicals in soils, we initiated a long term aging study explicitly examining sorption, desorption, and biodegradation in soils (see chapter 4). In this study, we measured sorption isotherms and desorption rates for biphenyl on Capac A and B soils horizons after 24 hours and 8 months of aging. We also measured biphenyl degradation rates and extents on these soils using a *Psuedomonas* species capable of completely mineralizing biphenyl in order to observe the effects of aging on bioavailability. The parameters for the biological and chemical assays were then compared in an effort to better understand the effects of aging on both biological and physico-chemical processes.

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Chapter 2

EFFECTS OF AGING ON THE SORPTION/DESORPTION OF CHLOROBENZENE ON SOILS WITH A RANGE OF ORGANIC CARBON CONTENT

Abstract

Soil-organic chemical contact time (aging) has been found to cause increased persistence of these compounds in the environment. There are few studies that have tested the effects of long-term aging and the role of organic matter content on contaminant sorption/desorption behavior and fate in soils. In this study, the sorption/desorption behavior of chlorobenzene on four soil types was evaluated after aging for periods of 24 hours and 14 months. The four soil types ranged in organic carbon content from 7.8 to 0.4 %. Sorption isotherms were prepared and evaluated after each aging period to observe changes in the uptake of chlorobenzene. Desorption kinetic profiles were generated after each aging period to observe changes in chlorobenzene release from soil, with desorption followed for up to four months. The data presented here demonstrates no increase in the uptake of chlorobenzene on 3 of 4 soils after 24 hours and 14 months of aging, indicating that equilibrium was reached quickly (24 hours or less). Initial desorption rates appear to be similar despite the differences in aging time, and desorption equilibrium was not reached on any soil type, indicating a large non-desorbable fraction. This non-desorbable fraction increased for all soil types with longer aging time.

Keywords – Sorption, desorption kinetics, chlorobenzene, aging, soils

Introduction

There are many studies which indicate that sorption and desorption in soils are not rapid, reversible processes, despite the assumption by many researchers that this is the case. Deviations from this assumption could have major effects on contaminant transport and fate. A study by Ball and Roberts (*1991*) indicated that sorption of tetrachlorobenzene was a slow process and could take hundreds of days to reach equilibrium, and that sorption coefficients on a low organic carbon (OC) aquifer material were an order of magnitude greater than those predicted by partition theory (*Chiou, 1979*). Similarly, Pignatello and Xing (*1996*) showed that equilibrium sorption coefficients (K_p) may increase between 1.3 and 10 times for long and short soil-chemical contact times (aging) and that sorption isotherms may become more non-linear with increased aging (*Xing and Pignatello, 1996*). Data from field studies have found that certain compounds (e.g. EDB, simazine) demonstrate unexpected persistence in soils compared to laboratory studies of binding and degradability in freshly spiked samples (*Steinberg, et al., 1987; Scribner, et al., 1992*). The formation of such a protected fraction was attributed to long pesticide-soil contact times. Numerous other investigators have found that the irreversible (non-desorbable) fraction of a chemical increased with increased aging (*Pavlostathis and Mathavan, 1992; McCall and Agin, 1985; Pignatello, 1990a*). Assuming these non-desorbable chemicals are biologically unavailable, this may explain their measured persistence. From these examples, it seems apparent that soil-chemical contact time (aging) does have an effect on sorption/desorption behavior, hence fate, and that these processes are not rapid and reversible. The specific effects of aging time on contaminant behavior, however, are not well defined or understood.

Despite a great deal of empirical evidence that aging can affect the sorption/desorption process, there are relatively few long term, laboratory controlled aging studies which explicitly measure sorption and desorption parameters. Most long-term aging studies have utilized field-contaminated soils. Steinberg et al. (*1987*) found that 1,2-dibromoethane (EDB) persisted in an agricultural field up to 19 years after its last known application. This is despite the fact that EDB is volatile (vapor pressure = 13.8 mm Hg), moderately water-soluble (water solubility = 4250 mg/L), has low affinity for soils, and is degraded rapidly by soil organisms under both aerobic (*Pignatello, 1986*) and anaerobic conditions (*Castro and Belser, 1968*). In the majority of these field studies, freshly added chemicals are "spiked" into clean soils and parameters such as extractability (*Hatzinger and Alexander, 1995*), biodegradability (*Steinberg, et al., 1987; Hatzinger and Alexander, et al., 1995*), bioavailability (*Scribner, et al., 1992*), or desorption (*Steinberg, et al., 1987; Scribner, et al., 1992; Pavlostathis and Mathavan, 1992; Pavlostathis and Jaglal, 1991*) are measured for both the freshly added and field-aged chemicals. Conclusions in these types of studies have been consistent in that field-aged chemicals all demonstrate reduced extractability, bioavailability, biodegradability, and a reduced extent of desorption. However, information from field studies can be limited because of uncertainty of the total chemical mass involved (*Harmon and Roberts, 1994*) and uncertainty (in some cases) about soil-chemical contact times. Furthermore, most aging studies have not explicitly measured sorption and desorption parameters.

There are very few, if any, studies that have explicitly analyzed the role of soil organic matter (SOM) in the aging process. Given the dominant role of SOM as a sorptive phase for organic contaminants in soils (*Chiou, 1979*), it seems reasonable to

expect that the effects of contaminant aging may be different in soils with different SOM contents. Although no studies have examined directly the role of SOM and aging, scrutiny of the literature demonstrates that there may be some relation between SOM content and the effects of aging. In a review paper on aging, Loehr and Webster (*1996*) concluded that the effect of aging time on sorption/desorption processes may be greater in soils with high organic carbon contents. It was observed recently that for dichlorophenol (DCP) the largest relative increase in the sorption coefficient (K) between 1 and 180 days occurred in soil (1.74 % OC) rather than in peat (54.07 % OC) (*Xing and Pignatello, 1996*). For the reverse process, desorption, some investigators have noticed the relationship between a larger resistant fraction and increased SOM (*Pignatello, 1990b; Carroll, et al., 1994*) for aged chemicals. In one of the most comprehensive studies on aging (*McCall and Agin, 1985*), there appeared to be a greater effect on $K_d$app (the apparent equilibrium distribution coefficient) of picloram aged in low OC soils (0.45 %) than in high OC soils (2.9 %). The $K_d$app was measured by a 2 minute desorption protocol after aging picloram on these soils for 0 and 300 days. In the low OC soil, the $K_d$app increased 5.4 times between 0 and 300 days, but only 1.6 times in the high OC soil. Also measured were $K_d$app values after sorption for 100 days and for desorption (after 100 days of sorption); the difference in these values represents the degree of hysteresis between a single sorption and desorption equilibrium point after 100 days. The difference in the values for the high OC soil was only 1.08 times (effectively the same; no hysteresis) whereas in the low OC soil the difference was 11.25 times. These changes indicate that the effect of aging is greater in low OC soils than in high OC soils. This may be in contrast to what some researchers have expected, but it agrees with the results

found by Xing and Pignatello (*1996*) and their study with DCP on peat and soil.

In this study we have conducted long term, laboratory controlled aging studies with the objective of explicitly measuring changes in sorption and desorption parameters with aging, and to evaluate the role of SOM content in the aging process. Sorption isotherms of chlorobenzene (CB) on four soil types with a range of SOM content (from 0.69 to 13.42 %) were measured after 24 hours and 14 months of aging. The degree of sorption is measured by K_p, the equilibrium partition coefficient, which is determined by the slope of the sorption isotherm. Then, desorption kinetics were measured for chlorobenzene (CB) on each soil after the sorption times mentioned above, with desorption being followed for up to four months.

Experimental Section

The soils used in this study were from the Colwood A horizon (fine-loamy, mixed, mesic Typic Haplaquoll), Schoolcraft A horizon, and the Capac A and B horizons (fine-loamy, mixed, mesic Aeric Ochraqualf). Soils were collected from areas located in southern Michigan and air-dried, ground, and sieved (2 mm). Sand, silt, clay, and OC content were done by the Michigan State University Plant and Soil Nutrient Lab (see Table 2.1). All soils were then gamma irradiated with 5 MRad at the University of Michigan Ford Nuclear Reactor Laboratory using a cobalt-60 irradiator (dose rates by Reuter-Stokes ion chamber). Soils were stored in 500-mL Nalgene bottles during irradiation and remained sealed until use.

Sorption Isotherms: The amounts of a particular soil and solution used to develop sorption isotherms were based on preliminary sorption experiments. The linear isotherm

Table 2.1. Characterization and properties of the soils used in this study.

Soil	% Sand	% Silt	% Clay	Type	% OC	*CEC
Colwood A	64.2	20.7	15.1	sandy loam	7.8	43.0
Capac A	54.6	24.0	21.4	sandy clay loam	3.3	24.4
Schoolcraft A	58.6	22.0	19.4	sandy loam	1.4	11.2
Capac B	60.0	20.0	20.0	sandy clay loam	0.4	9.6

*(CEC= cmol(+)/kg)

equation (x/m = K*Ce) was employed to estimate the amount of soil and solution needed to sorb 50 % of the added solute while also minimizing headspace volume. The tubes used were 20-mL glass ampules that were autoclaved prior to use. All additions of soil and solution to the ampules were carried out in a sterilized laminar flow hood. A mass of soil was weighed and transferred to the ampule using a metal spatula along with a plastic funnel. A 0.005 M $CaCl_2$ solution, which had been autoclaved for 25 minutes and amended with 200 mg/L NaN_3, was added to the ampules using a sterilized repipettor. These functions were carried out in the laminar flow hood and all items contacting soil or solution were autoclaved prior to use (spatulas, funnels, etc.).

Additions of the ^{14}C-chlorobenzene (CB) (Sigma Chemical Co., radiochemical purity > 97 %) stock solution (in acetone) and flame sealing of the ampules were carried out as follows. An aliquot of CB stock solution was added to the ampule using a 10 or 25 ul Hamilton syringe and the ampule was immediately flame sealed using an Ampulmatic flame sealer unit (Bioscience, Inc.). Aliquots used for the sorption isotherms were 3, 5, 10, and 15 ul of a low concentration CB stock and 3, 10, and 15 ul of a higher

concentration CB stock solution. The low concentration stock solution was 83-mg/L ^{14}C-CB and the high concentration stock solution contained the same concentration of ^{14}C-CB and an additional 28 mg/mL of unlabelled ("cold") CB. The stock solutions were stored in a -4° C freezer in amber reacti-vials with mininert valves when not in use. Each of the seven sorption isotherm points were done in triplicate. After flame sealing, the ampules were equilibrated ("aged") for either 24 hours or 14 months. To insure homogeneity, the tubes were shaken (reciprocating shaker) for either 24 hours (for 24-hour aging period) or 72 hours (for 14-month aging). After shaking, the tubes were either analyzed immediately (24 hour aging) or stored in the dark with periodic shaking (14 month aging). For analysis, each ampule was centrifuged at 635 x g for 7-9 minutes, the ampule broken at the neck, and a 1mL aliquot of the aqueous phase was added to 8 mL of scintillation fluid (RPI, Inc., Safety-Solve). The samples were shaken and the next day analyzed by liquid scintillation counting (Beckman LS 6500 multi-purpose scintillation counter). Values for each triplicate set of ampules were averaged and standard deviations calculated. The data were plotted as the amount sorbed (ug/g) versus concentration in solution (ug/L). Linear regression was used to compute the slope of the line, which corresponds to the equilibrium sorption coefficient (K_p). The K_p values were compared at each of the aging periods for each soil type.

Desorption Kinetics: Soil and solution were added to the ampules as described above, with the same amounts of soil and solution used as were used for the sorption experiments. A fixed volume of CB stock solution (5 uL) was added to all of the desorption ampules and the ampules were then flame sealed. The ampules were aged for the appropriate time period (24 hours or 14 months) and shaken and centrifuged as

described above. Then, a quadruplicate set of ampules were opened by cutting the stem (1.6 – 2.0 cm from the top of the ampule) using a ¼-inch glass drill bit (Sommer & Maca, Co.), then sampling the solution phase (200 uL) using a 200 uL Gilson Pipetman. This sample was analyzed using scintillation counting (after 24 hours) to arrive at the equilibrium concentration in solution (C_o) before desorption was initiated. Then a larger aliquot of the solution phase was removed (≈ 75-80 % of the total volume of solution) using a 25 mL gas-tight Hamilton syringe. The same volume of fresh solution (autoclaved 0.005 M $CaCl_2$ with 200 mg/L NaN_3) was then added to the ampule, again using the 25-mL Hamilton syringe. The syringe was rinsed with clean solution between withdrawal of the old solution and addition of the new. The ampule was then re-flame sealed and shaken by hand. At the appropriate time interval, the quadruplicate set of tubes was centrifuged at 635 x g (7-9 minutes) and the remainder of the stems were broken at the necks and a 1 mL aliquot of the aqueous phase was sampled and analyzed by scintillation counting (after 24 hours). This gives the concentration of CB that desorbs into solution after a given desorption time (C_f). The amount desorbed is: $C_f - [C_o$ + (the mass of CB remaining in the residual solution) ÷ (volume of residual solution)]; since only 75-80 % of the total solution volume was removed, an appreciable amount of solution remained, the residual solution, which mixed with the fresh solution added to initiate desorption. Desorption time intervals were: 0.083, 0.5, 1, 2, 4, 8, 12, 24, 72, 216, 648, and 2880 hours. Since four ampules were used for each desorption time interval, a total of 48 ampules were prepared in the same manner and incubated for the 24 or 14 month aging period. The concentration desorbed $C_f - (C_o$ + residual CB) was converted to the fraction of the total remaining in the soil (at t=0, the fraction in the soil is 1 and the

fraction desorbed is 0).

Analytical Procedures: CB concentrations were monitored during the aging regime to ensure that chemical or biological degradation did not occur. CB was analyzed by HPLC utilizing a Perkin-Elmer 250 binary liquid chromatography pump connected in series to a Waters 480 UV spectrophotometer and a INUS Beta Ram ^{14}C detector. Several ampules were chosen at random at several time points during the aging period (up to 14 months) and analyzed for possible degradation products. Samples were centrifuged (635 x g for 7-9 minutes) and a 3 to 4 mL aliquot of the solution was passed through a 0.2 um teflon filter. The filtrate ($\approx$ 200 uL) was analyzed on the system described above. Chromatograms were analyzed and were compared to those obtained initially from the analysis of CB at the beginning of the aging period. Peaks comprising the chromatograms had not changed qualitatively (based on retention times and peak shape) during the 14 month aging. Elution of the compound as a single peak on both the UV and ^{14}C detector was evidence of no degradation.

Statistical analysis: Sorption isotherms were analyzed for linearity using linear and non-linear regression analysis. Isotherms were fit to the Freundlich model ($x/m = KCe^n$) and the 95 % confidence interval (C.I.) for n was generated for the model. Isotherms were also analyzed for differences in slope between 24-hour sorption and 14 month sorption. This was accomplished by performing linear regression analysis with indicator variables. The variability in the model coefficients was tested for significance at the .995 level. Nonlinear regression analysis was performed on the desorption data using Sigmaplot graphing software. Parameters for the desorption equation were estimated using the Marquardt-Levenberg algorithm and standard deviations of each parameter are computed.

Results

Sorption Isotherms: Comparing K_p values from each aging period, it is evident that apparent sorption equilibrium is reached quickly on most soils tested (see Figure 2.1). For Schoolcraft A, Capac A, and Colwood A, the K_p after 24 hours is nearly identical to K_p after 14 months (see Table 2.2). The slopes of these isotherms are not statistically different (at the 0.005 level) between each aging period (P =0.015, 0.057, 0.295 for Colwood A, Capac A, and Schoolcraft A, respectively). The exception is CB sorption on Capac B, where a statistical difference (at 0.005) between isotherm slopes

Table 2.2. Linear sorption model ($x/m = K_p \bullet Ce$) data after 24 hours and 14 months of aging.

		K_p (L/Kg)	r^2
CB on Col. A	24 hour	14.2	0.9967
	14 month	13.1[a]	0.9976
CB on Cap. A	24 hour	3.96	0.9978
	14 month	4.15[a]	0.9988
CB on Schl. A	24 hour	1.19	0.9967
	14 month	1.22[a]	0.9967
CB on Cap. B	24 hour	0.29	0.9990
	14 month	0.36[b]	0.9991

[a] no statistically significant change in sorption at the .005 level
[b] a statistically significant increase in sorption at the .005 level

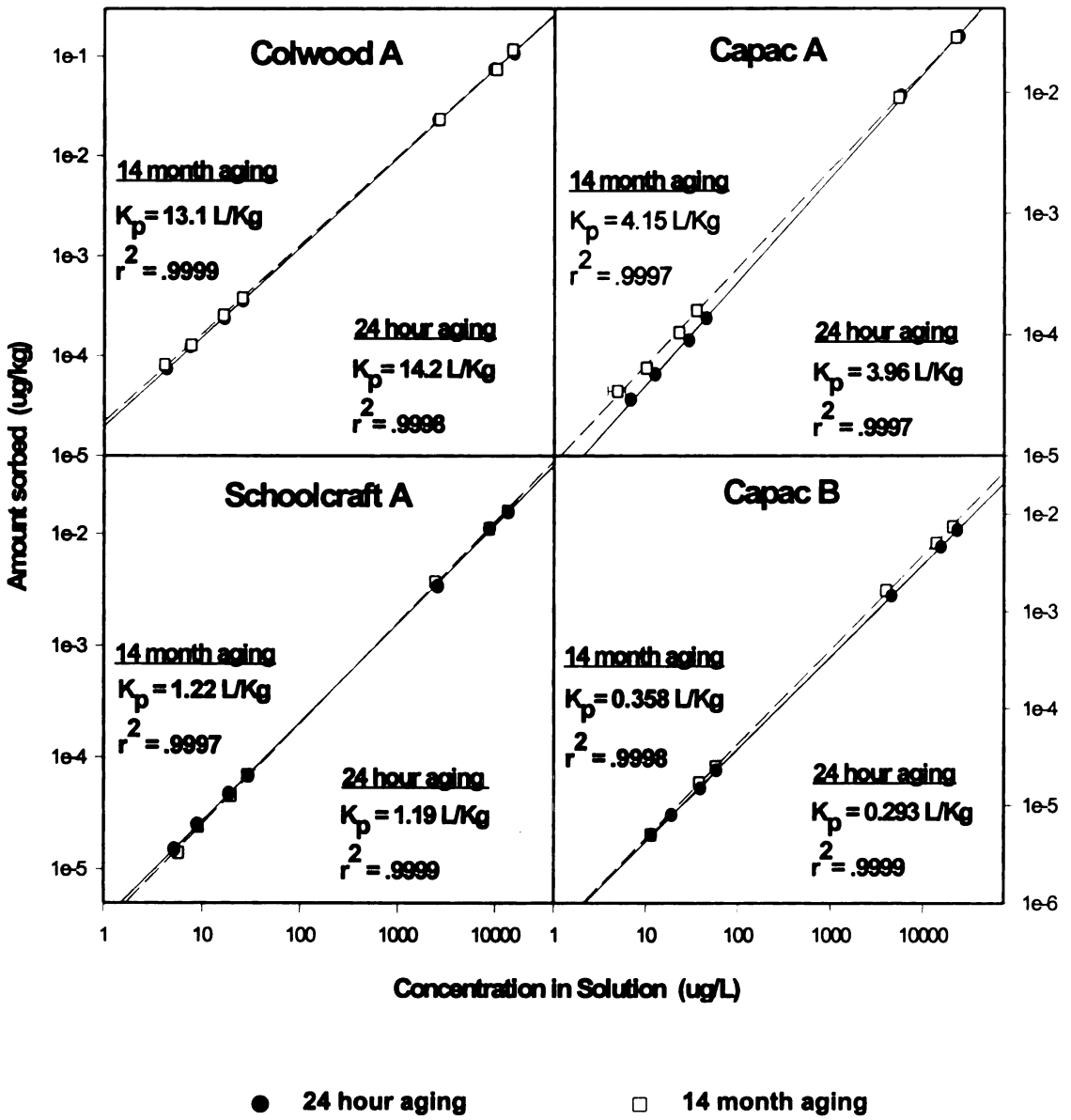

Figure 2.1. Sorption isotherms of CB on the four soil types after 24 hours and 14 months of aging.

Table 2.3. Freundlich isotherm ($x/m = K \bullet Ce^n$) parameters after 24 hours and 14 months of aging.

		K (95 % C.I.)	n (95 % C.I.)
CB on Col. A	24 hour	-0.004 – 0.017	0.908 – 1.274
	14 month	0.017 - 0.056	0.826 - 0.943
CB on Cap. A	24 hour	0.010 – 0.013	0.865 - 0.893
	14 month	0.009 - 0.010	0.905 - 0.908
CB on Schl. A	24 hour	0.001 – 0.007	0.789 – 0.961
	14 month	0.005 - 0.006	0.832 - 0.858
CB on Cap. B	24 hour	0.000 – 0.001	0.942 – 0.971
	14 month	0.001 - 0.001	0.895 - 0.938

was found to exist (P =0.000). For this soil type, which has the lowest OC content (0.4 %), K_p increased by 22 % from 24 hours to 14 months (Table 2.3). Isotherm data was fit to both the linear sorption model and the Freundlich model ($x/m = K*Ce^n$). The data demonstrating isotherm linearity, or near linearity, in the range tested, is the 24 hour CB sorption on Capac B (95 % C.I. of Freundlich coefficient, n = 0.942 - 0.971) data and the 24 hour CB sorption on Colwood A (n = 0.908 – 1.27) data. Linearity is assumed when the 95 % C.I. of "n" includes 1. The Freundlich equation parameters for all isotherms are listed in Table 2.3. When the isotherm data were fit using the linear isotherm model, r^2 values for all isotherms fell between .9967 and .9991 (linear plot). Parameters for the linear isotherm model are listed in Table 2.2. K_{om} values (calculated from K_p) appear to agree with literature values for CB on all soil types (Table 2.4).

Desorption Kinetics: A double exponential decay equation ($y=a*e(-k_1*t) + b*e(-k_2*t)$) was used for non-linear regression analysis of the desorption data. Use of this

Table 2.4. Organic matter normalized sorption values (K_{om}) for chlorobenzene.

Soil	K_p,24 hr. (L/Kg)	K_p,14 mo. (L/Kg)	$^1K_{om}$ (exp.) (L/Kg)	$^2K_{om}$ (calc.) (L/Kg)
Colwood A	14.2	13.1	105.81	72.56
Capac A	3.96	4.15	69.77	72.56
Schoolcraft A	1.19	1.22	49.42	72.56
Capac B	0.29	0.36	42.15	72.56

$^1K_{om}$ (exp.) = (K_p,24 hr.)/ f_{om} (fraction of organic matter); f_{om} = (% OC/100) • 1.72. $^2K_{om}$(calc.) from log K_{om} = 0.904 * log K_{ow} – 0.779 (*Chiou, et al., 1983*).

equation assumes that there are fast and slow sites (or "boxes") for sorption and desorption, similar to the two-box model (*Cameron and Klute, 1977*). The main parameters used to analyze the desorption data were the fast desorption rate constant (k_1), the slow desorption rate constant (k_2), fraction of chemical in the fast compartment (a), and the fraction of chemical in the slow compartment (b). Also utilized in the analysis was the fraction desorbed ($\mathbf{f_{des}}$) which gives a measure of the extent of total desorption after a given desorption period. This value was calculated by dividing the total amount observed to desorb (T_{des}) divided by the amount that should desorb assuming complete desorption reversibility (Eq_{des}).

$$\mathbf{f_{des} = T_{des} / Eq_{des}}$$

On the desorption plots (Figures 2.2 - 2.5) the value for Eq_{des} can be seen as the asymptote that should, theoretically, be approached by the desorption curve. If the experimental desorption curve reaches the asymptote, then $\mathbf{f_{des}} = 1$. The experimental $\mathbf{f_{des}}$ values after 24 hour and 14 month aging periods are summarized in Table 2.5. The

Table 2.5. Chlorobenzene desorption data after 24 hours and 14 months of aging.

	f_{des}, 24 hrs.	f_{des}, 14 mo.	% decrease
CB/Col. A	.93	.75	19 %
CB/Cap. A	.81	.66	19 %
CB/Schl. A	.80	.60	25 %
CB/Cap. B	.76	.70	8 %

Table 2.6. Desorption equation parameters ($y = a \bullet e^{(-k1t)} + b \bullet e^{(-k2t)}$) for chlorobenzene.

		a	b	k_1 (hr^{-1})	k_2 (hr^{-1})
CB/Col. A	24 hour	0.25	0.75	19.6 ± 2.9	1.7e-5 ± 6e-6
	14 month	0.25	0.75	18.3 ± 4.3	3.4e-17 ± 9e-6
CB/Cap. A	24 hour	0.24	0.76	19.1 ± 2.9	1.3e-5 ± 6e-6
	14 month	0.18	0.82	26.1 ± 6.6	5.8e-6 ± 5e-6
CB/Schl. A	24 hour	0.25	0.75	14.0 ± 4.0	1.7e-5 ± 1e-5
	14 month	0.15	0.85	23.6 ±6.6	2.5e-5 ± 5e-6
CB/Cap. B	24 hour	0.13	0.87	12.3 ± 3.4	1.8e-5 ± 6e-6
	14 month	0.10	0.90	314	2.0e-5 ± 8e-6

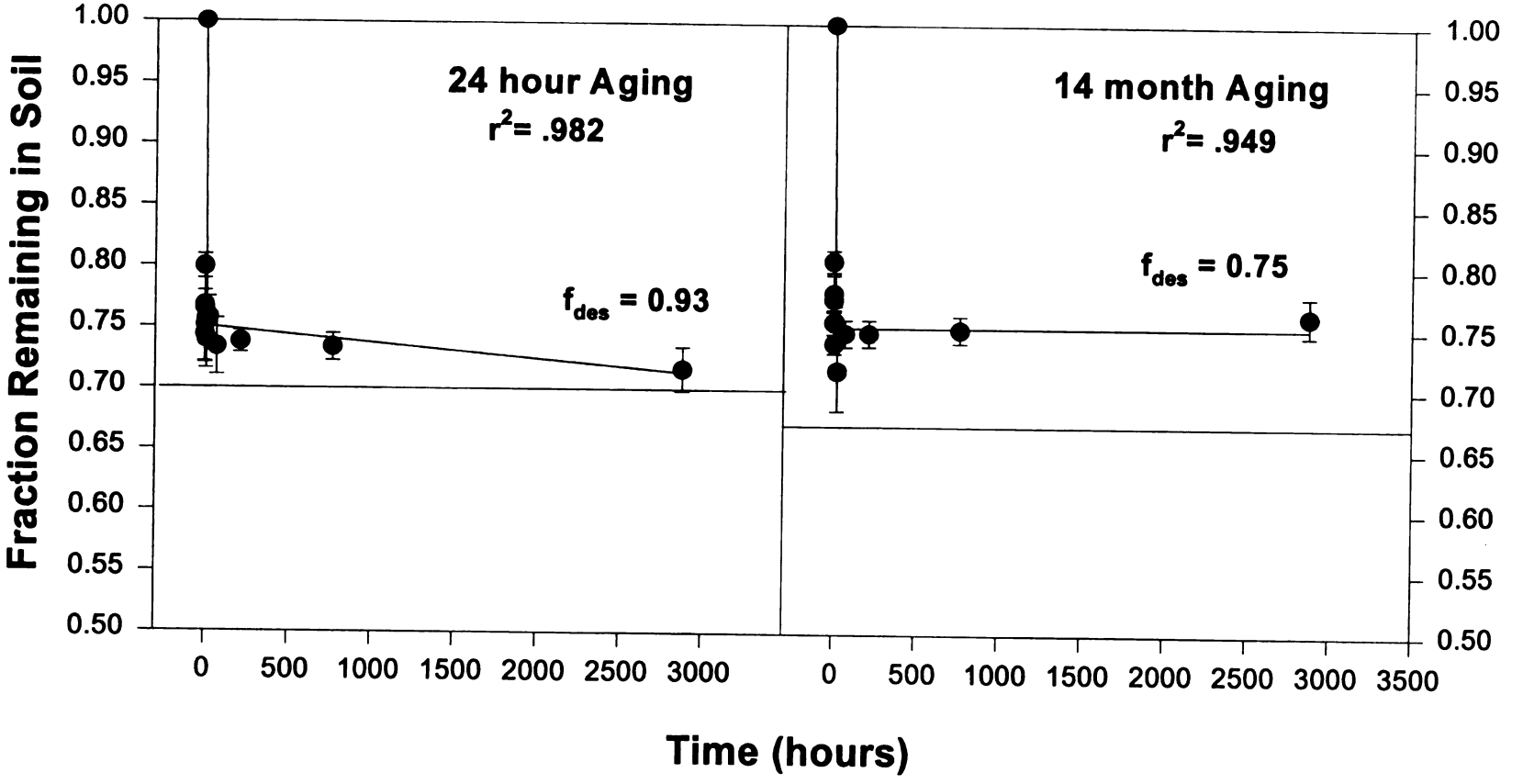

Figure 2.2. Desorption of CB on Colwood A after 24 hours and 14 months of aging.

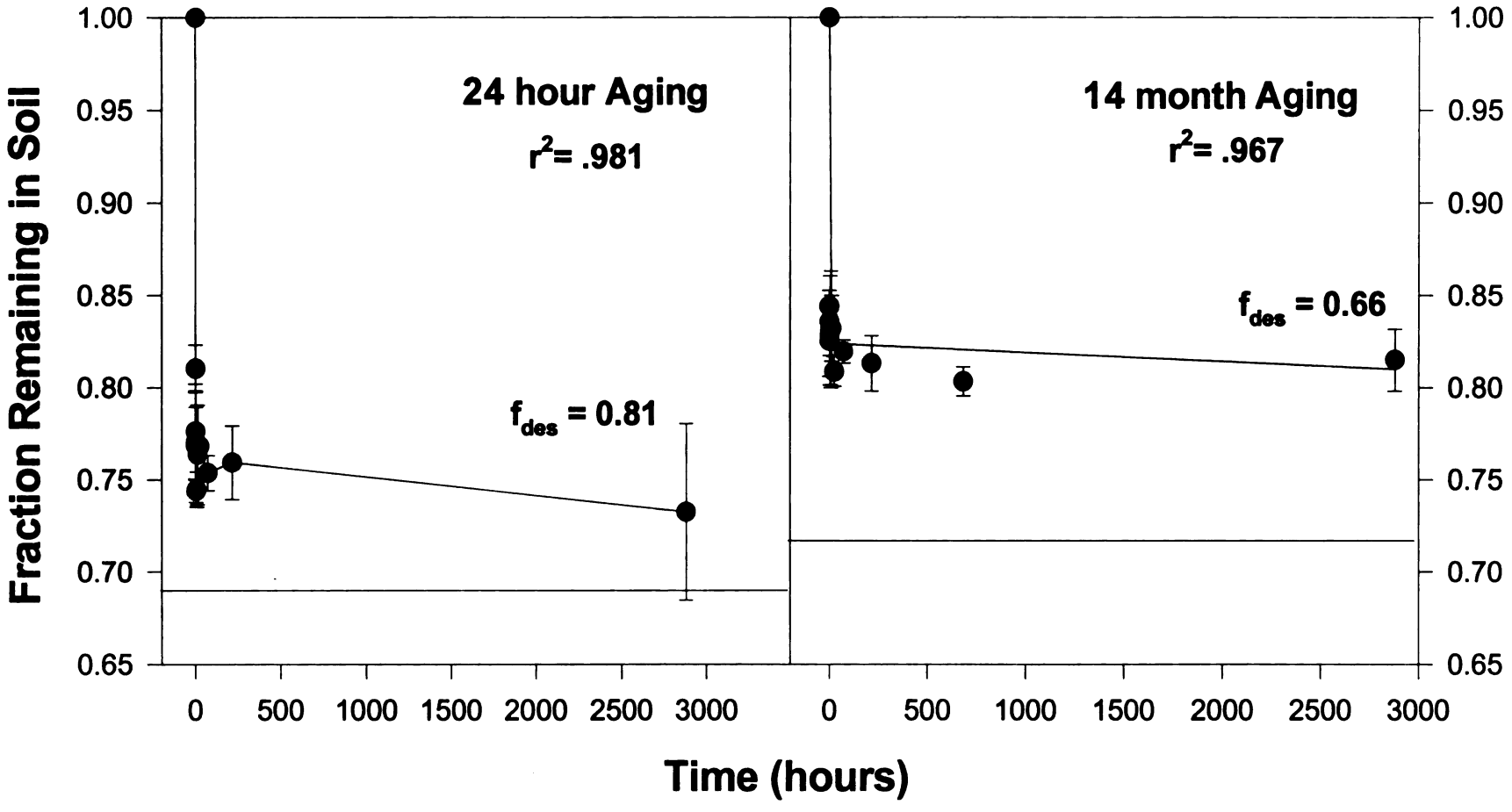

Figure 2.3. Desorption of CB on Capac A after 24 hours and 14 months of aging.

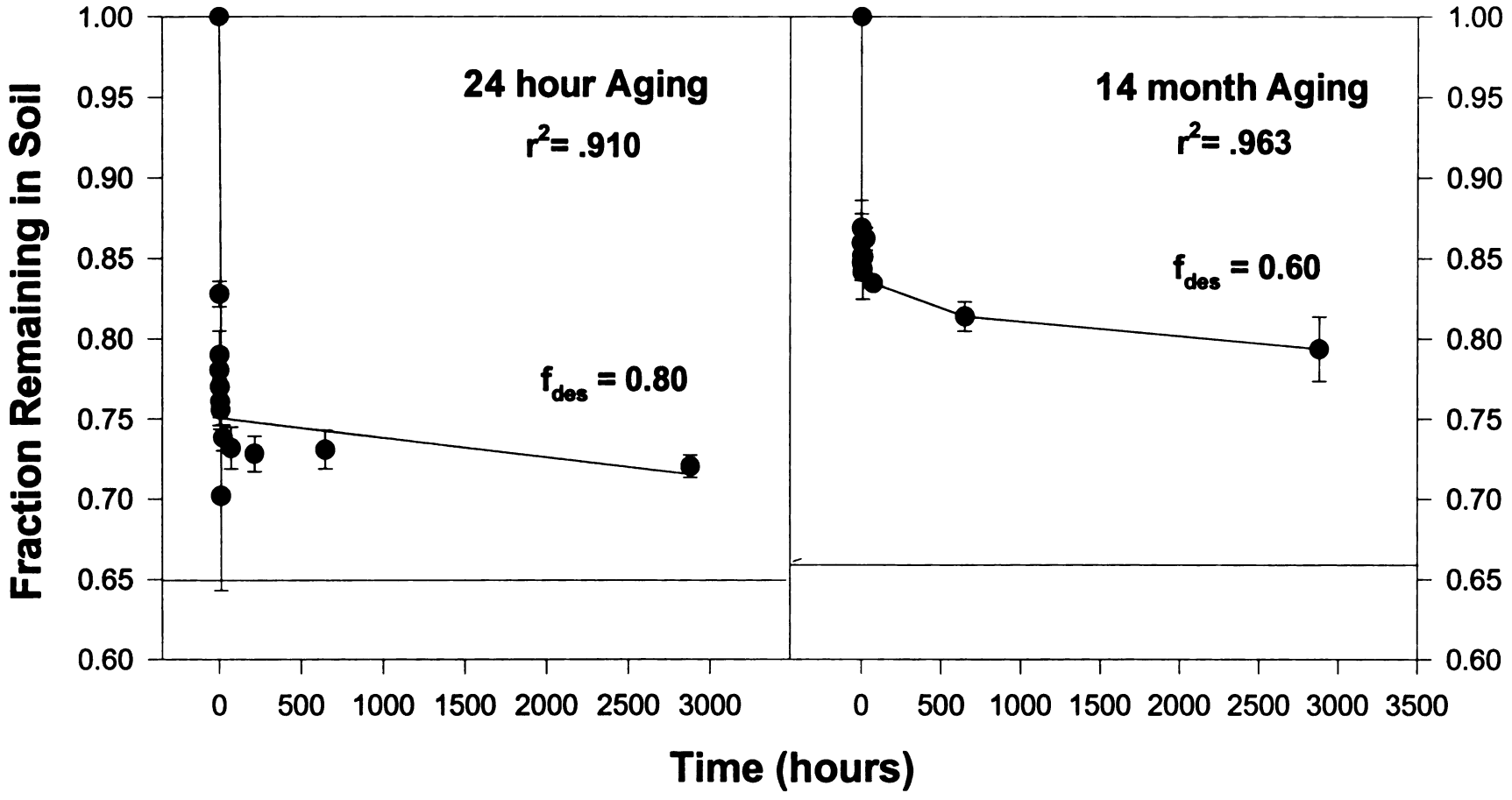

Figure 2.4. Desorption of CB from Schoolcraft A after 24 hours and 14 months of aging.

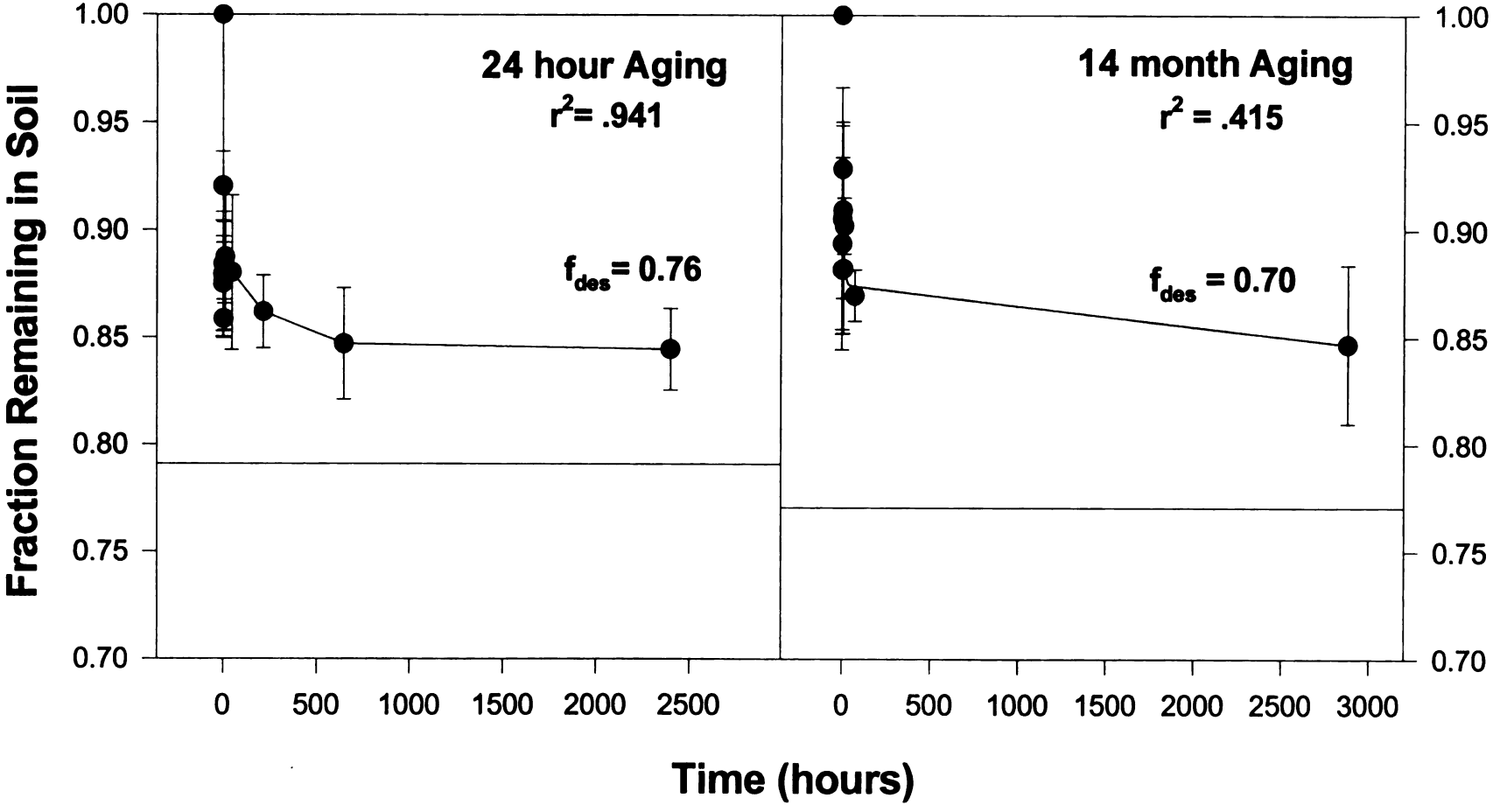

Figure 2.5. Desorption of CB on Capac B after 24 hours and 14 months of aging.

desorption equation parameters for the experimental data are given in Table 2.6.

In no case did all of the CB desorb completely. Even for samples that were aged for only 24 hours and then desorbed for 4 months, the most that desorbed (f_{des}) is approximately 0.93 (for Colwood A) (Figure 2.2 and Table 2.5). On the other soil types for the 24 hour aging time, the fraction desorbed is approximately 0.76-0.80, which means 20-24 % is bound "irreversibly" (on the time scales used in this study) after only 1 day of sorption (Figures 2.3, 2.4, 2.5 and Table 2.5). For CB on all soil types, the f_{des} decreased with increased aging time, which means that more was bound "irreversibly" for the samples that were aged longer (Table 2.5). This finding is in agreement with what many other investigators have found. The largest change in f_{des} was on Schoolcraft A; 0.80 desorbed after aging for 24 hours but only 0.60 desorbed after 14 months of aging (Figure 2.4 and Table 2.5). After aging for 14 months and then initiating desorption for four months, 40% of CB was found to resist desorption on Schoolcraft A.

There appears to be no effect of aging on the fast desorption rate constant (k_1) (Table 2.6). Initial desorption rates appear to be very rapid regardless of the aging time and desorption appears to be essentially complete after one to two hours of desorption time. Based on the modeling results using the double decay equation, the rate constant k_1 was the same for each soil type regardless of whether the sample was aged for 24 hours or 14 months. For example, k_1 for CB desorption from Colwood A after 24 hours of aging was 19.6 ± 2.9 hr^{-1}. The k_1 after 14 months of aging was 18.3 ± 4.3 hr^{-1}.

There also does not appear to be a consistent effect of aging on the slow desorption rate constant k_2 (Table 2.6). Again, the values for k_2 from the double decay equation are the same for each soil type regardless of the aging time. In a few cases the

variability in the k_2 estimates are large enough so that comparisons and conclusions are not possible, but in all other cases they are the same. For example, k_2 for CB desorption from Capac A after 24 hours of aging is $1.35 \times 10^{-5} \pm 5.7 \times 10^{-6}$ hr^{-1}. The k_2 after 14 months of aging is $5.80 \times 10^{-6} \pm 4.8 \times 10^{-6}$ hr^{-1}.

Although there was no increase in sorption due to aging (except on Capac B), aging did seem to effect the distribution of chemical within the soil matrix. For all soil types, except Colwood A, there was a decrease in the fraction of chemical residing in the fast compartment (a) and an increase in the fraction residing in the slow compartment (b) (Table 2.6). The fraction in "b" from the modeling data is analogous to the "irreversible" fraction (1 - f_{des}). On Colwood A, the amount in each compartment remained constant. Reasons for this behavior are not clear at this time.

Discussion

There seems to be little or no effect of aging on the apparent sorption equilibrium of CB in all soil types. Although there was an increase in K_p for the Capac B soil, the increase was very small. It appears that for CB, equilibrium is approached quickly in soils of moderate or high SOM content. The results from Table 2.4 demonstrate good agreement between calculated K_{om} and experimental K_{om}, which can be expected to vary up to 2 to 3 times for different soils (*Kile, et al., 1995*). This information provides some evidence that SOM is the dominant sorptive phase for CB in the soils tested.

Results from these experiments did not show any clear increase in non-linearity with aging time. This is in contrast to the observations of Xing and Pignatello (*1996*) and Weber and Huang (*1996*). Xing and Pignatello (*1996*) observed increases in non-

linearity of isotherms for dichlorobenzene (DCB) and dichlorophenol (DCP) between 1 and 180 days. This was attributed to the fact that SOM has both partition and adsorption domains (dual-mode sorption) and that the adsorption domains are reached only given long soil-chemical contact times since these domains are internal in the SOM matrix (*Xing and Pignatello, 1996*). The adsorption component gives the isotherm increasing non-linearity, which only becomes apparent with long soil-chemical contact times. The isotherms observed in this study do not appear to be consistent with a dual-mode sorption mechanism. According to the results presented here, in one case (Colwood A), isotherm linearity decreased with aging time, but in another case (Capac A), linearity increased with aging time (Table 2.2). These results also did not show increased non-linearity in relatively low OM soils. The most linear isotherms were found on the highest and lowest OM soils, Colwood A and Capac B, respectively (see Table 2.2).

The use of the linear sorption model versus the Freundlich model is an issue that is difficult to resolve. In cases where the Freundlich exponent was found to be farthest from 1 (Schoolcraft A data), apparently indicating non-linearity (when n=1, the isotherm is linear), r^2 values for the linear model are greater than 0.9967 (linear plot) (see Tables 2.2 and 2.3). If the 95 % C.I. of "n" does not include 1, then the Freundlich model provides a better fit to the data than the linear model, and the use of the more parameterized (Freundlich) model is justified statistically. So, in some cases, the Freundlich model is more appropriate, but in other cases the linear model is more appropriate. On a practical level, which overrides statistical significance, the linear model provides a very good approximation of the sorption behavior of CB on these soils and a very accurate fit to the data. For reasons of practicality, consistency, and accuracy

the linear model is the model of choice for this study.

The statistically significant increase in K_p on Capac B with aging time is consistent with evidence from other studies indicating that aging has a greater effect on sorption in relatively low OM soils (*McCall and Agin, 1985; Xing and Pignatello, 1996*). However, the magnitude of the increase observed here is relatively small compared to that observed by Ball and Roberts (*1991*). They observed an order of magnitude increase in the long-term sorption of tetrachlorobenzene in an aquifer material (0.021 % O.C.) over the amount of sorption expected based on organic matter partitioning. Here, the long-term sorption of CB on Capac B is approximately the same (52.32 L/Kg) as the amount of sorption expected based on organic matter partitioning (72.56 L/Kg). Although, it is possible that this discrepancy could be accounted for by the differences in the chemicals studied and the OC content of the soils. As mentioned earlier, it was observed that for dichlorophenol (DCP) the largest relative increase in the sorption coefficient (K) between 1 and 180 days occurred in soil (1.74 % OC) rather than in peat (54.07 % OC) (*Xing and Pignatello, 1996*). The magnitude of the increase for DCP due to aging is $\approx$ 175 %; in this study, the increase for CB is only $\approx$ 22 %. Results from McCall and Agin (*1985*) also demonstrate an increased effect of aging in low OM soils. There appears to be a trend of increased effect of aging in soils of low OC content, but the magnitude of this effect does not appear to be consistent.

The desorption kinetics of CB in this study shows that there is an increase in the "irreversible" fraction (or a decrease in f_{des}) with increased aging time for all soils. This is in agreement with observations from many other studies (*Pignatello, 1990a; Pavlostathis and Mathavan, 1992*). There does not appear to be any correlation to the

increase in irreversible fraction and SOM content, but this relationship may be obscured by the large error associated with the Capac B desorption data (Figure 2.5). This soil was the most difficult to work with because of its low sorption capacity and the resultant need for a high soil:solution ratio. This made the soil slurry difficult to remix after centrifugation, which was a problem during desorption kinetics where precise sampling times were important. This could have helped contribute to the large uncertainty of some of this data. If one neglects the Capac B data, there does appear to be a greater increase in the irreversible fraction with time in soils with decreased SOM content, but with only three soils this conclusion is difficult to make with any certainty.

Another surprising observation is that for CB and soils aged for only 24 hours, there is a significant irreversible fraction even when desorption was performed for up to four months. This data set indicates that diffusion is unlikely to be the main process governing sorption/desorption behavior. Previous work has suggested that sorption and desorption of organic chemicals in soils is reversible in accordance with a retarded diffusion mechanism (*Wu and Gschwend, 1986*). The data presented here, along with data from other recent studies on the irreversibility of PAH sorption/desorption (*Kan, et al., 1994; Fu, et al., 1994*), appear contradictory to the aforementioned hypothesis. The size of the desorption resistant fraction observed for PAH's of 30-50 *% (Fu, et al., 1994)* is very similar in magnitude to the desorption resistant fraction for CB found in this study. The rapid formation of an "irreversible" (desorption resistant) fraction suggests a specific physical or chemical sorption interaction, rather than retarded diffusion, as the dominant mechanism.

It is very difficult to discern from the data whether the slow "tailing" of chemical

in the desorption graphs has actually "plateaued" or if it is approaching the asymptote at a very slow rate. Even with quadruplicate samples, the error bars are large enough to make this conclusion unreachable. In some cases there appears to be a "plateau" and in other cases it appears that there may be an extremely slow net desorption process still taking place. Regardless, on a practical level it appears that the net desorption process has stopped after approximately one day and there is little or no change from one day to four months. This means there is a significant irreversible (non-desorbable) fraction of CB, which forms rapidly with aging. This finding was unexpected from the standpoint that CB is a non-polar compound thought to be unreactive in soils.

Examination of the kinetic parameters shows that there appears to be no effect of aging on the slow or fast desorption rate constants (k_1 or k_2). In all cases, the rate constants are nearly the same between 24 hours and 14 months. These results are in contrast to McCall and Agin (*1985*) who observed no change in the fast desorption rate constant with aging time, but there was a decrease in the slow desorption rate constant. Their data was for picloram, which is a larger, more polar molecule than CB, aged in soils for 1 and 200 days. These results also contrast those of Carmichael, et al. (*1997*) which found that the desorption rates (not rate constants) for fresh and added PAH's were different by several orders of magnitude. If there are actual differences in k_1 due to aging, which are not easily discernable with the method used here, it would appear that these differences must be extremely small and perhaps negligible on a practical level. These results are not easily attributable to simple intraparticle diffusion. If diffusion were operative, one would expect the shape of the desorption curve to be markedly different for the 14 month sample. The curve should show a long, slow "tailing" towards the

asymptote and have reduced kinetic coefficients. Schulten (*1995*) has suggested that the interaction of SOM and organic chemicals is one in which the humic substances are penetrated and disrupted by an organic compound, which increases the overall energy state of the complex. Given an appropriate period of time (aging) the complex finds a more relaxed state due to structural or conformational rearrangements characterized by shrinking of the void space around the pollutant molecule. The complex is now more apt to sequester the compound permanently, possibly leading to what is observed as the irreversible fraction on our desorption profiles. Although the kinetic coefficients and the amount sorbed do not change with aging, the distribution of compound within the fast and slow compartments does change with aging. In all cases, except Colwood A, the fraction of CB in the "slow" compartment (b) increased with aging time. This could indicate that movement into the "slow" compartment should not be viewed as diffusion deep into the soil matrix, but as a static process where the compound becomes bound at one physical location on the soil particle. The slow compartment may not be a physically distant area of the soil particle, but a kinetically limited site located in the same region as non-kinetically limited sites.

Field studies have also shown markedly decreased bioavailability of aged pesticide residues. In the field, the rapidly desorbable fraction (observable as the fraction in "a" in the desorption plots) would be expected to move into the aqueous phase to reestablish equilibrium as pesticides are removed by biodegradation, leaching, plant uptake, or volatilization. This fraction of the soil-applied pesticides would be rapidly dissipated, leaving only the irreversible fraction. This fraction would likely be highly immobile and very difficult to access, and hence difficult to degrade. Increased aging

times would promote the formation of such a bound fraction. This is exactly what has been observed for compounds such as EDB and simazine that have been applied continuously over long periods of time (*Steinberg, et al., 1987; Scribner, et al., 1992*).

The findings discussed herein show that aging of CB in soils, as performed in a laboratory setting, has an effect on the distribution of CB within the soil matrix and decreases the amount desorbed. Aging of CB in soils had little or no effect on other factors such as the rate of desorption and the extent of sorption. The effect of aging on apparent sorption equilibrium may be related to SOM content, with soils of low organic content approaching equilibrium more slowly. The relation between SOM content and desorption is still unclear as no conclusive trends were established, although it is possible that desorption is less reversible in soils with very low OM content.

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Chapter 3

EFFECTS OF AGING ON THE SORPTION/DESORPTION BEHAVIOR OF EDB, CHLOROBENZENE, 2,4-D, AND ATRAZINE

Abstract

Field studies have demonstrated that prolonged pesticide-soil contact times (aging) leads to unexpected persistence of these compounds in the environment. Although this phenomena is well documented in the field, there have been very few controlled laboratory studies that have tested the effects of long-term aging and the role of differing sorbates on contaminant sorption/desorption behavior and fate in soils. This study was initiated to examine the sorption/desorption behavior of chlorobenzene (CB), 1,2-dibromoethane (EDB), atrazine (AT), and 2,4-dichlorophenoxyacetic acid (2,4-D) on one soil type after 24 hours, 1 month, and 14 months of aging. Sorption isotherms were prepared and evaluated after each aging period to observe changes in the uptake of each compound by soil. Desorption kinetic curves were generated after each aging period to observe changes in release from soil, with desorption being followed for up to four months. The data indicates increases in sorption for all compounds except CB, indicating that for 2,4-D, EDB, and AT, equilibrium was not reached in 24 hours or less. Initial desorption rates appear to be the same despite differences in aging times. Desorption equilibrium was not reached for any chemical or any aging time, except 2,4-D after aging for 24 hours. In this case, desorption was found to be reversible and equilibrium was attained. In all other cases, a large non-desorbable fraction was evident.

Keywords – atrazine, 2,4-D, EDB, aging, sorption, desorption kinetics, soils

Introduction

Although laboratory studies of organic contaminant sorption by soils often employ equilibration times of 24 hours or less, several recent studies have indicated that sorption is not a rapid process and may take long time periods (hundreds of days) to reach equilibrium (*Ball and Roberts, 1991; Pignatello and Xing, 1996*). Furthermore, several desorption studies have found that the desorption resistant (irreversible) fraction of a chemical increases with increased soil-chemical contact time (aging) (*Pignatello, 1990*; *Pavlostathis and Mathavan, 1992*). Data from field studies have indicated that certain field weathered or aged compounds (e.g. EDB, simazine) demonstrate unexpected persistence despite being readily degradable by soil microorganisms (*Steinberg, et al., 1987; Scribner, 1992*). These observations suggest that aging does affect sorption/desorption behavior, bioavailability, and biodegradability of organic contaminants and pesticides in soils. Despite the dramatic effects attributed to aging on contaminant binding and persistence, there are very few long-term, laboratory controlled studies which explicitly measure sorption/desorption parameters after different aging times. Consequently, little is known about the effects of aging on contaminant fate as might be influenced by sorbent and sorbate properties.

Several researchers have observed that increasingly hydrophobic compounds exhibit slower sorption/desorption kinetics in soils (*Karickhoff and Morris, 1985; Brusseau and Rao, 1989b*). In contrast, Oliver (*1985*) found that desorption behavior of aged non-polar organics in sediments was largely independent of adsorbate properties. The compounds studied exhibited nearly a four order of magnitude range in hydrophobicity, as measured by K_{ow} (octanol-water partition coefficient), but only

included relatively non-polar chlorinated hydrocarbons. Several other studies have examined the effects of aging of both polar (and/or compounds with polar functional groups) and non-polar organic compounds. Xing and Pignatello (*1996*) examined sorption isotherms of dichlorobenzene (non-polar) and dichlorophenol (polar) in soil after 0 and 30 days of aging and found that the K_p increased only 1.3 times for dichlorobenzene (DCB; log K_p= 3.38) but 2.7 times for dichlorophenol (DCP; log K_p= 2.75). This would suggest that the non-polar compound, although slightly more hydrophobic, had faster sorption kinetics than the polar compound. These results are in agreement with the results of another study (*Brusseau and Rao, 1989a*) in which inverse linear free energy relationships (LFER) were observed between sorption rate coefficients (log k) and sorption equilibrium coefficients (log K_p) for both non-polar and polar compounds. Among compounds with similar partition coefficients, the polar compounds exhibited considerably slower sorption/desorption kinetics. They attributed this to the increased reactivity of polar compounds (and/or compounds with polar functional groups). Brusseau and Rao (*1989a*) suggested that polar compounds must diffuse through soil organic matter (a physical non-equilibrium process or PNE) where they are also subject to specific chemical interactions due to their polar functional groups (a chemical non-equilibrium processes or CNE). These authors presented evidence that polar compounds are rate-limited due to diffusion (PNE) and CNE whereas non-polar compounds are rate limited solely by diffusion. Polar compounds, such as atrazine, picloram, and chlorophenols, which have reactive functional groups, are known to form specific interactions with soil components (*Hayes, 1970; Li and Felbeck, 1972; Nearpass, 1976*). When the results of Xing and Pignatello (*1996*) are viewed in this

context, DCP would be expected to exhibit a larger increase in K_p upon aging than DCB, as was observed. Based upon the data of Brusseau and Rao (*1989a*), the relatively similar log K_p values for DCB and DCP would translate to a log k value for dichlorophenol that is two orders of magnitude slower than that for dichlorobenzene.

The objective of this study was to evaluate the effects of aging on sorption dynamics of polar and non-polar compounds in soils utilizing long-term laboratory controlled aging regimes. Sorption isotherms and desorption kinetics of chlorobenzene (CB), EDB, atrazine (AT), and 2,4-D on a Capac A soil were measured after 24 hours, 1 month, and 14 months, with desorption being followed for up to four months.

Experimental Section

A Capac A horizon soil (fine-loamy, mixed, mesic Aeric Ochraqualf) was used in this study. The soil was collected from southern Michigan, air dried, ground, and sieved (2 mm). Sand, silt, clay, and organic carbon (OC) content were determined by the Michigan State University Plant and Soil Nutrient Lab. This soil is a sandy clay loam with a 3.3 % OC content. It is composed of 54.6, 24.0, and 21.4 % sand, silt, and clay, respectively. The soil was then gamma irradiated with 5 MRad at the University of Michigan Ford Nuclear Reactor Laboratory using a cobalt-60 irradiator (dose rates by Reuter-Stokes ion chamber). The soil was then stored in 500 mL Nalgene bottles during irradiation and remained sealed until use.

Sorption Isotherms: The quantities of soil and solution used to develop sorption isotherms corresponded to the amount needed to sorb $\approx$ 50% of the added solute while minimizing headspace volume. Either 20 mL glass ampules (for EDB and

chlorobenzene) or 20 mL Corex glass tubes (for 2,4-D and AT) were utilized for the sorption/desorption experiments. The ampules were closed by flame sealing and the tubes were closed using teflon lined screw caps. The tubes and ampules were autoclaved prior to use. A mass of soil was weighed and transferred to the ampule/corex tube using an autoclaved metal spatula along with an autoclaved plastic funnel. A 0.005 M $CaCl_2$ solution, which had been autoclaved for 25 minutes and amended with 200 mg/L NaN_3, was added to the tubes using a sterilized repipettor. All additions of soil and solution to the ampules and tubes were carried out in a laminar flow hood and all items contacting soil or solution were autoclaved prior to use (funnels, spatulas, etc.).

Acetone stock solutions of the following compounds were prepared: ^{14}C-chlorobenzene (CB)(radiochemical purity (RP) > 97 %), ^{14}C-1,2 dibromoethane (EDB)(RP > 98 %), ^{14}C-2,4-dichlorophenoxyacetic acid (2,4-D) (RP > 97 %), and ^{14}C-atrazine (AT)(RP > 93 %) (were obtained from Sigma Chemical Co.). Stock solutions for each compound consised of a low concentration stock, in which the specific compound is all ^{14}C labeled, and a high concentration stock, which contains ^{14}C compound and non-labeled ("cold") compound. The stock solutions were stored in amber reacti-vials with mininert valves in a -4° C freezer while not in use. An aliquot of the stock solution of a specific compound was added to the ampule/corex tube using a 10, 25, or 100 uL Hamilton syringe and the ampule was immediately flame sealed using an Ampulmatic flame sealing unit (Bioscience, Inc.); Corex glass tubes were immediately sealed with screw-on caps. Aliquots used for the sorption isotherms were from both the low and high concentration stock solutions to cover a 3-4 order of magnitude range in initial solution concentration. Seven initial solute concentrations were utilized (in

triplicate) for each compound. After sealing, the ampules/corex tubes were equilibrated ("aged") for either 24 hours, 1month, or 14 months. Immediately after closure the ampules/tubes were shaken on a reciprocating shaker for either 24 (for 24 hour aging period) or 72 hour (for 1 and 14 month aging) periods. After shaking, the ampules/tubes were either analyzed immediately (24 hour aging) or stored in the dark with periodic shaking (1 and 14 month aging). Prior to analysis, ampules were centrifuged at 635 x g for 7 to 9 minutes and a 1mL aliquot of the aqueous phase was removed and added to 8 mL of scintillation fluid. Tubes were handled in the same manner except that they were centrifuged at 6722 x g for 7 to 9 minutes. The samples were then shaken, stored in the dark overnight, and the next day analyzed by liquid scintillation counting (Beckman LS 6500) to determine the aqueous phase concentrations; the amount of solute sorbed was determined by difference. Linear regression was used to compute the slope (or sorption coefficient, K_p) of the sorption isotherm on a plot of amount sorbed (ug/Kg) versus concentration in solution (ug/L).

Desorption Kinetics: Soil and solution were added to the ampules/tubes as described above, with the same amounts of soil and solution used as for the sorption experiments. A single initial solute concentration was used for each chemical. These were then aged for the appropriate time period (24 hours, 1 month, or 14 months) and shaken and centrifuged as described for the sorption isotherms. Then, a quadruplicate set of ampules were opened by cutting the stem (1.6 – 2.0 cm from the top of the ampule) using a ¼-inch glass drill bit (Sommer & Maca, Co.), and sampling the solution phase (200 uL) using a 200 uL pipetman. Tubes were sampled in triplicate by removing the caps and taking a 1 mL sample of the solution phase. This sample was analyzed using liquid scintillation

counting (after 24 hours) (Beckman LS 6500) to arrive at the equilibrium concentration in solution (C_o) before desorption was initiated. Then a larger aliquot of the solution phase was removed (≈ 75-80 % of the total volume of solution) using a 10 or 25 mL gas-tight Hamilton syringe. The same volume of fresh solution (autoclaved 0.005 M $CaCl_2$ with 200 mg/L NaN_3) was then added to the ampule/tube, again using the 10 or 25 mL Hamilton syringe. The syringe was rinsed with clean solution between withdrawal of the old solution and addition of the new. The ampule was then re-flame sealed and shaken by hand, and the tubes were re-capped and shaken by hand. At the appropriate time interval, the quadruplicate set of ampules were centrifuged at 635 x g (7 to 9 minutes), the remainder of the stems were broken at the neck, and a 1 mL aliquot of the aqueous phase was sampled and analyzed by liquid scintillation counting (after 24 hours). This gives the concentration of CB that desorbs in solution after a given desorption time (C_f). The amount desorbed is: $C_f - [C_o$ + (the mass of CB remaining in the residual solution) ÷ (volume of residual solution)]. The tubes were treated in the same manner as the ampules, except that triplicate samples were analyzed and these were centrifuged at 6722 x g for 7 to 9 minutes. Desorption time intervals were: 0.083, 0.5, 1, 2, 4, 8, 12, 24, 72, 216, 648, and 2880 hours. Since four ampules were used for each desorption time interval, a total of 48 ampules were prepared in the same manner and incubated for the 24 hour, 1 month, or 14 month aging period. Thirty-six tubes were prepared in the same manner and incubated for the aging periods stated above. The concentration desorbed C_f – (C_o + residual CB) was converted to the fraction of the total remaining in the soil (at t=0, the fraction in the soil is 1 and the fraction desorbed is 0).

Analytical Procedures: High-performance liquid chromatography (HPLC) analysis was

used to determine the radiochemical purity and stability of the ^{14}C-CB, ^{14}C-EDB, ^{14}C-AT, and ^{14}C-2,4-D for the 14 month aging period. After receiving the ^{14}C compounds, acetone stock solutions were prepared and stored in a –4° C freezer until they were ready to use. Prior to first use, an aliquot of the stock solution was analyzed utilizing a Perkin-Elmer 250 binary liquid chromatography pump connected in series to a Waters 480 UV spectrophotometer and a INUS Beta Ram ^{14}C detector. Radiochemical purity was estimated by injecting ≈ 0.025 uCi from the acetone stock solution. Elution of the compound as a single peak on both the UV and ^{14}C detector was evidence of radiochemical purity. The relative peak areas of the parent compound and other non-simultaneously eluting peaks was used to quantitate the radiochemical purity. The compounds were delivered from Sigma as 93-98 % radiochemically pure and our results verified this. This procedure was repeated before each aging experiment. After the 14 month aging period, several tubes (for each compound) were chosen at random and analyzed for possible degradation products. Samples were centrifuged and a 3 to 4 mL aliquot was passed through a 0.2 um teflon filter. The filtrate (≈ 200 uL) was analyzed by HPLC as described above. Chromatograms were analyzed and were compared to those obtained initially from the analysis of radiochemical purity. Peaks comprising the chromatograms had not changed qualitatively (based on retention times and peak shape) during the 14 month aging period, except for AT. AT showed significant chemical degradation (> 20 %) for the 14 month period, but not for the 1 month aging period.

Statistical analysis: Sorption isotherms were analyzed for linearity using non-linear regression analysis. Isotherms were fit to the Freundlich model ($x/m = K* Ce^n$) and the 95 % confidence interval (C.I.) for n was calculated. Isotherms were also analyzed for

differences in slope between 24 hour sorption and 14 month sorption. This was accomplished by performing linear regression analysis with indicator variables. The variability in the model coefficients were tested for significance at the 0.99 level. Nonlinear regression analysis was performed on the desorption data. Parameters for the desorption equation were estimated using the Marquardt-Levenberg algorithm and standard deviations of each parameter are computed.

Results

Sorption Isotherms: Comparing K_p values (Figure 3.1 and Table 3.1) for the aging periods of 24 hours and 1 month, there is very little difference in apparent sorption for any compound except 2,4-D. EDB, CB, and AT had no statistically significant (at the 0.01 level) increase in sorption from 24 hours to 1 month. 2,4-D did show a statistically significant (P = 0.001) increase in the slope of the sorption isotherm between 24 hours and 1 month (Table 3.1). At 14 months of aging, 2,4-D and EDB both had an increase in K_p from the corresponding values at 24 hours and 1 month (P = 0.000 for both), whereas CB still showed no increase in K_p for any aging period. Also, AT showed a statistically significant, albeit small, decrease in K_p at 1 month. Sorption of AT at 14 months could not be evaluated due to chemical conversion of AT to hydroxy-AT. This was confirmed with HPLC analysis by matching the retention times of the degradation product and an authentic standard. There appears to be good agreement between experimental K_{om} (calculated from K_p) and calculated K_{om} values for all compounds (Table 3.2).

The isotherm data were fit to both the Freundlich sorption model ($x/m=K*Ce^n$), where x/m is the concentration in soil and Ce is the aqueous phase concentration, and the

Table 3.1. Linear sorption model (x/m = K_p*Ce) data for EDB, CB, AT, and 2,4-D.

		K_p (L/Kg)	r^2
EDB on Cap. A	24 hour	0.73	0.9999
	1 month	0.72[a]	0.9965
	14 month	1.26[b]	0.9992
CB on Cap. A	24 hour	3.96	0.9978
	1 month	3.37	0.9995
	14 month	4.15[a]	0.9988
AT on Cap. A	24 hour	3.24	0.9980
	1 month	2.82[c]	0.9932
	14 month	N.D.	N.D.
2,4-D on Cap. A	24 hour	0.62	0.9981
	1 month	0.66[b]	0.9992
	14 month	0.91[b]	0.9961

[a] no statistically significant increase in sorption from 24 hour sample at the .01 level
[b] a statistically significant increase in sorption from 24 hour sample at the .01 level
[c] a statistically significant decrease in sorption from 24 hour sample at the .01 level

linear sorption model. The Freundlich isotherm data showed a slight degree of non-linearity as indicated by the Freundlich coefficient "n". The most linear isotherms were found to be for 24 hour 2,4-D sorption (n = 0.939 - 1.18; 95 % C.I.), 24 hour EDB sorption (n = 0.966 - 0.995), and 1 month CB sorption (n = 1.00 -1.03). The Freundlich isotherm parameters are listed in Table 3.3. When the data was fit using the linear model (n=1), all isotherms had r^2 values of 0.9932 or greater (Table 3.1).

Desorption Kinetics: A double exponential decay equation ($f=a*e(-k_1*t) + b*e(-k_2*t)$ was used for non-linear regression analysis of the desorption data. Use of this equation assumes that there are fast and slow sites (or "boxes") for sorption and desorption, similar to the two-box model (*Cameron and Klute, 1977*). The parameters used to analyze the

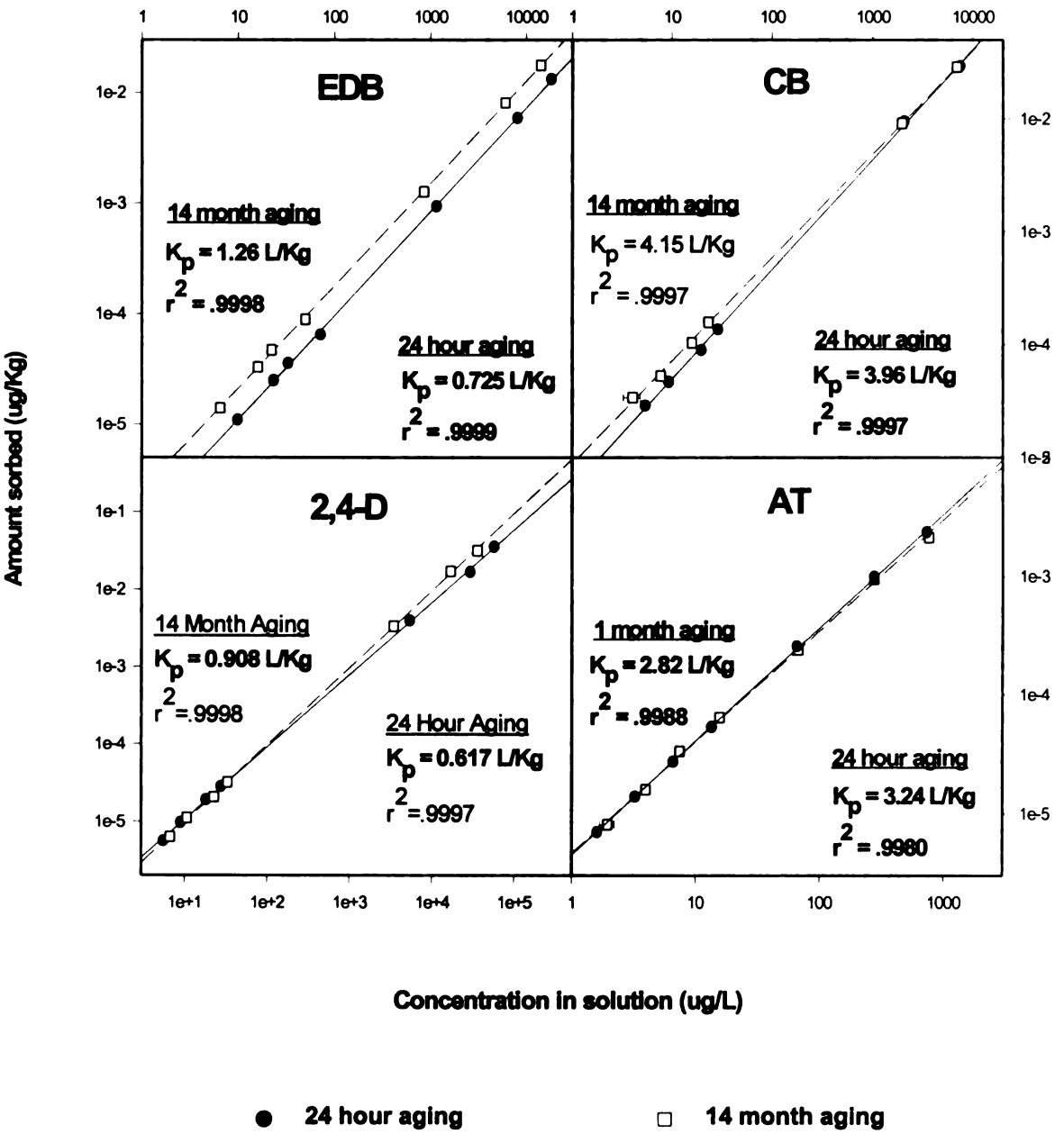

Figure 3.1. Sorption isotherms of CB, EDB, 2,4-D, and AT after 24 hours and 14 months (or 1 month for AT) of aging.

Table 3.2. Organic matter normalized sorption values (K_{om}) values for EDB, CB, and AT.

	K_p,24 hr. (L/Kg)	K_p,14 (for AT, 1 mo.) (L/Kg)	K_{ow}	$^1K_{om}$ (exp.) (L/Kg)	$^2K_{om}$ (calc.) (L/Kg)
EDB	0.73	1.26	57.54	12.77	6.49
CB	3.96	4.15	831.76	69.77	72.56
AT	3.24	2.82	363.08	57.08	34.30

$^1K_{om}$ (exp.) = (K_p,24 hr.)/ f_{om} (fraction of organic matter); f_{om} = (% OC/100) * 1.72. $^2K_{om}$(calc.) from log K_{om} = 0.904 * log K_{ow} – 0.779 (*Chiou, et al., 1983).*

Table 3.3. Freundlich isotherm ($x/m = K*Ce^n$) parameters after 24 hours, 1 month, and 14 months of aging.

		K (95 % C.I.)	n (95 % C.I.)
CB	24 hour	0.010 – 0.013	0.865 – 0.893
	1 month	0.002 – 0.003	1.004 – 1.032
	14 month	0.009 – 0.010	0.905 - 0.908
EDB	24 hour	0.001 – 0.001	0.966 - 0.995
	1 month	0.002 – 0.004	0.827 - 0.884
	14 month	0.002 – 0.003	0.915 – 0.935
AT	24 hour	0.005 – 0.007	0.875 – 0.926
	1 month	0.005 – 0.012	0.772 – 0.901
	14 month	N.D.	N.D.
2,4-D	24 hour	0.000 – 0.001	0.939 – 1.180
	1 month	0.001 – 0.002	0.905 – 0.953
	14 month	0.001 – 0.006	0.794 – 0.952

desorption data were the fast desorption rate constant (k_1), the slow desorption rate constant (k_2), fraction of chemical in the fast compartment (a), and the fraction of chemical in the slow compartment (b). Also utilized in the analysis was the fraction desorbed (f_{des}), which gives a measure of the extent of total desorption. This value was calculated by dividing the total amount observed to desorb (T_{des}) divided by the amount that should desorb assuming complete desorption reversibility (Eq_{des}).

$$f_{des} = T_{des} / Eq_{des}$$

On the desorption plots (Figures 3.2 - 3.7) the value for Eq_{des} can be seen as the asymptote that should, theoretically, be approached by the desorption curve. If the experimental desorption curve reaches the asymptote, then $f_{des} = 1$.

The desorption curves are shown in Figures 3.2 - 3.7. In only one case did all of the sorbed chemical desorb almost completely. This was for the 24 hour sorption of 2,4-D, where f_{des} is approximately 0.90 (Figure 3.2). For the 14 month and 1 month samples, a considerably smaller fraction of 2,4-D desorbed (0.58 and 0.68, respectively) (Figures 3.2 and 3.3, respectively). When the desorption intervals for 2,4-D were increased beyond four hours to 4 months, the f_{des} increased to .98 and .74 for the 24 hour and 14 month 2,4-D samples, respectively (Figure 3.4). This means that for the 2,4-D sample aged 24 hours, 98 % desorbed after a four month desorption interval, while 90 % had desorbed after a four hour desorption interval.

For all compounds tested, f_{des} decreased with increased aging time. This means a greater portion of chemical was bound "irreversibly" for the samples that were aged longer. The largest change in f_{des} from 24 hours to 1month was for AT (28.6 %) (Table 3.4 and Figure 3.5). The largest change in f_{des} from the 24 hour aging period to the 14

month period was for EDB (46.1 %) (Table 3.4 and Figure 3.6). For EDB, f_{des} = 0.36 for the 14 month aging period, meaning that nearly 64 % of EDB was bound irreversibly to soil after 14 months of aging followed by 4 hours of desorption (Figure 3.6). There was very little, if any, increase in this value even after desorption was extended to 4 months (Figure 3.7). The f_{des} values are summarized in Table 3.4.

For this study, when comparing desorption data among all compounds, a four hour desorption interval was utilized so that the sorption period substantially exceeded the desorption period. This was done to minimize significant re-sorption occurring along with desorption, since these processes occur simultaneously, especially for the 24 hour aged samples. Essentially, this is the method of initial rates for calculating rates of chemical reactions (*Atkins, 1994*).

There does not appear to be any effect of aging on the fast or slow desorption rate constants (k_1 or k_2, respectively) for any compounds tested (Table 3.5). In all cases, the rate constant is the same for each aging period, or in the case of EDB, the variability in k

Table 3.4 Desorption data (f_{des} at 4 hours of desorption) after 24 hours, 1, and 14 months.

	f_{des}, 24 hr.	f_{des}, 1mo.	% decrease (24 hr. to 1 mo.)	f_{des}, 14 mo.	% decrease (24 hr. to 14 mo.)
EDB/Cap. A	.67	.60	11.4 %	.36	46.1 %
CB/Cap. A	.83	.66	19.9 %	.60	27.0 %
AT/Cap. A	.79	.56	28.6 %	N.D.	N.D.
24D/Cap. A	.90	.68	24.7 %	.58	35.3 %

Table 3.5. Desorption equation ($y=a \bullet e^{(-k1 \bullet t)} + b \bullet e^{(-k2 \bullet t)}$) parameters after 24 hours, 1 month and 14 months of aging.

		a	b	k_1 (hr^{-1})	k_2 (hr^{-1})
EDB	24 hour	0.16	0.84	31.3 ± 13	2.0e-15 ± 4e-3
	1 month	0.10	0.90	301.2 ± 4e+4	5.8e-3 ± 3e-4
	14 month	0.05	0.95	287.5 ± 2e+5	3.8e-4 ± 2e-3
CB	24 hour	0.22	0.78	24.0 ± 3	1.1e-2 ± 3e-3
	1 month	0.20	0.80	23.0 ± 5	3.7e-3 ± 5e-3
	14 month	0.17	0.83	30.5 ± 6	2.6e-4 ± 3e-3
AT	24 hour	0.27	0.73	21.4 ± 4	1.2e-2 ± 7e-3
	1 month	0.15	0.85	24.7 ± 4	6.9e-3 ± 2e-3
	14 month	N.D.	N.D.	N.D.	N.D.
2,4-D	24 hour	0.27	0.73	15.7 ± 5	1.4e-2 ± 1e-2
	1 month	0.20	0.79	11.9 ± 5	3.4e-15 ± 1e-2
	14 month	0.15	0.85	9.5 ± 1	6.1e-3 ± 2e-3

is too large to draw any conclusions (see Table 3.5).

Aging had a dramatic effect on the distribution of the chemical within the soil matrix. For all compounds tested, the fraction of compound residing in the fast compartment decreased progressively with aging time (Table 3.5) and the fraction in "b" increased. The fraction in "b" is similar to the "irreversible" fraction (1- f_{des}). The largest decrease in the fraction in the fast compartment (a) between 24 hours and 1 month was for AT (45.4 % decrease). The largest decrease between 24 hours and 14 months was for EDB (68.1 % decrease).

Discussion

We observed a compound specific effect of aging on the apparent sorption equilibrium. The effect was largest for EDB and was not observed for CB. EDB showed a 74 % increase in K_p between 24 hours and 14 months equilibration, but had no measurable increase between 24 hours and 1 month. The K_p for AT actually decreased slightly between 24 hours and 1 month equilibration; chemical degradation prohibited evaluation of the K_p for AT aged for 14 months. The AT desorption curves generated utilizing 1 and 4 month desorption intervals show clear evidence of re-sorption, indicating that sorption equilibrium had not been reached at 1 month. Based on this, it seems likely that the decrease in K_p for AT at 1 month as compared to 24 hours was a manifestation of sorption non-equilibrium. In contrast, 2,4-D had a statistically significant increase in the apparent 24 hour K_p at both 1 month and 14 months of aging (see Table 3.2). These data demonstrate that for some compounds the 24 hour K_p may underestimate the degree of sorption in soils.

There is very good agreement between the experimental K_{om} and K_{om} values

calculated from empirical relationships between K_{ow} and K_{om} (Table 3.2). Measured K_{om} values utilizing different soils can be expected to vary up to 2 to 3 times (*Kile, 1995*). There is also good agreement between the values generated here and literature values, except in the case of EDB. For CB, a K_{om} of 47.86 L/Kg has been reported by Chiou, et al. (*1983*), which is very close to the value of 72.56 L/Kg reported here. Reported K_{om} values for AT vary widely from 27 to 230 L/Kg (converted from K_{oc}) (*Montgomery, 1993*), but the values reported here are within this range. Reported K_{om} values reported for EDB do not agree as well as those for the other compounds. Values between 21.1 to 94 L/Kg are reported by Montgomery (*1993*) and between 59.9 and 78.0 L/Kg are reported by Steinberg, et al. (*1987*). These values are much larger than the values reported here, by an order of magnitude in some cases. The earlier reported K_{om} values for EDB seem very high given its relatively low K_{ow} value. An empirical equation (*Chiou, et al., 1983*) based on K_{ow} predicts a K_{om} of 12.77 L/Kg (Table 3.2). The experimental value of 6.49 L/Kg reported here is much closer to the expected K_{om} for EDB than the values reported earlier.

Results from this study demonstrated no clear increase in non-linearity with aging. The CB sorption isotherm is more linear at 14 months (n=0.905-0.908) and 1 month (n=1.00-1.03) than at 24 hours (n=0.864-0.893), whereas the EDB isotherm is most linear at 24 hours (n=0.966-0.995) and least linear at 1 month (n=0.827-0.884). These results are in agreement to a previous study using chlorobenzene on several soil types (*Sharer, 1999*) showing no clear increase in non-linearity with increased aging time. These results are in contrast to those of Weber and Huang (*1996*) and Xing and Pignatello (*1996*). Xing and Pignatello (*1996*) observed increases in non-linearity of

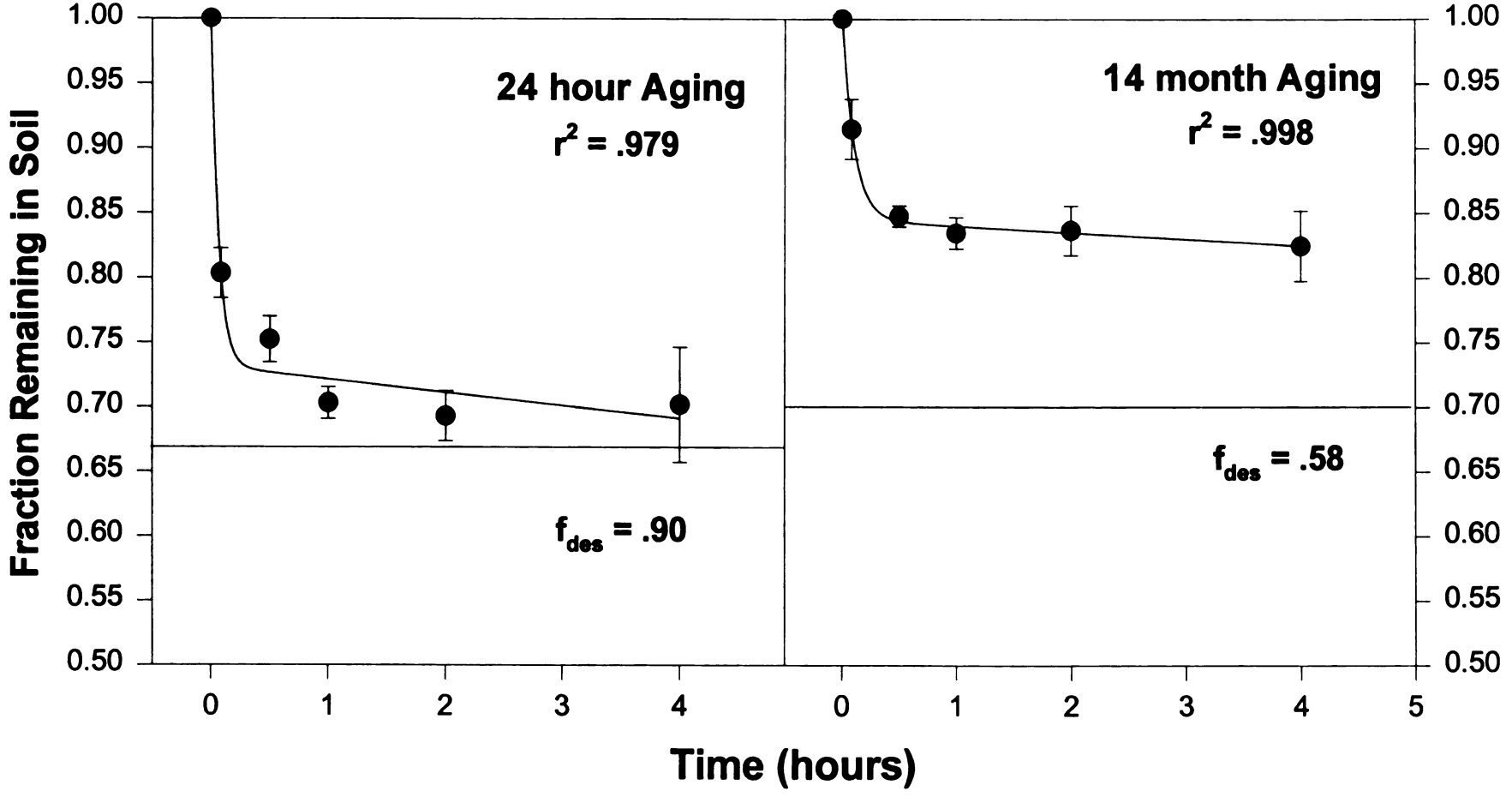

Figure 3.2. Desorption kinetics of 2,4-D after a 24 hour and a 14 month aging period.

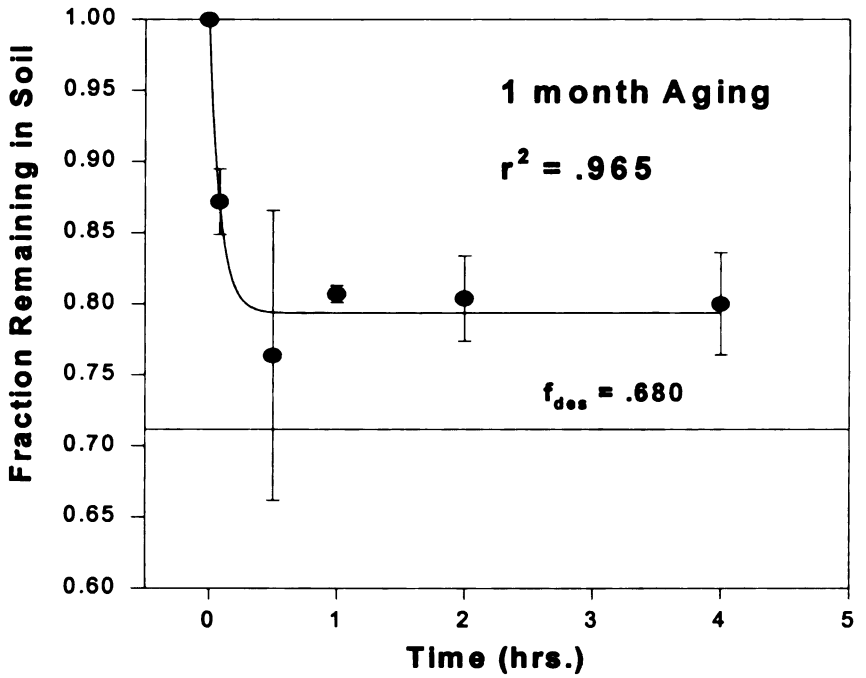

Figure 3.3. Desorption kinetics of 2,4-D on Capac A after a 1 month aging period.

isotherms for dichlorobenzene (DCB) and dichlorophenol (DCP) between 1 and 180 days. This was attributed to the fact that SOM has both partition and adsorption domains (dual-mode sorption) and that the adsorption domains are reached only given long soil-chemical contact times since these domains are internal in the SOM matrix (*Xing and Pignatello, 1996*). The adsorption component gives the isotherm increasing non-linearity that only becomes apparent with long soil-chemical contact times. The isotherms observed in this study do not exhibit consistent increases in non-linearity with increased contact time, so this data would not appear to support a dual-mode sorption mechanism.

The linear and Freundlich sorption models were used to fit the experimental data. Visual inspection of the data show the isotherms to be very linear. Although, in some cases, Freundlich coefficients indicate some non-linearity (i.e. 1 month EDB sorption

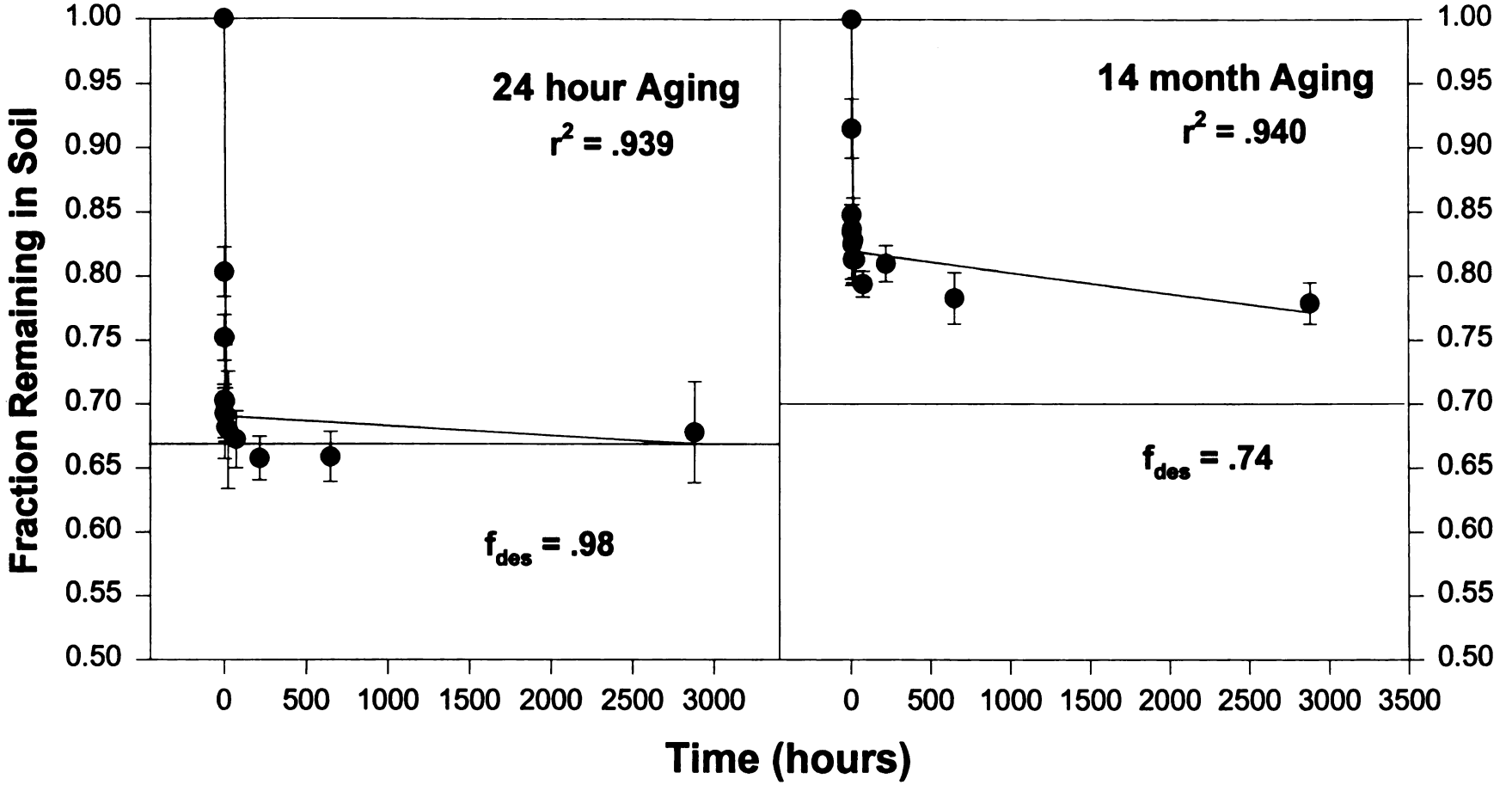

Figure 3.4. Desorption kinetics of 2,4-D on Capac A after a desorption interval of 2800 hours.

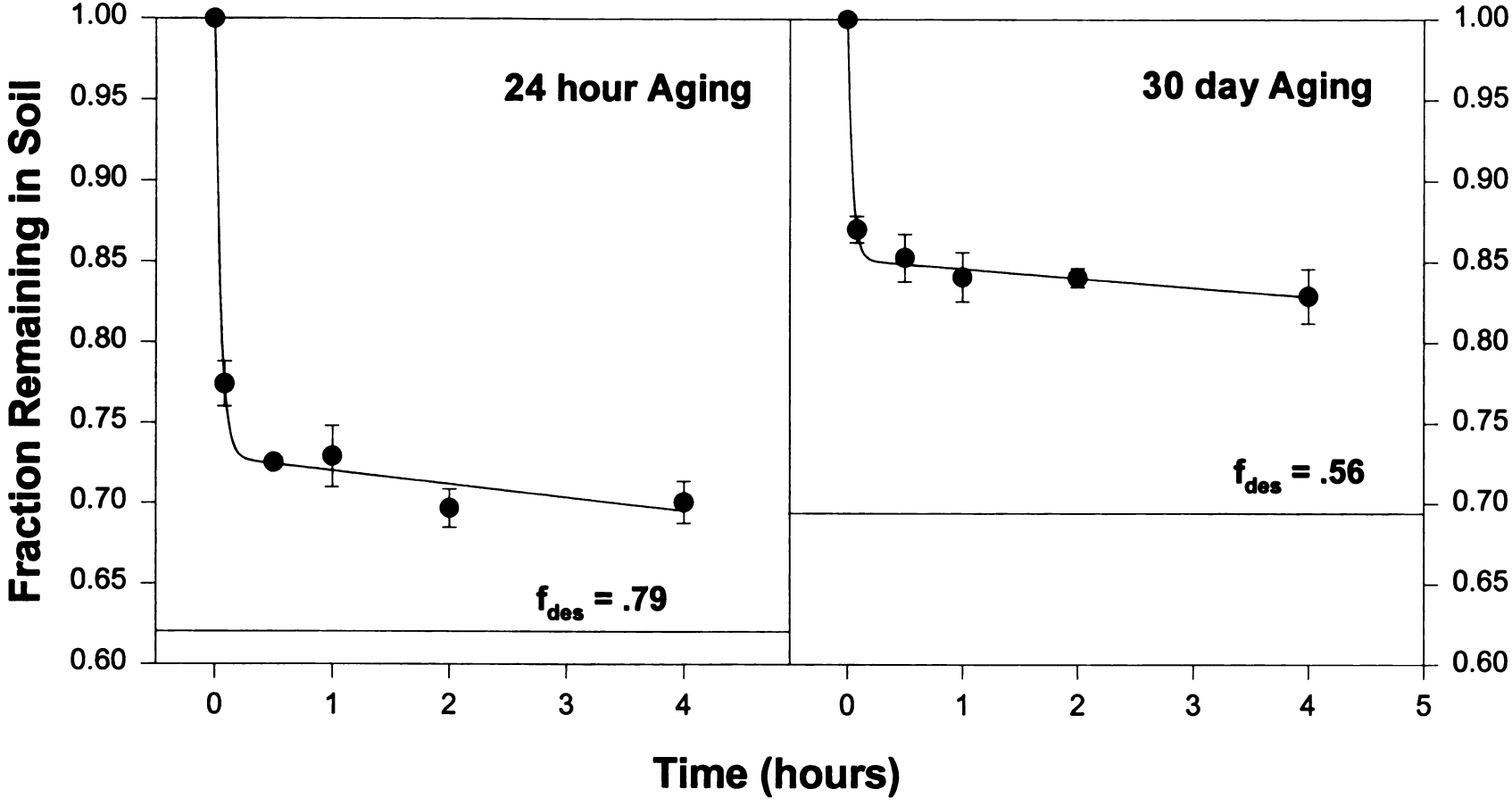

Figure 3.5. Desorption kinetics of AT after aging periods of 24 hours and 1 month.

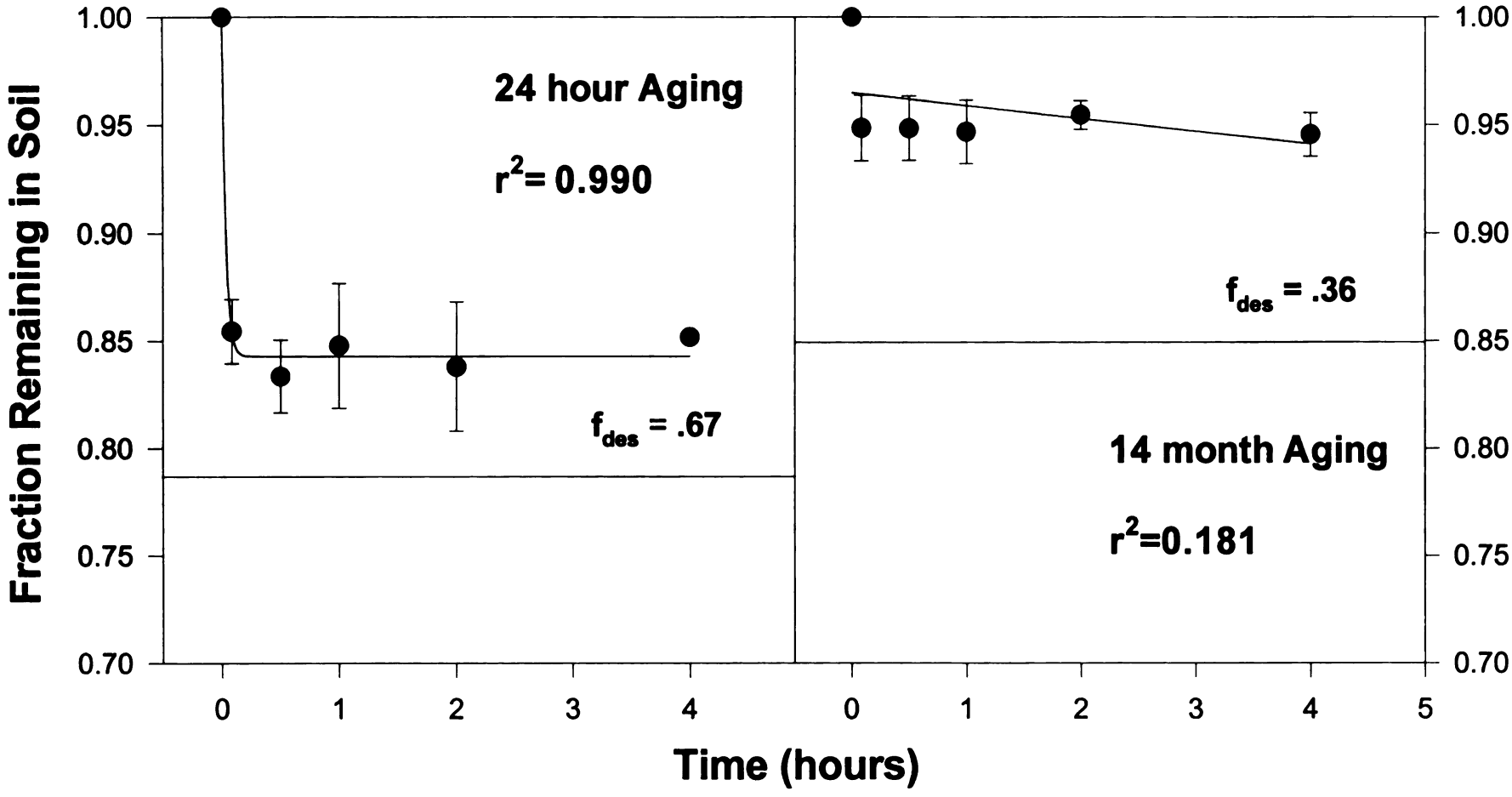

Figure 3.6. Desorption kinetics of EDB after aging for 24 hours and 14 months.

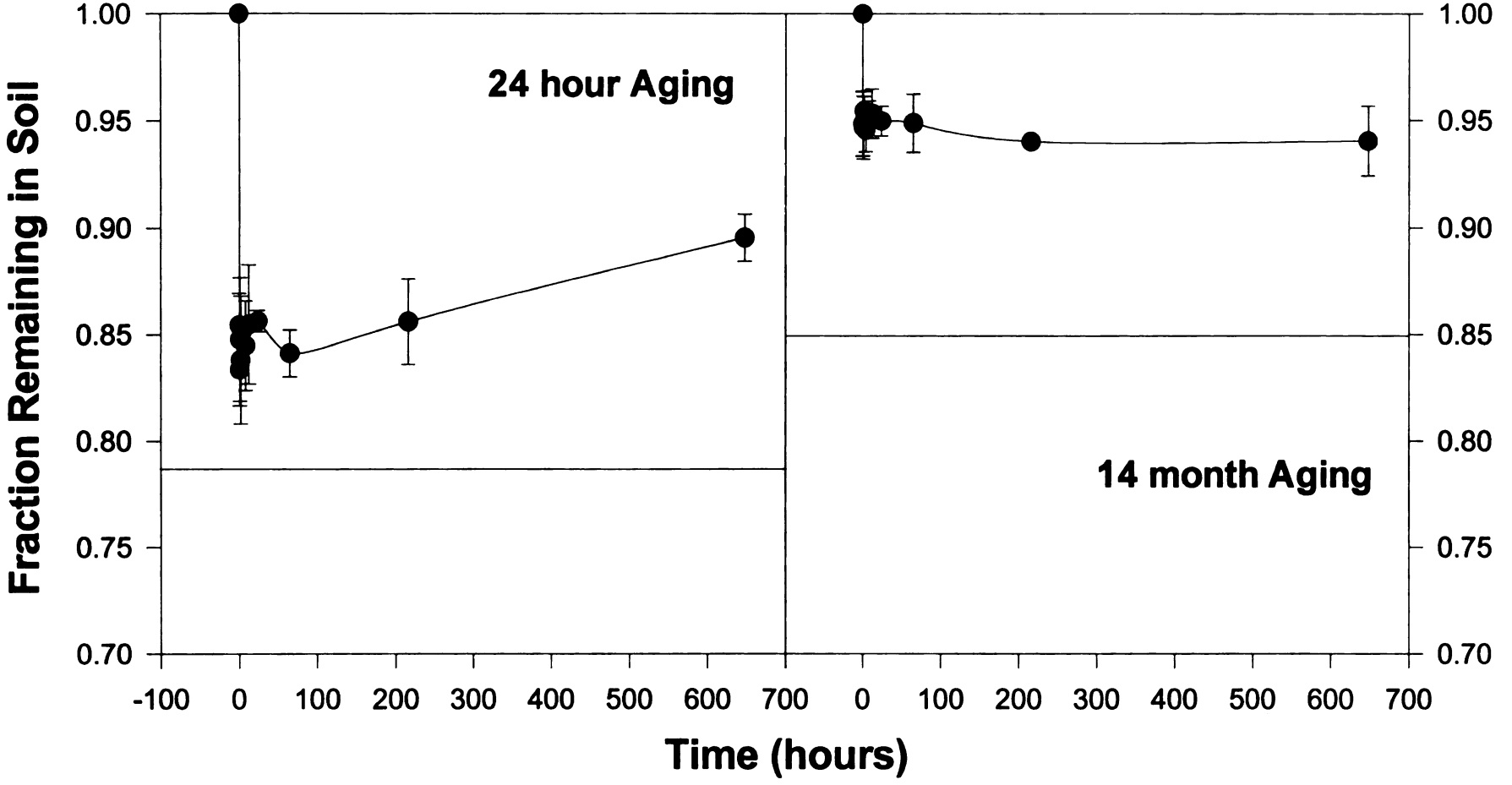

Figure 3.7. Desorption kinetics of EDB after desorption intervals of up to 650 hours.

isotherm, n = 0.827-0.884), the r^2 values for the linear model are never below 0.9932. If the 95 % C.I. of "n" for the Freundlich model includes one, the linear model is more appropriate statistically because the extra parameter becomes unnecessary. Conversely, if one is outside the confidence interval, then the use of the more parameterized (Freundlich) model is justified statistically. For this data set, in some cases the linear model is more appropriate and in some cases the Freundlich model is more appropriate.

We are unable to conclude that aging time has more of an effect on the sorption behavior of polar (Type II) compounds (*Brusseau and Rao, 1989a*) than on non-polar (Type I) compounds, such as CB and EDB. Although there was no effect of aging on the sorption coefficients of CB, there was a dramatic effect on EDB. For the polar (Type II) compounds, 2,4-D had an increase in sorption after 1 month, whereas AT did not. EDB has a lower K_p value than CB and both are Type I compounds, and therefore, according to Brusseau and Rao (*1989a*), EDB should have faster sorption kinetic behavior. They developed linear free energy relationships (LFER's) which predict that compounds with higher sorption coefficients (K_p) should have slower sorption/desorption behavior. Their data predicts that EDB should have a log k (sorption rate coefficient) approximately 5 times larger than CB. Their data also predicts that for Type I and Type II compounds with similar K_p values, the Type II compound should have a log k approximately two orders of magnitude smaller than the Type I compound. This behavior was not observed here and hence it is apparent that these generalizations do not always explain the behavior of specific compounds such as EDB. Likewise, these concepts do not explain why 2,4-D showed an increase in sorption after 1 month whereas AT did not.

One of the most interesting aspects of this study is the difference in

sorption/desorption behavior between CB and EDB upon aging. Although there was no increase in apparent K_p for CB with increased aging time, a large increase in K_p was observed for EDB subject to the same aging regimen. These results are very surprising given that both compounds are halogenated hydrocarbons, are relatively non-polar, and have similar molecular volumes (0.144 nm^3 and 0.170 nm^3 for EDB and CB, respectively). Furthermore, using the Wilke-Chang relationship, calculated diffusivities in water are nearly equal for these compounds (9.22 x 10^{-6} cm^2/sec for CB; 10.15 x 10^{-6} cm^2/sec for EDB) (*Wilke and Chang, 1955*). Based on these physico-chemical characteristics, one would predict a priori that these compounds should behave similarly in soil. If any differences in sorption characteristics existed, one would predict that CB, rather than EDB, would have an increase in apparent K_p due to aging. Previous researchers have concluded that increasingly hydrophobic compounds (water solubilities of CB and EDB are 500 and 4250 mg/L, respectively) approach sorption equilibrium more slowly. Our observation that CB equilibrates very rapidly and EDB very slowly, contradicts this relationship and suggests that compound specific interactions may be an important determinant of sorption kinetic behavior. Interestingly, EDB has been shown to have unexpected persistence in field soils (*Steinberg, et al., 1987*) and results presented here indicate that EDB exhibits sorption behavior that is unpredictable from its physical and chemical properties.

Spectral evidence has shown that compounds like EDB and 1,2-DCA exist as different conformational isomers in soils. This may help in part to explain the unexpected behavior of EDB observed in field studies. These compounds are known to associate more strongly with clay surfaces in the gauche conformer (*Aochi, et al., 1992*)

and with humics in the anti conformer (*Aochi and Farmer, 1997*). Sorption of these molecules is thought to occur by a pore filling mechanism in soils as deduced from spectroscopic evidence (*Aochi and Farmer, 1997*). This pore filling mechanism has been used to help explain the resistant fraction of DCA and EDB in soils and clays. The resistant fraction of DCA in clay minerals appears to be consistent with the existence of the chemical in a narrow network of pores where it experiences intense electrical fields (*Aochi and Farmer, 1995*). It is possible that the increased rotational freedom about the C-C single bond of this molecule enables it to reach a lowered (stable) energy state in soils, which could account for the unexpected sorption/desorption behavior of EDB. A relatively inflexible, rigid molecule like CB may not be able to reach this more relaxed energy state in soils.

Desorption data shows that there is an increase in the "irreversible" (non-desorbable) fraction (or a decrease in f_{des}) with increased aging time for all compounds tested (Table 3.4). This is in agreement with observations from a previous study done on CB (*Sharer, 1999*) where the irreversible fraction of CB was found to increase on four soil types with increased aging time. Other studies have also found that the irreversible fraction increases with equilibration time (*Pignatello, 1990; Pavlostathis and Mathavan, 1992*). There does not appear to be any correlation between the magnitude of f_{des} and compound type. Although at 1 month AT and 2,4-D show the largest decrease in f_{des}, at 14 months EDB has the largest decrease and CB the smallest (see Table 3.3). Furthermore, the actual fraction desorbed after the one month aging period is very similar among compounds. After 14 months of aging, EDB has the largest bound fraction. Based on the work of Brusseau and Rao (*1989a*) indicating that polar compounds are

subject to slower sorption/desorption behavior, our hypothesis was that there would be a greater "irreversible" fraction due to aging for 2,4-D and AT than for CB and EDB. However, these data indicate that aging does not have more of an effect on the desorption behavior of polar compounds such as 2,4-D and AT than on non-polar compounds.

The distribution of chemical within the fast (a) and slow (b) compartments in soil does change with aging, with an increase in the slow fraction for longer periods of aging for all compounds tested. In contrast, the kinetic data (k_1 and k_2) shows that aging has no effect on the rate of desorption. These results are in contrast to McCall and Agin (*1985*) who observed no change in the fast desorption rate constant with aging time, but there was a decrease in the slow desorption rate constant. Their data was for picloram, a relatively polar compound, aged in soils for 1 and 200 days. These results also contrast those of Carmichael, et al. (*1997*) which found that the desorption rates (not rate constants) for fresh and field contaminated PAH's were different by several orders of magnitude. It should be mentioned that although k_1 is very difficult to measure accurately by the method described here, it seems apparent that if aging does have an effect on k_1, the effect must be very small and perhaps negligible. As was also the case in a previous study (*Sharer, 1999*), it was found that in most cases a substantial fraction of the compound was not desorbed even for samples aged for only 24 hours and desorbed for up to four months. This observation is consistent with the findings of Kan, et al. (*1994*) and Fu, et al. (*1994*) who showed that the desorption behavior of PAH's in soils was irreversible. The size of the irreversible fraction of PAH's was found to be 30-50 % of the total mass applied after seven days of sorption and up to hundreds of days of desorption. It is interesting to note that 2,4-D was the only compound that demonstrated

sorption reversibility after 24 hour contact times (≈ 98 % desorbs after 4 months of desorption) (Figure 3.2). However, the sorption reversibility disappeared upon aging with the soil. After 1 month, ≈ 92 % of 2,4-D desorbed and after 14 months of aging, only ≈ 73 % desorbed (Figures 3.3 and 3.4). The desorption resistant fraction seen in the 24 hour samples is an indication that diffusion may not be the main mechanism controlling desorption behavior, as these samples would be expected to show ideal (or near ideal) sorption/desorption behavior after sorption for only 24 hours and desorption for four months.

This study has demonstrated that aging has an effect on sorption for some compounds but not for others on a common soil type. EDB and 2,4-D show clear indications of an increase in sorption, whereas CB does not, and AT does not for the 1 month sorption period. Indirect evidence indicates that AT sorption does increase after a longer period of equilibration. Aging has no effect on the desorption rates of any compound tested. Aging does affect the amount of a compound desorbed with an increase in the irreversible (non-desorbable) fraction with increased aging time. There does not seem to be a correlation between the extent of desorption and compound type, indicating that aging does not have more of an effect on the desorption of 2,4-D and AT than on CB and EDB. Aging also has an effect on the distribution of a chemical between the fast and slow sites in soil, with a greater portion residing in the slow fraction for longer aging times. This trend was observed for all chemicals tested. It seems clear that the behavior of chemicals in soils is compound specific and can not always be predicted from physical-chemical characteristics. A much larger data set is needed to ascertain whether the behavior of EDB is anomalous due to some unknown chemistry or if many

compounds exhibit behavior that is unpredictable due to aging. Based on our results generalizations about effects of aging on the sorption behavior of organic chemicals in soils should be avoided.

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Chapter 4

EFFECTS OF AGING ON THE BIOAVAILABILITY AND SORPTION /DESORPTION BEHAVIOR OF BIPHENYL IN SOILS

Abstract

Aging (soil-chemical contact time) is known to lead to unexpected persistence of organic contaminants in the environment. A highly mobile and easily degradable soil fumigant, EDB, has been found in agricultural field soils almost twenty years after its last known application. The effects of aging on bioavailability, one of the main variables for determining the persistence of organic chemicals in the environment, is a poorly understood process. There are very few studies that have tested the effects of long-term aging on chemical dynamics in soils and have related these effects to bioavailability tests of these aged compounds. In this study, sorption/desorption behavior of biphenyl (BP) on two soil types (Capac A and Capac B) was evaluated for aging times of 24 hours and 8 months. Then bioavailability experiments of BP on the same soils were performed after aging times of 24 hours to 6 months. Sorption isotherms and desorption kinetic profiles were prepared to analyze changes in uptake and release, respectively, due to aging of BP from a physico-chemical standpoint. Mineralization kinetics of BP to $^{14}CO_2$ by a strain of *Pseudomonas putida* was used to assess changes in bioavailability due to aging from a biological standpoint. Data indicates that there is an increase in sorption with aging time for BP on both soil types. The rate of BP desorption does not change with increased aging time. The extent of BP mineralization was found to decrease with aging time.

Keywords – Bioavailability, biphenyl, sorption, desorption, aging, soils

Introduction

Sorption/desorption behavior of organic chemicals in soils is an important determinant governing the bioavailability of these compounds to bacteria. Limited bioavailability of these compounds may cause increased persistence in natural environments such as soils. Bioavailability also determines the toxicological and herbicidal activity of organic contaminants and pesticides in the environment. The bioavailability of a compound can be limited by sorption to soils which decreases the extent of degradation by microbes *(Wszolek and Alexander, 1979; Steen, et al., 1980).* Most researchers have assumed that before a sorbed molecule can be degraded by a bacterium, it first has to diffuse to the solid-liquid interface, then partition into the aqueous phase, where it is available for microbial degradation *(Harms and Zehnder, 1995).* The conclusion that sorbed substrates are unavailable to bacteria, and that desorption is a prerequisite for degradation, have been validated in studies by Ogram, et al. *(1985)* and Steen, et al. *(1980).* Other researchers (*Guerin and Boyd, 1992*) have concluded that generalizations regarding availability of sorbed contaminants are inappropriate. They provided evidence for the direct access of soil-sorbed naphthalene by one species of bacteria but not another. This may be because of organism specific properties such as attachment, motility, or affinity for the particular substrate.

In cases where bacteria can only use dissolved substrates, sorption can limit bioavailability in two ways: 1) Decreasing aqueous phase concentrations to low levels due to sorption and thereby limiting rates of degradation, and 2) Limiting the extent of biodegradation due to small desorption rates (a desorption limited process) *(Harms and Zehnder, 1995).* These factors will limit the initial biodegradation rate but limited extents

of biodegradation can be overcome if bacteria are able to enhance desorption. Several studies have concluded that bacteria are able to enhance desorption, indicating that desorption is slow relative to biodegradation and that biodegradation increases desorption. Harms and Zehnder *(1995)* found that 3-chlorodibenzofuran desorption was driven by cells attached to teflon sorbents. They concluded that bioavailability was dependent on the specific affinity of a bacteria for a specific substrate and the tendency of that organism to adhere to a surface. Rijnaarts, et al. *(1990)* also found that microbes enhanced desorption and that initial rates of biodegradation were consistently higher than initial desorption rates. The study of Guerin and Boyd *(1992)* found that one bacterial species was able to enhance desorption whereas another species was not.

Because many field soils have been contaminated for periods of months to years, conclusions from short-term bioavailability studies may be inappropriate for situations where the soil-chemical contact time (aging) is long. Observations from field studies have demonstrated that aged chemicals are less bioavailable than freshly added ones *(Steinberg, et al.,1987; Scribner, et al., 1992).* A study by Weissenfels, et al. *(1992)* demonstrated that the strength of PAH sorption to soils, which may increase with aging, decreased the amount degraded. They also concluded that freshly added chemicals do not accurately mimic the behavior of aged chemicals. Hatzinger and Alexander (*1995*) showed that the extent of freshly added phenanthrene mineralized was greater than the extent mineralized for aged phenanthrene in a muck soil (11.22 % OC). They found no difference in the extent mineralized for freshly added (O days) and aged (84 days) phenanthrene in a loamy soil (2.33 % OC). Rates of degradation were decreased for aged phenanthrene on both the loam and the muck. In a sandy soil (1.34 % OC), they found

no difference in the rate or extent of degradation for aged versus freshly added phenanthrene. 4-Nitrophenol was added to the loam and muck soils and mineralization was assessed at 0, 40, and 103 days. In both soil types, rates and extents of mineralization decreased with increased aging time. These results show the effect of aging on biodegradation and indicate that in many cases aging has an effect on both the rate and extent of biodegradation.

One study has explicitly measured both desorption and biodegradation rates for freshly added and aged chemicals (*Carmichael, et al., 1997*). Desorption rates of chrysene and phenanthrene (both PAH's) were found to be much faster than observed mineralization rates for freshly added compounds in this study. They also found that desorption rates for field-aged chemicals were equal to or slower than mineralization rates, so it was concluded that desorption of aged PAH's may control their fate and availability. This may explain why the persistence of PAH's has been observed even in soils that have active populations of PAH-degrading organisms. These results are in agreement with those of Guerin and Boyd *(1993)* which found that initial mineralization rates (IMR's) for aged compounds were slower than for freshly added.

In order to better understand the effects of aging on bioavailability and on the fate of chemicals in soils, we initiated a long-term aging study explicitly examining sorption, desorption, and biodegradation in soils. In this study, sorption of biphenyl on Capac A and B soil horizons after was evaluated 24 hours and 8 months of aging. Also, biphenyl desorption rates were measured after these periods of aging. Finally, biphenyl biodegradation in these soils using a *Psuedomonas* species was evaluated to observe the effects of aging on bioavailability. Results from the biological and chemical assays were

then compared in an effort to better understand the effects of aging on both biological and physico-chemical processes.

Experimental Section

Soils used in this study were Capac A and B horizon (fine-loamy, mixed, mesic Aeric Ochraqualf) soils collected from southern Michigan. These soils were prepared using the same methods as in chapter 2. Capac A has a sand, silt , and clay content of 54.6, 24, and 21.4 %, respectively, and an OC content of 3.3 %. Capac B has a sand, silt, and clay content of 60, 20, and 20 %, respectively, and an OC content of 0.4 %. All soils were then gamma irradiated with 5 MRad at the University of Michigan Ford Nuclear Reactor Laboratory using a cobalt-60 irradiator (dose rates by Reuter-Stokes ion chamber). Soils were stored in 500 mL Nalgene bottles during irradiation and remained sealed until use.

Sorption isotherms: The amounts of a particular soil and solution used to develop sorption isotherms were based on preliminary sorption experiments. The linear isotherm equation ($x/m = KCe$) was employed to estimate the amount of soil and solution needed to sorb 50 % of the added BP while also minimizing headspace volume. The tubes used were 20 mL glass ampules which were autoclaved prior to use. All additions of soil and solution to the ampules were carried out in a sterilized laminar flow hood. A mass of soil was weighed and transferred to the ampule using a metal spatula along with a plastic funnel. A 0.005 M $CaCl_2$ solution, which had been autoclaved for 25 minutes and amended with 200 mg/L NaN_3, was added to the ampules using a sterilized repipettor. These functions were carried out in the laminar flow hood and all items contacting soil or

solution were autoclaved prior to use (spatulas, funnels, etc.).

Additions of the ^{14}C-Biphenyl (BP) (radiochemical purity > 98 %; Sigma Chemical Co.) stock solution (in acetone) and flame sealing of the ampules were carried out in a chemical fume hood. An aliquot of BP stock solution was added to the ampule using a 10 or 25 ul Hamilton syringe and the ampule was immediately flame sealed using an Ampulmatic flame sealer unit (Bioscience, Inc.). Aliquots used for the sorption isotherms were 2, 5, 10, and 20 ul of a low concentration BP stock and 10, 25, and 70 ul of a higher concentration BP stock solution. The low concentration stock solution was initially 2.84 uCi/mL ^{14}C-BP and the high concentration stock solution contained initially 16.6 uCi/mL ^{14}C-BP. The stock solutions were stored in a -4° C freezer in amber reacti-vials with mininert valves when not in use. Each of the seven sorption isotherm points were done in triplicate. After flame sealing, the ampules were equilibrated ("aged") for either 24 hours or 8 months. To insure homogeneity, the tubes were shaken (reciprocating shaker) for either 24 hours (for 24 hour aging period) or 72 hours (for 8 month aging). After shaking, the tubes were either analyzed immediately (24 hour aging) or stored in the dark with periodic shaking (8 month aging). For analysis, each ampule was centrifuged at 635 x g for 7-9 minutes, the ampule broken at the neck, and a 1mL aliquot of the aqueous phase was added to 8 mL of scintillation fluid (RPI, Inc., Safety-Solve). The samples were shaken and the next day analyzed by liquid scintillation counting (Beckman LS 6500 multi-purpose scintillation counter). Values for each triplicate set of ampules were averaged and standard deviations calculated. The data were plotted as the amount sorbed (ug/Kg) versus concentration in solution (ug/L). Linear regression was used to compute the slope of the line, which corresponds to the

equilibrium sorption coefficient (K_p). The K_p values were compared at each of the aging periods for each soil type.

Desorption Kinetics: Soil and solution were added to the ampules as described above, with the same amounts of soil and solution used as were used for the sorption experiments. A fixed volume of BP stock solution (10 uL) was added to all of the desorption ampules and the ampules were then flame sealed. The ampules were aged for the appropriate time period (24 hours or 8 months) and shaken and centrifuged as described above. Then, a quadruplicate set of ampules were opened by cutting the stem (1.6 – 2.0 cm from the top of the ampule) using a ¼-inch glass drill bit (Sommer & Maca, Co.), then sampling the solution phase (200 uL) using a 200 uL Gilson Pipetman. This sample was analyzed using scintillation counting (after 24 hours) to arrive at the equilibrium concentration in solution (C_o) before desorption was initiated. Then a larger aliquot of the solution phase was removed (≈ 75-80 % of the total volume of solution) using a 25 mL gas-tight Hamilton syringe. The same volume of fresh solution (autoclaved 0.005 M $CaCl_2$ with 200 mg/L NaN_3) was then added to the ampule, again using the 25 mL Hamilton syringe. The syringe was rinsed with clean solution between withdrawal of the old solution and addition of the new. The ampule was then re-flame sealed and shaken by hand. At the appropriate time interval, the quadruplicate set of tubes was centrifuged at 635 x g (7-9 minutes) and the remainder of the stems were broken at the neck and a 1 mL aliquot of the aqueous phase was sampled and analyzed by scintillation counting (after 24 hours); this gives the concentration of BP that desorbs in solution after a given desorption time (C_f). The amount desorbed is: $C_f - [C_o$ + (the mass of BP remaining in the residual solution) ÷ (volume of residual solution)]; since only 75-

80 % of the total solution volume was removed, an appreciable amount of solution remained, the residual solution, which mixed with the fresh solution added to initiate desorption. Desorption time intervals were: 0.083, 0.5, 1, 2, 4, 8, 12, 24, 72, 216, 648, and 2880 hours. Since four ampules were used for each desorption time interval, a total of 48 ampules were prepared in the same manner and incubated for the 24 or 8 month aging period. The concentration desorbed $C_f - (C_o$ + residual BP) was converted to the fraction of the total remaining in the soil (at t=0, the fraction in the soil is 1 and the fraction desorbed is 0).

Statistical analysis: Sorption isotherms were analyzed for linearity using non-linear regression analysis. Isotherms were fit to the Freundlich model ($x/m = K \bullet Ce^n$) and the 95 % confidence interval (C.I.) for n was generated for the model. Isotherms were also analyzed for differences in slope between 24 hour sorption and 8 month sorption. This was accomplished by performing linear regression analysis with indicator variables. The variability in the model coefficients were tested for significance at the 0.99 level. Nonlinear regression analysis was performed on the desorption data using Sigmaplot graphing software. Parameters for the desorption equation were estimated using the Marquardt-Levenberg algorithm and standard deviations of each parameter are computed.

Bioavailability assays: To evaluate the availability of soil-sorbed biphenyl to the biphenyl degrader (*Psuedomonas putida* P106), a mineralization assay, adapted from the method described by Guerin and Boyd (*1992*), was used. Soil-free controls and soil slurries were set up in 160-ml serum bottles sealed with Teflon-coated butyl stoppers. Sterile soil (7.5 g) (gamma irradiated as for the sorption/desorption experiments) was placed into each bottle, and variable volumes of sterile phosphate buffer (20 mM) and

non-radioactive biphenyl stock solution were added to obtain the appropriate concentrations. Approximately 0.1 μCi of ^{14}C-biphenyl was added to each serum vial separately from the addition of "cold" biphenyl. Soil slurries were shaken for 24 hours and then stored in dark with periodic shaking for the prescribed aging period. Soil-free controls were prepared in sterile soil extracts. Cells harvested at early stationary phase were used as inocula. Cell density in serum bottles was ~10^6 CFU/ml for strain P106. At precise time intervals, 1 ml suspension and 1 ml headspace were withdrawn from each bottle and injected into to a sealed tube which served as a $^{14}CO_2$ trap. The tube contained 1ml of 2 N HCl and was sealed with a rubber stopper. Filter paper in the tube was soaked with 2N NaOH which was used to trap the ^{14}C. After the assay, the filter paper strip was transferred to a scintillation vial containing 10 ml scintillation fluid, and the center cup which held the filter paper was washed with 2 ml 50% (v/v) ethanol to remove any residual ^{14}C. Samples were left overnight in the dark before being analyzed by liquid scintillation counting.

Data analysis: Percentage of the initial radioactivity converted to $^{14}CO_2$ was plotted versus time. Mineralization data were fitted to a first-order kinetic equation:

$$P = Pmax\ [1 - \exp(-k \bullet t)]$$

where P is the percentage of initial radioactivity mineralized, Pmax is the maximal percent mineralized, k is the first-order rate constant, and t is time. The initial mineralization rate (IMR, ug• L^{-1}•min^{-1}) is the product of Pmax, k, and initial biphenyl concentration:

$$IMR = k\ (min^{-1}) \bullet P_{max} \bullet [Biphenyl]\ (\mu g \bullet L^{-1})$$

In soil free systems, at substrate concentrations below the half saturation constant of the organism, and with non-growing cells, mineralization rates are linearly proportional to the substrate concentration. Thus, a linear control line was established relating IMR to aqueous biphenyl concentrations. In soil slurries if sorbed biphenyl is unavailable to bacteria, only biphenyl in the aqueous phase can be degraded in soil slurries. Under this assumption, IMR values of soil slurries should be equal to those in a soil free control with the same aqueous phase biphenyl concentration, i.e. they should fall on the soil free control line. IMR of soil slurries above the soil-free control line, indicates that bacteria have access to sorbed biphenyl or that desorption is rapid relative to degradation.

Results

The sorption isotherms of biphenyl (BP) on Capac A and B show that BP had a statistically significant increase (at the 0.01 level) in sorption from 24 hours to 8 months (Figures 4.1 and 4.2). The increase in sorption on Capac B was less than the increase on Capac A. Sorption data were fit to the Freundlich equation, $x/m = KCe^n$, where x/m is the concentration of sorbed BP (ug/Kg), Ce is the aqueous BP concentration (ug/L) , K is the sorption coefficient, and n is the coefficient of linearity (Table 4.1). When sorption data are fit to the linear form of the Freundlich equation (n = 1), the isotherms appear linear in the range tested (r^2 values range from .9970 - .9997 for the linear plot). Evaluation of the Freundlich isotherm parameters show some evidence of non-linearity (n slightly less than 1). For Capac A, these values appeared to increase (become more linear) from the 24 hour to 8 month aging interval. For Capac B, these values remained essentially constant.

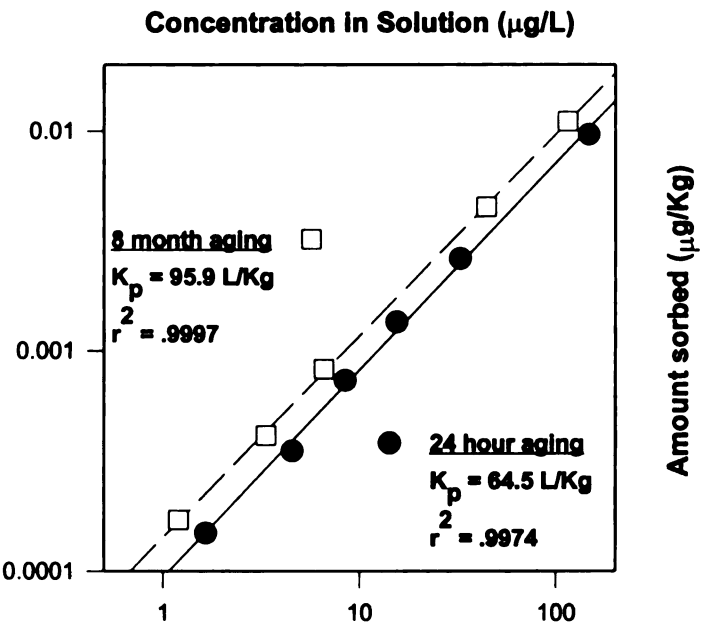

Figure 4.1. BP sorption on Capac A after 24 hours and 8 months of aging.

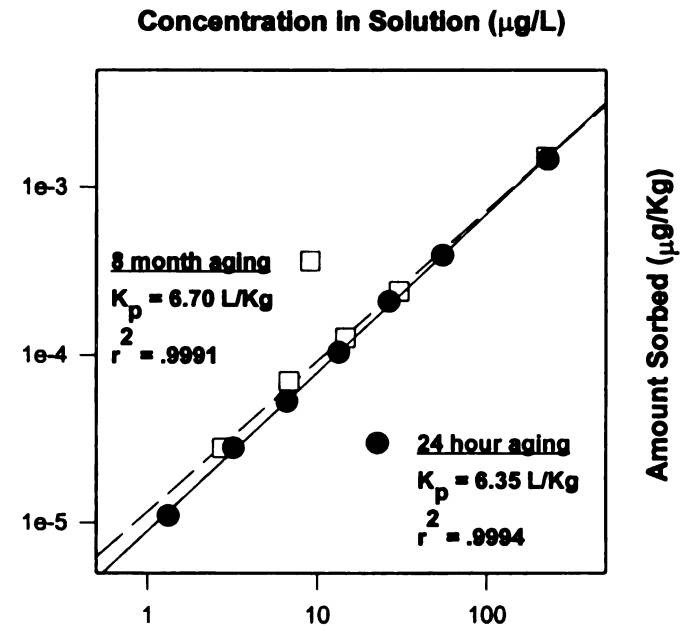

Figure 4.2. BP sorption on Capac B after 24 hours and 8 months of aging.

Table 4.1. Freundlich isotherm ($x/m = K \bullet Ce^n$) parameters after 24 hours and 8 months of aging time.

		K (95 % C.I.)	n (95 % C.I.)
BP / Cap. A	24 hour	0.099 – 0.140	0.843 – 0.914
	8 month	0.115 – 0.148	0.907 – 0.961
BP / Cap. B	24 hour	0.009 – 0.011	0.905 – 0.930
	8 month	0.009 – 0.012	0.888 – 0.940

Desorption kinetic data was evaluated using the double decay equation ($y = a \bullet e^{(-k1t)} + b \bullet e^{(-k2t)}$) where y is the fraction of chemical remaining in the soil, k_1 and k_2 are the fast and slow desorption rate constants, respectively, and "a" and "b" are the fraction of chemical residing in the fast (a) or slow (b) sites. Parameters from the double decay equation are listed in Table 4.2. Also utilized in the analysis of desorption data was the fraction desorbed ($\mathbf{f_{des}}$), which gives a measure of the extent of total desorption. This value was calculated by dividing the total amount observed to desorb (T_{des}) divided by the amount that should desorb assuming complete desorption reversibility (Eq_{des}):

$$\mathbf{f_{des} = T_{des} / Eq_{des}}$$

On the desorption plots (Figures 4.3-4.4), the value for Eq_{des} can be seen as the asymptote that should, theoretically, be approached by the desorption curve. If the experimental desorption curve reaches the asymptote, then $\mathbf{f_{des}} = 1$. Also listed in Figures 4.3 and 4.4 are the r^2 values which indicate the goodness of fit of the double decay equation to the experimental data. The experimental data points (average of quadruplicate values) are shown along with a plot of the regression line generated by the double decay equation. For this study, when comparing desorption data, a four hour

Table 4.2. Desorption equation ($y=a \bullet e^{(-k1 \bullet t)} + b \bullet e^{(-k2 \bullet t)}$) parameters after 24 hours and 8 months of aging.

		a	b	k_1 (hr^{-1})	k_2 (hr^{-1})
BP / Cap. A	24 hour	0.16	0.84	13.8 ± 5.3	1.7e-2 ± 8.5e-3
	8 month	0.16	0.84	15.2 ± 2.0	9.4e-3 ± 2.8e-3
BP / Cap. B	24 hour	0.26	0.74	20.8 ± 1.9	2.5e-2 ± 3.2e-3
	8 month	0.22	0.78	14.6 ± 3.8	2.6e-2 ± 8.8e-3

desorption interval was utilized so that the sorption interval substantially exceeded the desorption period. This was done to minimize significant resorption occurring along with desorption, since these processes occur simultaneously, especially for the 24 hour aged samples which may not have reached sorption equilibrium. Essentially, this is the method of initial rates for calculating rates of chemical reactions (*Atkins, 1994*).

Aging appeared to have little effect on the desorption rate constants of BP. The fast desorption rate constant (k_1) is nearly identical on Capac A after 24 hours and 8 months of aging (13.77 ± 5.3 hr^{-1} and 15.23 ± 2.0 hr^{-1}, respectively). This trend also holds on Capac B after 24 hours and 8 months of aging (20.8 ± 1.9 hr^{-1} and 14.57 ± 3.8 hr^{-1}, respectively). The slow desorption rate constant (k_2) also varies little with aging (see Table 4.2). The fraction of BP residing in the fast (a) and slow (b) compartments changes little with aging on Capac A. The fraction in each compartment does change with aging on Capac B (Table 4.2). Correspondingly, the fraction desorbed (f_{des}) after four hours decreases for Capac B (.67 to .58) whereas f_{des} actually increases slightly on Capac A with aging (from .70 to .76) (see Figures 4.3 and 4.4).

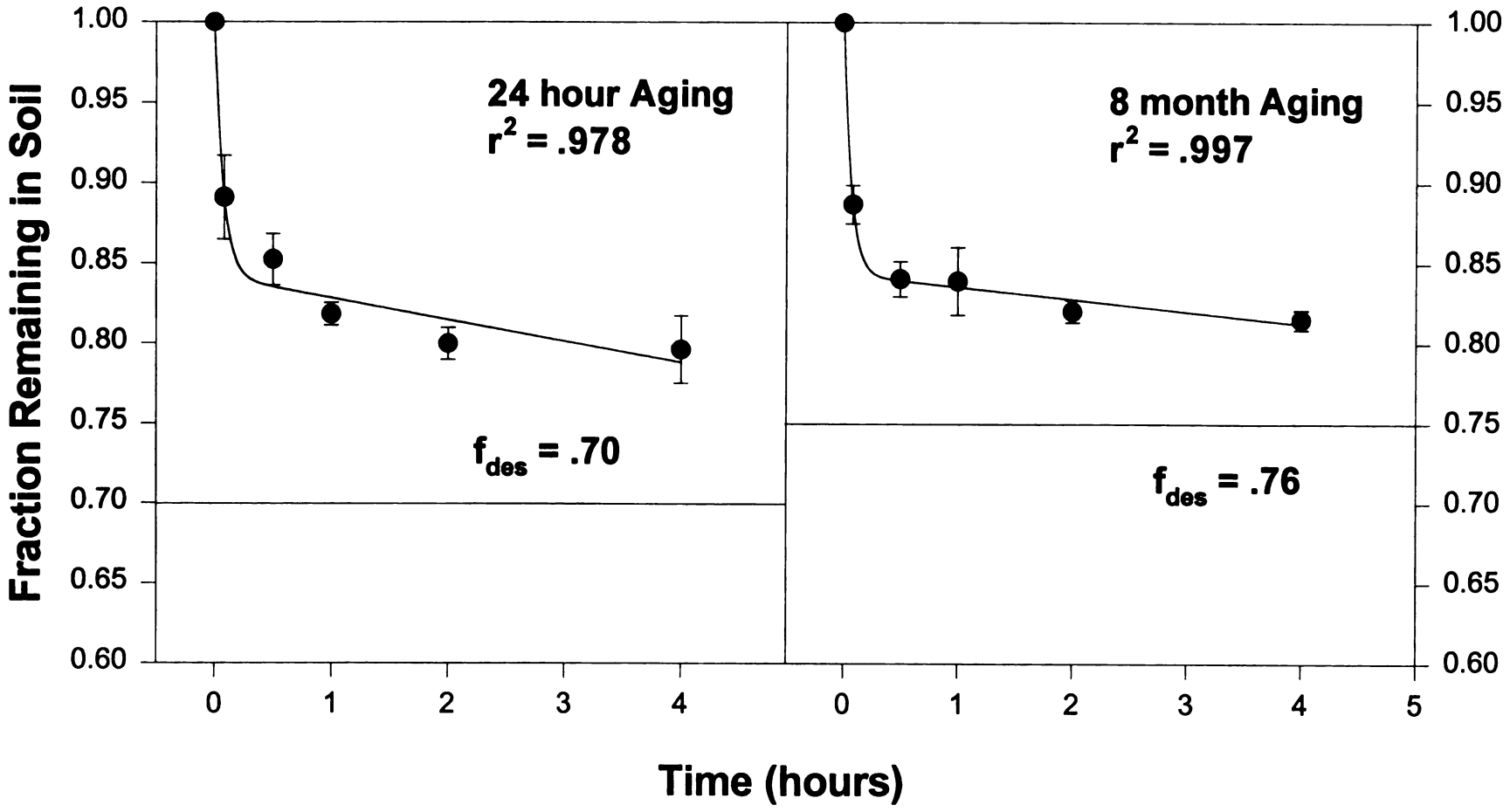

Figure 4.3. Desorption kinetics of BP on Capac A after 24 hours and 8 months of aging.

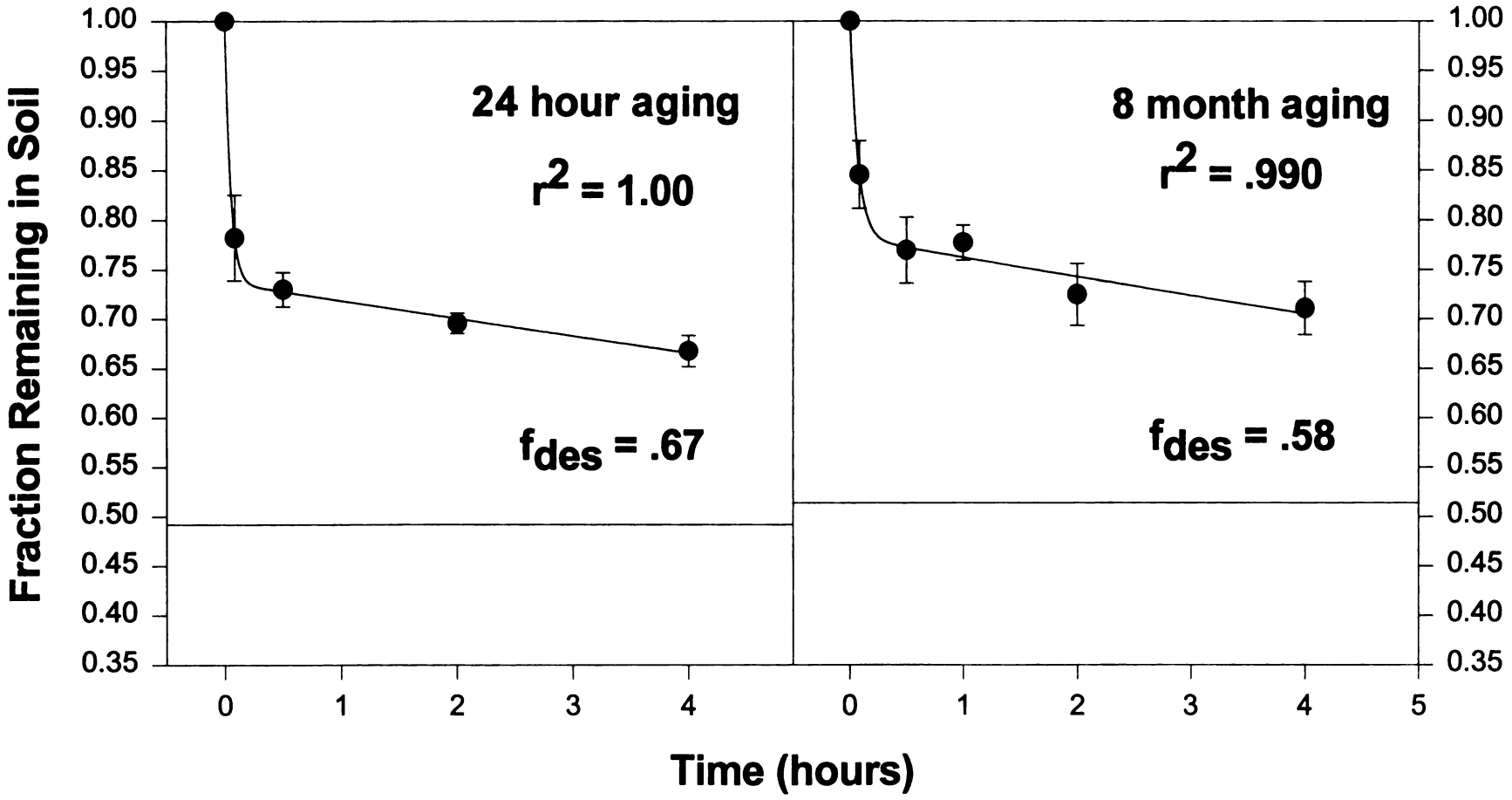

Figure 4.4. Desorption kinetics of BP on Capac B after 24 hours and 8 months of aging.

Biological data for the mineralization of ^{14}C-BP to $^{14}CO_2$ by *Pseudomonas putida* P106 is shown in Figure 4.5 and 4.6. On both Capac A and B, the extent of BP mineralized to CO_2 decreases progressively with the length of aging time prior to inoculation of the soil slurries (1 day to 6 months) with *P. putida* P106.

Table 4.3 gives a direct comparison of the biological and chemical data. Data from the respective experiments were compared using the first order decay model ($A_0=A_1e^{(-k*t)}$), where A_o is the amount of chemical at t=0 hours, A_t is the amount at any point in time, t is time in hours, and k is the first order rate constant. For this study, the first four hours of desorption were compared directly to the first four hours of biodegradation. The biological experiments measured biodegradation for 6 hours, so comparisons between the two systems beyond 6 hours was not possible. Four hours was the longest common time point measured for these systems. It is clear that the rate constant for biological degradation is much faster than the rate constant for desorption by almost two orders of magnitude and this trend is consistent on both soil types. An important observation is that neither the biological nor the desorption rate constant decrease with aging, which was highly unexpected.

Discussion

Sorption isotherms of BP indicate that sorption is nearly complete on Capac B after 24 hours, but not on Capac A. Although isotherms on both soils showed a statistically significant (at the .01 level) increase in sorption, the increase in sorption on Capac B was relatively small. The sorption isotherms can be fit adequately to the linear form of the Freundlich equation (n = 1); r^2 values were > .9970. When fitting the data to

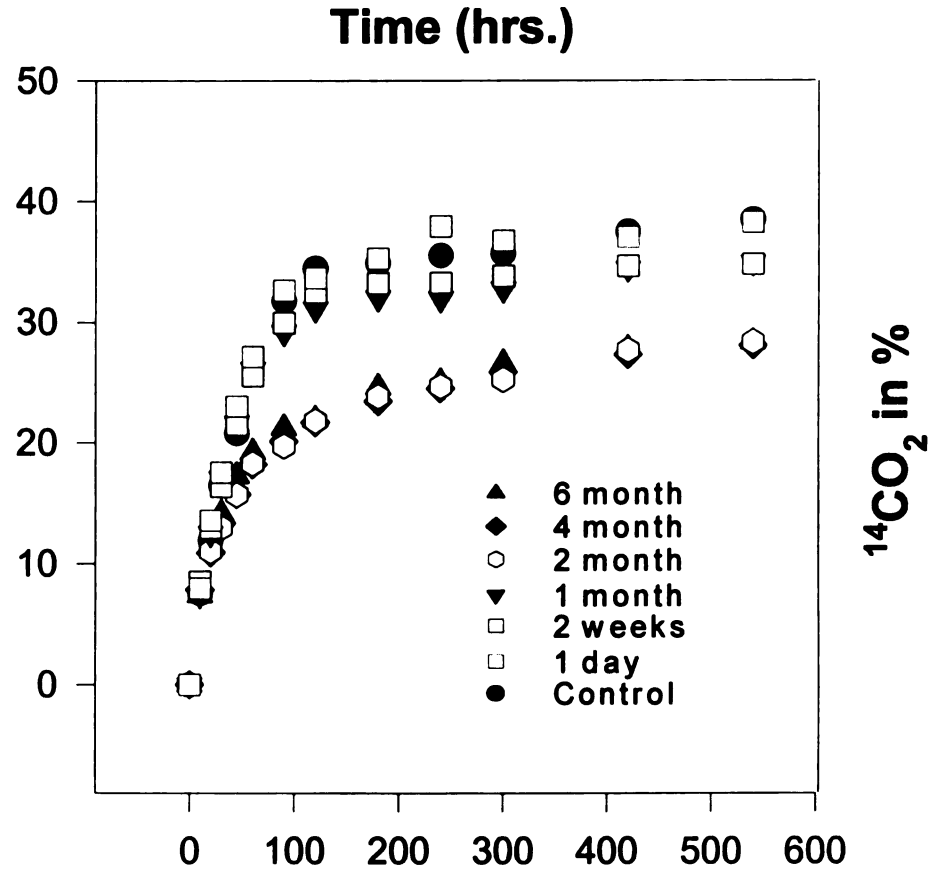

Figure 4.5. Mineralization kinetics of BP to $^{14}CO_2$ by *P. putida* after different aging periods on Capac A.

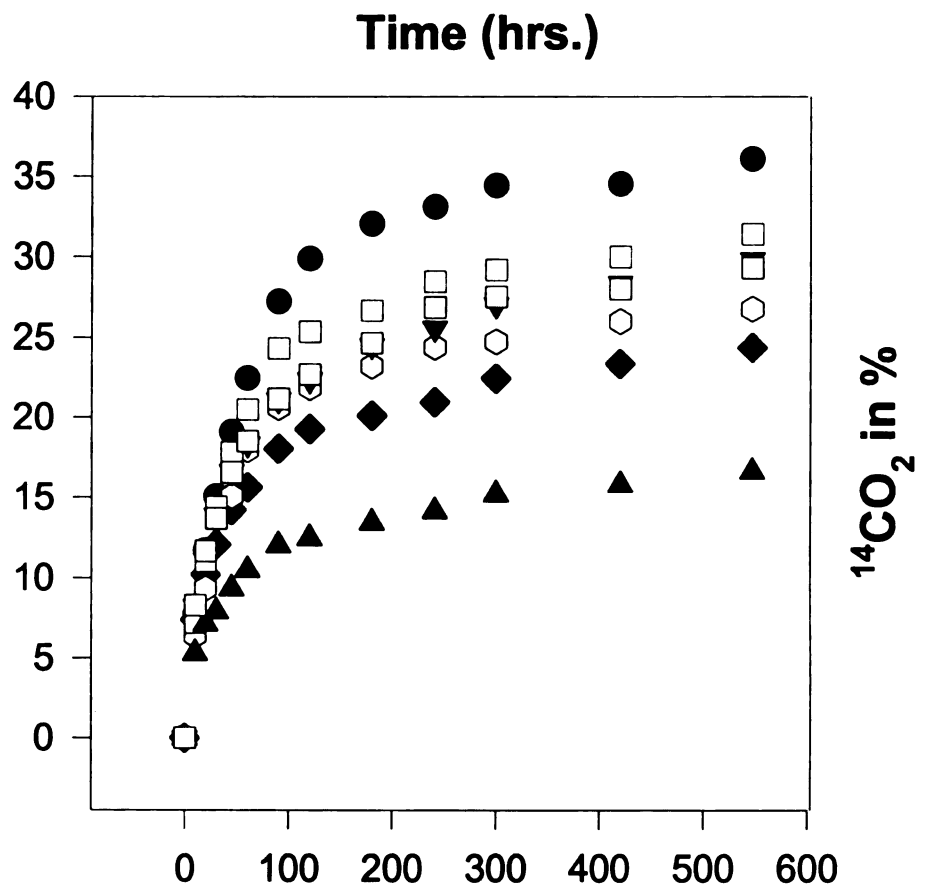

Figure 4.6. Mineralization kinetics of BP to $^{14}CO_2$ by *P. putida* after different aging periods on Capac B. For legend, follow figure 4.5.

Table 4.3. Comparison of biological and chemical assays of biphenyl after 24 hours and 6 to 8 months of aging.

	Chemical data				Biological data	
	K_p	k (hr^{-1})	f_{des}	irreversible	k (hr^{-1})	fraction degraded
Capac A						
24 hour	65	4.44e-2	.70	.30	1.31	.38
6/8 month*	96	3.56e-2	.76	.24	1.45	.25
Capac B						
24 hour	6.4	7.45e-2	.67	.33	1.27	.28
6/8 month*	6.7	6.78e-2	.58	.42	1.46	.14

K_p = L/Kg ; all data based on the first 4 hours of desorption or mineralization.
* chemical assay done after 8 months of aging, biological done after 6 months of aging

the conventional form of the Freundlich equation, there is some evidence of non-linearity from the fact that the n values are less than 1. The values of n, however, remain constant or increase slightly when comparing data at 24 hours of equilibration time to those at 8 months. This is in contrast to the results of Xing and Pignatello (*1996*) who observed increasing non-linearity of sorption isotherms (decreases in n) for dichlorobenzene and dichlorophenol on a sandy loam soil after equilibration times of 1 and 180 days. This was attributed to the fact that SOM has both partition and adsorption domains (dual-mode sorption) and that the adsorption domains are reached only given long soil-chemical contact times since these domains are internal in the SOM matrix (*Xing and Pignatello, 1996*). The adsorption component gives the isotherm increasing non-linearity that only becomes apparent with long soil-chemical contact times. The isotherms observed in this

study and in previous studies (*Sharer, 1999a; Sharer, 1999b*) do not appear to be consistent with a dual-mode sorption mechanism.

The desorption data indicates that the desorption rate of BP is the same whether the sample has been aged for 24 hours or 8 months on both soil types. This behavior is consistent on both Capac A and Capac B. This is in agreement with results from two studies using a variety of compounds and soils (*Sharer, 1999a; Sharer, 1999b*), although in contrast to studies by McCall and Agin (*1985*) and Carmichael, et al. (*1997*). McCall and Agin (*1985*) found that the fast desorption rate constant did not decrease with increased aging time, but the slow desorption rate constant did, for freshly added and aged picloram. The study by Carmichael, et al. (*1997*) found that desorption rates, not rate constants, decreased dramatically for fresh versus field contaminated (aged) PAH's. The fraction of compound residing in the fast and slow compartments changed on the Capac B soil, but remained the same on the Capac A soil. For Capac B, 26 % of sorbed BP was located in the fast compartment after 24 hours of aging and 22 % after 8 months of aging. For Capac A, the fraction in the fast compartment remained constant at $\approx$ 16 % and the fraction desorbed actually increased slightly with aging (from 70 to 76 %). Both these results are unexpected and are in contrast to almost all other data obtained by this desorption technique. Biphenyl desorption on Capac B was characterized by a decrease in the fraction desorbed with increased aging time. This result is consistent with the general observations from two previous studies (*Sharer, 1999a; Sharer, 1999b*) and from results by Pignatello (*1990*) and Pavlostathis and Mathavan (*1992*).

The biological data showing the mineralization of ^{14}C-BP clearly demonstrates a progressive decrease in the amount degraded with increased aging time on both soil

types. For example, the amount mineralized to CO_2 after a 24 hour aging period is 32-33 %, and after a 6 month aging period, the amount mineralized is only 14-15 %. It would be expected that if an increase in sorption occurs for BP due to increased aging, this should cause a concomitant decrease in the initial rate of biodegradation of BP, due to a lower solution concentration. This would manifest itself as a reduction in the slope of the initial part of the mineralization curve (Figures 4.5 and 4.6). From inspection of these graphs, there does not appear to be such a reduction in slope, except possibly in the case of the 6 month aging of BP on Capac B. Given the fact that the desorption rates of BP do not change with aging, a reduction in the initial rate of biodegradation would only be expected due to a reduction in the initial solution concentration and this was not indicated from the sorption isotherms for Capac B. There was a decrease in initial solution concentration for BP on Capac A due to aging. It seems likely that the decrease in initial solution concentration due to aging was not large enough to become evident as a reduction in the initial slope of the mineralization curves. These sorption/desorption results are consistent with the observation that there is no reduction in the rate of biodegradation due to aging as reflected by the mineralization curves themselves and by the first order mineralization rate constants, which also do not change with aging (Table 4.3).

The mineralization curves of BP on Capac B are consistent with the desorption data. The mineralization curves appear to have no initial decrease in slope with increased aging, with the possible exception of the 6 month aged sample. This is consistent with the sorption data which shows that sorption of BP on Capac B increases only very slightly with aging. Also, the desorption rate of BP does not change with aging, so again

desorption would not be expected to influence differentially the initial slope of the mineralization curves. There is, however, a decrease in the irreversible (non-desorbable) fraction of BP with aging, along with an increased fraction of BP in the slow compartment based on the modeling data. This would cause a decrease in the extent of mineralization, consistent with our observations (Figure 4.6).

There is a decrease in the extent of mineralization of BP in Capac A after 2 and 6 months of aging; the magnitude of this decrease was considerably smaller than in the Capac B soil. The results are difficult to resolve in terms of the sorption/desorption data which show an increase in sorption but no increase in the irreversible (non-desorbable) fraction with aging. The increase in sorption due to aging is greater on Capac A, so it would be expected that there would be a larger decrease in the extent mineralized on Capac A. However, it should be noted that the sorption/desorption behavior of BP on the Capac A soil is unique. All other combinations of compounds and soils (*Sharer, 1999a; Sharer, 1999b*) show an increase in the non-desorbable fraction with aging.

A comparison of the first order desorption rate constants and biodegradation rate constants show the latter to be two orders of magnitude greater. This suggests that the systems described here are desorption limited (desorption slow relative to biodegradation, Table 4.3) and that the irreversible fraction is not accessed by microbes. However, distinguishing whether the irreversible (non-desorbable) fraction is truly irreversible or just extremely rate-limited is difficult due to the time scale of the mineralization assay. It may be that for the time scale of the mineralization assay this portion of BP did not desorb, but desorption may occur on a longer time scale typical in field situations. However, studies of field weathered soils have indicated the existence of a truly

biologically unavailable fraction which may correspond to the non-desorbable fractions observed here. For example, EDB, a compound readily degraded by soil microorganisms in non-aged laboratory assays, is known to persist in field soils for nearly 20 years after its last application (*Steinberg, et al.,1987*). Thus, our data and the observations from field weathered soils indicate that the non-desorbable fraction observed here may not be accessible to microbes on any pertinent time scale. The 24 hour aging desorption data supports this assertion. After aging for 24 hours and then desorbing for four months, there is still an appreciable fraction that is non-desorbable for both BP and EDB (*Sharer, 1999b*).

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