Persistence of 1,2-Dibromoethane in Soils: Entrapment in Inraparticle Micropores

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Persistence of 1,2-Dibromoethane in Soils: Entrapment in Intraparticle Micropores

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■ The soil fumigant 1,2-dibromoethane (EDB) was found in agricultural topsoils up to 19 years after its last known application. This residual EDB was highly resistant to both mobilization (desorption into air and water) and microbial degradation in contrast to freshly added EDB. Release of the residual EDB into aqueous solution was extremely slow at 25 °C but highly temperature dependent. Treatment of release as a radial diffusion process yielded effective intraparticle diffusivities of (2–8) × 10^{-17} cm^2/s and half-equilibration times in a 1:2 soil–water suspension of 2–3 decades at 25 °C. Aerobic degradation of residual EDB by indigenous microbes was negligible after 38 days compared to rapid removal and mineralization of added [^{14}C]EDB. The release of residual EDB was greatly enhanced by pulverization of the soil. The results show that the residual EDB is trapped in soil micropores other than the interlayers of expandable clays where release is influenced by extreme tortuosity or steric restriction.

Introduction

More than 20 million pounds of 1,2-dibromoethane (EDB) was used for soil fumigation in the U.S. before it was banned in 1983 by the U.S. Environmental Protection Agency because of its potential carcinogenicity and because it was detected in groundwater supplies. EDB is volatile (vapor pressure 13.8 mmHg and estimated Henry's law constant 8.2 × 10^{-4} atm m^3/mol at 25 °C) (*1*, *2*) and moderately water soluble (4250 mg/L at 25 °C) (*3*). It also has a low affinity for soils as evidenced by low soil–water partition coefficients K_p or carbon-referenced soil–water partition coefficients K_{oc} derived from sorption isotherms (*4*, this study). In addition, when added at nanogram per gram concentrations to surface soil suspensions, EDB is degraded rapidly (within days) by soil microbes under both aerobic (*5*) and anaerobic (*6*, *7*) conditions. These observations suggest that EDB should disappear rapidly from surface soils following application. We have, however, found up to 200 ng/g EDB in the topsoil of tobacco fields in Connecticut, as long as 19 years after its last known application (see below). Our objective was to understand this unexpected persistence, because residual EDB could be a continued source of groundwater contamination. Our results indicate that it persists because of tenacious sorption to the soil.

Neutral organic compounds are sorbed by soils and sediments by partitioning into soil organic phases and adsorption on mineral surfaces. Most experiments in the laboratory have been conducted for short times, where sorption/desorption is usually described as rapid (requiring

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periods of hours to achieve equilibrium) and reversible. Many compounds in soil/sediment systems, however, exhibit hysteretic sorption/desorption isotherms, which have prompted examinations of the kinetics and reversibility of these processes. In a study of polychlorobiphenyl (PCB) congeners, Di Toro and Horzempa (*8*) ascribed the hysteresis to "reversible" and "resistant" fractions of added chemical. Karickhoff (*9*) modeled sorption of hydrophobic aromatic hydrocarbons as a two-stage kinetic process, whereby the chemical is fractioned into a "labile" state (equilibrium occurring within about 1 h) and a "nonlabile" state. Curl and Keolelan (*10*) suggested that competitive sorption by natural adsorbates could describe hysteresis.

Gschwend and Wu (*11*) claimed that nonreversibility was an artifact and that sorption of PCB congeners was completely reversible in a 48-h equilibration period when precautions were taken to eliminate or account for nonsettling microparticles in the aqueous phase. Later these authors (*12*) described a radial diffusion model for sorption kinetics whereby compounds diffuse in or out of the interstices of natural particles, which were assumed to be aggregates of smaller particles, and diffusion is retarded by microscale partitioning of the compound between intraaggregate pore fluids and the surrounding pore solid surfaces or organic phases. According to this model, highly hydrophobic compounds with octanol–water coefficients $K_{ow} = 10^5$–10^8 could require up to several months to diffuse from silt size particles containing a few percent organic carbon. EDB, having a K_{ow} of 86 (this study), should be released from soil quickly (within hours) according to this model.

Adequate description of these sorptive processes is crucial for predicting the fate and transport of organic contaminants in the environment; clearly, at this point they are only poorly understood (*13*). This report describes the desorption and bioavailability of residual EDB from fumigated soils (hereafter referred to as "native" EDB) compared with added ^{14}C-labeled EDB. The results suggest that native EDB is entrapped in intraparticle micropores associated with extreme steric restriction or tortuosity and, therefore, cannot rapidly dissipate or be degraded.

Experimental Section

Soils. Cheshire fine sandy loam was obtained from the Lockwood Farm of the Connecticut Agricultural Experiment Station in Hamden, CT, from a plot that was fumigated once at about 70 kg/ha in July 1985 by injection of EDB (Aldrich, 99%) at a depth of 15 cm and 25 cm apart in a grid. Samples of two other soils were collected from former tobacco farms in Warehouse Point, CT, and Broad Brook, CT. EDB is presumed to have been applied to these fields according to standard agricultural practices at the rate of 70 kg/ha, but the frequency and total quantities are unknown. EDB use at the Warehouse Point site was halted in 1983 as a result of the nationwide ban, whereas the last known application to the Broad Brook soil occurred in 1973 due to the conversion of the farm from tobacco to nursery crops. Samples collected for this study were from 0 to 20 cm below the surface. Soil classification and mechanical analysis of all three soils have been given elsewhere (*14*).

A portion of each soil was passed, as collected, through a 2-mm sieve and refrigerated to be used for biodegradation experiments. The remainder was air-dried and sieved through a 2-mm sieve. To obtain wet-sieved size fractions, the air-dried soils were suspended in water, allowed to stand for 3 days, and then sieved wet or centrifuged by standard techniques to give particle size fractions of 0–2, 2–53, 53–106, and 106–250 μm. These fractions were refrigerated wet and used within 2 weeks. Total organic carbon (TOC) was determined by CO_2 evolution from combusted soil that had been pulverized and treated with HCl.

Determination of EDB in Soil. This method has been described previously (*14*). Briefly, the soil was extracted with methanol in a glass screw-cap vial with a Teflon-lined silicone rubber septum (Pierce Chemical Co.) at 75 °C. EDB was then transferred to hexane after dilution of the extract with water, and the hexane layer was analyzed by gas chromatography (GC). EDB in some extracts was verified by gas chromatography–mass spectrometry (*14*).

Volatilization. Soil (0.76 g) was placed loosely into a Pasteur pipet in line with a column of Tenax GC adsorbent (20/35 mesh, 0.2 g). A stream of dry N_2 gas at 15 mL/min was passed through for 3.5 days and the EDB collected on the Tenax. The Tenax was then eluted with hexane (2 × 5 mL) and EDB determined by GC. The soil was then extracted with methanol and analyzed for the remaining EDB. Control experiments showed that Tenax traps EDB quantitatively from the vapor phase.

K_p Determination. All experiments were carried out in duplicate. Air-dried soil (5 g) and 10 mL of water containing 0.01 M $CaCl_2$ (to aid in obtaining a clear supernatant) and 200 mg/L NaN_3 (to eliminate microbial degradation) were placed in screw-cap septum vials along with a small volume of aqueous [1,2-^{14}C]EDB (New England Nuclear, Boston, MA; 98% purity, 23 mCi/mmol) corresponding to 10, 20, 50, or 100 ng/g of soil. The vials were shaken gently at 25 ± 0.2 °C for 24 or 72 h. The vials were then centrifuged, and 1.00 mL of the supernatant was counted in 15 mL of Opti-Fluor liquid scintillation fluid (Packard Instrument Co., Downers Grove, IL). Counts were quench-corrected by the external standard ratio method with quench curves. The concentration of sorbed EDB was calculated from the difference between added and supernatant counts. K_p was determined from the slope of linear plots of sorbed vs aqueous EDB concentrations, which were highly correlated in each case ($r^2 > 0.95$).

The apparent K_p for native EDB was determined under the same conditions except that the [^{14}C]EDB amendment was eliminated. After centrifugation, 5 mL of the aqueous layer was extracted into 1 mL of hexane and analyzed for EDB by GC. K_p was taken as the ratio of sorbed EDB (determined by methanol extraction as above) to aqueous EDB concentrations.

Octanol–Water Partition Coefficient. Stock [^{14}C]-EDB was partitioned between equal volumes of hexane and water to remove any water-soluble impurities, and 20 μL of the hexane layer containing 1 × 10^5 disintegrations per minute (dpm) (157 ng) was added to 1 mL of 1-octanol and 12 mL of distilled water in 14-mL screw-cap vials, in triplicate. After being shaken vigorously for 30 s, the vials were centrifuged (2000 rpm, 10 min) in an inverted position, and 1.00 mL of the aqueous layer was sampled by syringe through the septum of the inverted vial. The vial was then opened, and 0.50 mL of the octanol layer was sampled. The samples were counted in 15 mL of Opti-Fluor.

Release into Aqueous Solution: Purge Technique. In some experiments, the rate of release of EDB from the soil was determined by a purge technique similar to published methods (*9*, *15*). Purging was performed in 250-mL glass gas washing bottles without the fritted glass normally used for gas dispersion. Gas was introduced into the bottles via an 8 mm diameter inlet tube. The exit gases were conveyed via Teflon tubing (1.5-mm o.d., 0.5-mm i.d.)

Table I. Apparent EDB Partition Coefficients and Other Data for Soils

soil	time between sampling and last fumigation, years	total organic carbon, %	native EDB, ng/g	apparent 24-h K_p, mL/g[a] based on sorption of added [^{14}C]EDB	apparent 24-h K_p, mL/g[a] based on desorption of native EDB
Lockwood	0.9	1.11	130	1.49 ± 0.04[b]	230[c]
Warehouse Point	3	1.61	125	2.08 ± 0.2	300
Broad Brook	13	1.65	27	1.70 ± 0.2	170

[a] Suspensions of 5 g of soil in 10 mL of water, 25 °C. [b] The 95% confidence limits of slope of sorbed vs aqueous ^{14}C concentrations. [c] Estimated uncertainty, ±12%.

to two traps placed in series containing 10 mL of hexane in glass 14-mL screw-cap septum vials. Gas flow rates were adjusted by use of a Linde flow meter with a fine metering valve.

To the bottles was added either 100 mL of distilled water or 10 g of soil and 100 mL of 200 mg/L NaN_3 in distilled water. An aliquot of [^{14}C]EDB was added through a Teflon tube, and the contents were stirred at room temperature, with a Teflon-coated magnetic stirring bar, for 5 min (distilled water) or 3 h (soil suspensions) before purging was initiated. Purging was performed for 10-min periods, after which time gas flow was stopped, and the hexane traps were changed. An aliquot of the hexane was added to 10 mL of scintillation fluid, and the amount of radioactive EDB removed was determined.

Release into Aqueous Solution: Batch Methods. Release of EDB at different temperatures was investigated as follows. Soil suspensions (1 g of soil and 5 mL of 0.01 M $CaCl_2$) contained in Teflon-lined screw-cap test tubes were placed in an aluminum heating block or incubator. The suspensions were not shaken during incubation to avoid mechanical disintegration of particles (*12*). Checks at 25 and 75 °C showed that gentle agitation periodically by hand or continuously by orbital shaking (60 rpm) had no effect on release over the time periods used. At intervals, replicate vials were centrifuged, and the supernatant was transferred to a vial containing 2 mL of hexane. The soil was washed with an additional 5 mL of 0.01 M $CaCl_2$ in the same vial. After centrifugation, the aqueous phase was combined with the original supernatant, extracted with hexane, and analyzed by GC. The soil was then extracted with methanol as above to determine the EDB remaining in the soil. The results of duplicate samples at each time point agreed within ±10%.

Desorption rate for the diffusion modeling study was determined with the 2–53-μm size fraction. Wet soil (equivalent to 4 g dry) was suspended in aqueous medium (8 mL) containing 0.01 M $CaCl_2$ and 200 mg/L sodium azide in 14-mL screw-cap vials. After centrifugation, the supernatant was discarded and replaced with fresh medium. The vials were then mixed on a hematology mixer (Fisher) in an incubator at 25 °C. This provided gentle agitation to keep the soils in suspension. At each time point, two of the replicate vials were centrifuged, and 5 mL of the clear supernatant was extracted with 1 mL of hexane and analyzed by GC.

To determine EDB release from pulverized soil, air-dried soil (1 g) was placed in the capsule of a mechanical ball mill (Wig-L-Bug, Crescent Dental Manufacturing Co., Chicago, IL) for varying periods. The capsule was opened, quickly dropped into a 40-mL vial containing 25 mL of water, and shaken for 15 min. The vial was then centrifuged, and an aliquot of the clear supernatant was extracted with hexane for EDB determination by GC.

Note on volatilization losses of EDB during sampling: The Henry's law constant for EDB predicts that 3.2% of total EDB will be in the headspace at equilibrium in a 1:1 air/water mixture at 25 °C. Experimentally, using [^{14}C]EDB in distilled water, we found 2 ± 0.5% in the headspace at 20 °C. In the desorption studies described above, vials contained much less than 50% by volume of headspace and were always cooled to room temperature before sampling. Samples were obtained with a glass pipet, taking care not to agitate the solution or allow bubbles of air to run up the pipet. Under these conditions, volatilization losses during sampling were unimportant.

Biodegradation Studies. For biodegradation experiments, soil (1.70 ± 0.01 g on a dry weight basis), autoclaved distilled water (2.0 mL), and [^{14}C]EDB in 160 μL of autoclaved distilled water were placed in sterile screw-cap septum vials. Samples used as controls contained an additional 500 mg/L NaN_3 as biocide. The vials were shaken gently at 23–28 °C horizontally in an orbital shaker at 60 revolutions per minute (rpm). Two replicates were sacrificed at each time point and extracted with methanol by the method described above to obtain total EDB. Total EDB was then determined by GC analysis of the hexane layer. [^{14}C]EDB was determined by scintillation counting of 1.00 mL of the hexane layer in 15 mL of Opti-Fluor. The difference between the total EDB and [^{14}C]EDB was taken as undegraded native EDB.

The remaining methanol-extracted soil from each time point was further treated to determine the amount of fixed ^{14}C and, thus, the amount of [^{14}C]EDB converted into cellular materials. The soil was allowed to stand overnight in 0.5 M HCl and dried at 120 °C for 1 h, and a weighed portion was combusted in a biological oxidizer as described previously (*5*).

Two additional replicates were sacrificed at each time point for determination and confirmation of evolved $^{14}CO_2$ by a purge method (*5*).

Results

The time from last known fumigation to sampling ranged from 0.9 to 13 years for the three agricultural sites (Table I). EDB concentration varied with subsurface depth and location at each site; for experiments reported here, one sample from the top 20 cm was chosen from each site, and the EDB concentrations are given in Table I. Topsoil samples from a fourth agricultural site in Simsbury, CT, which was last fumigated with EDB 19 years prior to sampling, gave EDB concentrations in the range 1–32 ng/g (unpublished data). These results indicate a high degree of resistance of EDB to mobilization and degradation in the field.

The native EDB is essentially nonvolatile. Air-drying soil samples in a Buchner funnel under aspirator suction for 24 h did not decrease EDB concentrations. Passing a stream of dry N_2 at the rate of about 30 volumes of gas per volume of soil per minute for 3.5 days through a sample of Lockwood soil removed only about 8% EDB. This contrasts sharply with observations by Wade (*16*) that the bulk of EDB volatilizes within a few hours at 20 °C from soils that had been exposed to EDB for 2 h before purging.

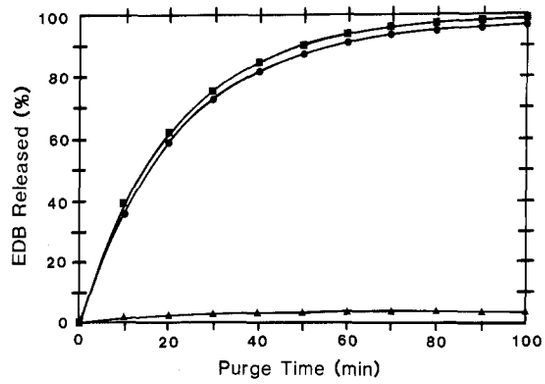


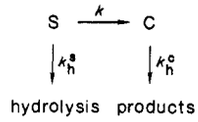
Figure 1. Removal of EDB from soil suspension by N_2 purging. (Bottom curve) Removal of native EDB from Lockwood soil. (Middle curve) Removal of a [^{14}C]EDB spike (10 ng/g) from the same soil after a 3-h equilibration period. (Top curve) Removal of [^{14}C]EDB (10 ng/mL) from distilled water.

Also, we found previously (*14*) that vigorous conditions—methanol at 75 °C for 24 h—were required to extract EDB quantitatively from the environmental samples. By contrast, much milder conditions gave quantitative recovery from spiked samples, even when they were allowed to stand for several days before extraction.

Partition coefficients based on sorption isotherms of [^{14}C]EDB and on desorption of native EDB for the three soils are given in Table I. Sorption of [^{14}C]EDB appeared close to "equilibrium" after 24 h, since the resulting K_p's increased by an average of only 14% after a 72-h period. The corresponding K_{oc} values (in the range 103–134) are in agreement with the values found by others (*4*). The octanol–water partition coefficient K_{ow} of EDB was found to be 86 ± 6 (mean ± standard deviation of triplicates). The K_{oc} is somewhat higher (by a factor of 1.4–3.6) than predicted by several empirical linear free energy relationships between K_{oc} and K_{ow} that have been developed by others (*13*). These relationships assume that the dominant sorbate–sorbent interaction is hydrophobic partitioning of sorbate into the soil organic matter. However, as pointed out before (*13*), other, nonhydrophobic contributions to the sorption process could increase the K_{oc} values. The important point to be made about these data is that the K_p's based on desorption of the native EDB for the same equilibration period were about 2 orders of magnitude greater than the K_p's from sorption isotherms (Table I). Clearly, the native EDB is far from equilibrium with the bulk aqueous phase.

Release of native EDB into aqueous solution from the Lockwood soil suspensions by purging with N_2 gas (Figure 1) showed that, whereas the freshly added EDB (3-h equilibration time) was rapidly removed from the soil, native EDB was removed much more slowly. Purging for a period of 100 min removed the freshly added EDB completely while less than 5% of the native EDB was removed.

Release of native EDB from the Lockwood soil was highly temperature dependent (Figure 2). Apparent activation parameters were obtained by treating EDB release as a first-order process. Aqueous hydrolysis of EDB is a competing reaction, especially at higher temperatures (*17–19*). The effect of hydrolysis would be to reduce both aqueous- and solid-phase EDB concentrations. The pertinent reactions are



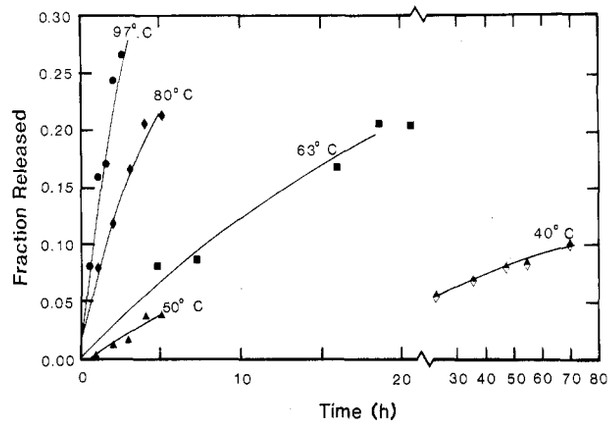


Figure 2. Effect of temperature on native EDB release from Lockwood soil. Fraction released = [C]/([S] + [C]) (see text).

where S = EDB associated with solid, C = EDB in aqueous solution, k is the desorption rate constant, and k_h^s and k_h^c are the first-order hydrolysis rate constants for the sorbed and aqueous states, respectively.

As the following discussion will show, hydrolysis can be ignored if it is assumed that hydrolysis rate constants are equal for the solid-phase and aqueous-phase states of EDB. Macalady and Wolfe (*20, 21*) showed that alkaline hydrolysis is greatly slowed for sediment-associated molecules compared to molecules in solution but that neutral (pH-independent) hydrolysis was unaffected by sorption over a broad spectrum of compound type and solvolytic mechanism. EDB hydrolysis is pH-independent in the range 4–9 (*17, 18*).

Under the assumption that $k_h^s = k_h^c = k_h$, the following rate expressions for the above reactions hold:

$$d[C]/dt = k[S] - k_h[C] \quad (1)$$

$$-d[S]/dt = k[S] + k_h[S] \quad (2)$$

Integration of eq 2 yields

$$[S] = [S]_0 e^{-(k+k_h)t} \quad (3)$$

where $[S]_0$ is initial EDB concentration in the solid. Substitution of eq 3 into eq 1 and solving the resulting differential equation gives eq 4. Substitution of eq 3 into eq 4 and rearranging terms gives eq 5.

$$[C] = [S]_0(e^{-kt} - e^{-(k+k_h)t}) \quad (4)$$

$$\ln [\text{fraction remaining}] = \ln \left[1 - \frac{[C]}{[S] + [C]} \right] = -kt \quad (5)$$

Equation 5 now allows calculation of the first-order desorption rate constants without the need for hydrolysis rate constants. The data from Figure 2 at each temperature fit eq 5 well ($r^2 > 0.91$ in all cases). The Eyring plot shown in Figure 3 yields the apparent activation enthalpy $\Delta H^{\ddagger}$ = 66 ± 11 kJ/mol (15.7 ± 2.5 kcal/mol).

The release of EDB from soil particles into aqueous solution may alternatively be treated as diffusion from a porous adsorbent. An analytical solution is available (*22*) for radial diffusion from uniform spheres of equal radius into a well-stirred solution of limited volume; the exact equation (eq 6.33 of ref 22), which is not reproduced here, is of the form

$$C_t/C_e = f(D_{eff}t/r^2)^{1/2} \quad (6)$$

where C_t/C_e is the fractional equilibrium (i.e., the ratio of

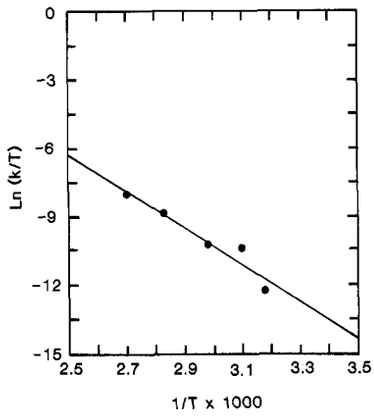


Figure 3. Eyring plot for native EDB desorption from Lockwood whole soil using first-order rate constants from the data in Figure 2.

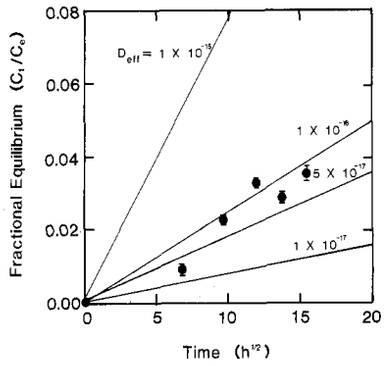


Figure 4. Release of native EDB at 25 °C from Lockwood 2–53-μm particles and theoretical curves based on a diffusion equation for various diffusivities D_{eff} (cm^2/s) for the mean particle radius. Error bars represent the range of duplicates.

Table II. Best Fit Values of Effective Diffusivity D_{eff} and Time Required To Reach 50% of Equilibrium According to a Radial Diffusion Equation

soil	mean particle radius, μm	D_{eff} for best fit to data, cm^2/s[a]	time for 50% of equilibrium, years
Lockwood	13.8	8×10^{-17}	23
Warehouse Point	13.8	2×10^{-17}	31

[a] By visual inspection of plots.

the mass amount of EDB in bulk solution at time t to its amount at equilibrium, $t = \infty$), D_{eff} is the effective diffusion coefficient of EDB within particles, and r is the particle radius. In adopting this approach, it is assumed that initially EDB is evenly distributed within the particles and that diffusion into bulk solution occurs until equilibrium governed by the K_p calculated from sorption isotherms (Table I) is established. Within a particle size range, the mean particle radius may be used to approximate the ideal case of uniform particle size (*23*). Wet-sieving techniques were used to insure that water-stable particles were being represented in the experiments.

Figure 4 shows the fractional equilibrium vs $t^{1/2}$ for the 2–53-μm size fraction obtained from wet-sieved Lockwood soil and the theoretical curves for several D_{eff} corresponding to the mean particle radius of 13.8 μm. The 2–53-μm fraction of the Warehouse Point soil gave similar results. The values of D_{eff} that best fit the data together with estimates of the times needed to reach 50% equilibrium are listed in Table II for the Lockwood and Warehouse Point soils. These numbers indicate an extremely slow approach to equilibrium.

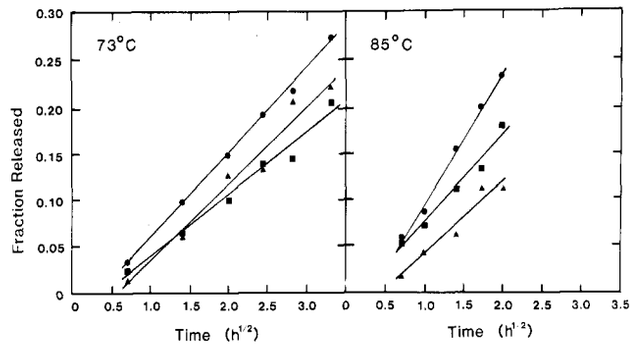


Figure 5. Release of native EDB at two temperatures as a function of particle size for the Lockwood soil: (circles) 2–53 μm, (squares) 53–106 μm, and (triangles) 106–250 μm. Each point is the mean of duplicate samples that agreed to within ±8%. Lines represent the least-square fit of means.

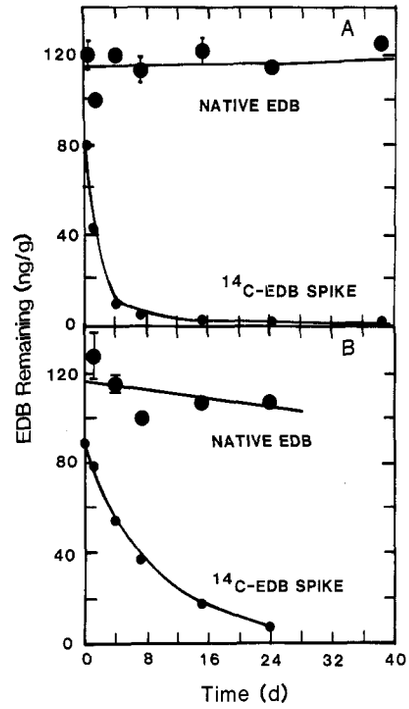


Figure 6. EDB degradation in soil suspensions by indigenous microbes showing the persistence of native EDB compared to a freshly added [^{14}C]EDB spike: (A) Lockwood soil and (B) Warehouse Point soil. The range of duplicates, when larger than the size of the symbol, is indicated by error bars.

Equation 6 predicts an inverse relationship between fractional equilibrium and particle radius. To test this, EDB release from different size fractions obtained from wet-sieved soil was measured at 73 and 85 °C (Figure 5). Since K_p (and thus C_e) at these high temperatures is unknown, we used C_t/S_0, where S_0 is the initial amount in the solid, in place of C_t/C_e. This is valid for comparison purposes because C_e is proportional to S_0. Also, hydrolysis was ignored because it would have the same effect on all fractions.

The fraction released (C_t/S_0) was found to be highly linearly correlated with $t^{1/2}$ in all cases ($r^2 > 0.96$). The slopes corresponding to the two larger fractions (53–106 and 106–250 μm) are not significantly different at the 95% confidence level at either temperature. The slope corresponding to the smallest fraction (2–53 μm) is significantly different from both larger fractions at 85 °C, but only from the 53–106-μm fraction at 73 °C. Furthermore, the smallest (2–53-μm) fraction releases EDB at most 2-fold faster than the other fractions when, according to eq 6, the

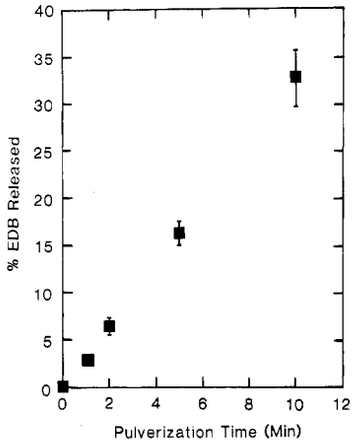


Figure 7. Percent of EDB released from the Warehouse Point soil into water as a function of pulverization time in a ball mill. The range of duplicate determinations, when larger than the size of the symbol, is indicated by error bars.

relative rates should be 6.5:2.2:1 for the 2–53-, 53–106-, and 106–250-μm fractions, respectively. Therefore, the results show only weak dependence on particle size.

Not only is the native EDB released slowly, but it is also not readily available for degradation by soil microbes. Figure 6 shows the time course of aerobic degradation of a freshly added spike of [^{14}C]EDB compared to that of native EDB in two soils. The Lockwood soil transformed more than 90% of a [^{14}C]EDB spike within 4 days, converting 46 ± 7% of the carbon to $^{14}CO_2$ and leaving 54 ± 3% as ^{14}C associated with solids. This solid-bound label was unextractable by hot methanol and presumed to be cell constituents (*5*). The Warehouse Point soil transformed the spike more slowly, requiring about 22 days to degrade more than 90% of the added EDB. Similar amounts of $^{14}CO_2$ (45 ± 5%) and cell constituents (52 ± 6%) were produced. Azide-poisoned controls showed no loss of [^{14}C]EDB (data not shown), no production of $^{14}CO_2$, and <6% unextractable ^{14}C, confirming the above biodegradation of the added EDB. The extent of mineralization of EDB observed here is similar to other surface soils (*5*). The difference in rates between the two soils may simply reflect a larger population of active degraders in the Lockwood soil, or other uncontrolled factors specific to the soils. In contrast to the spike, essentially no degradation of the native EDB occurred in either soil. These results also indicate slow exchange between native EDB and added [^{14}C]EDB.

Mechanical breakup of the soil particles in a ball mill resulted in accelerated release of EDB. Figure 7 shows that the amount of EDB released from the Warehouse Point soil during a 15-min extraction with water increased with time of pulverization from less than 0.1% before pulverization to greater than 30% after pulverization for 10 min. Similar results were obtained for the Lockwood soil. This also held for smaller size fractions; for example, pulverization of the silt plus clay fractions (0–50 μm) for 10 min resulted in a 20-fold increase in released EDB over the unpulverized material (data not shown). The rise in temperature of the soil on pulverization (maximum of 8.5 °C, most of it occurring within the first 2 min) was far from sufficient to account for the enhanced release. Pulverization also accelerated release into the vapor phase; the release of EDB was 40% from a sample pulverized for 5 min compared to 8% from an unpulverized sample in a stream of N_2 as described above.

The distribution of EDB among water-stable particle size fractions below 250 μm was determined for the Lockwood and Warehouse Point soils (Table III). The results show that EDB was at maximum concentration in the very fine sand fraction (53–106 μm), declining with larger or smaller size fractions, and at minimum concentration in the clay fraction (<2 μm).

Table III. EDB Concentration in Size Fractions Obtained from Wet-Sieved Soils

	EDB concn, ng/g[a]	
diameter range, μm	Lockwood soil	Warehouse Point soil
106–250	69 ± 18	104 ± 10
53–106	142 ± 5	164 ± 12
2–53	111 ± 1	66 ± 3
0–2	21 ± 1	34 ± 1

[a] Range of duplicate analyses.

Discussion

EDB in the fumigated soils is extremely resistant to volatilization, release into aqueous solution, and degradation by indigenous soil microbes, which were simultaneously able to rapidly degrade freshly added [^{14}C]EDB at comparable concentrations. Pulverization promoted release, both to the aqueous and the gaseous phases. The results suggest that EDB is entrapped in soil micropores. Obviously, EDB in inaccessible regions becomes available as these regions are exposed by pulverization. The inertness to microbial degradation (Figure 6) suggests that EDB is present at micropore sites that are sterically inaccessible to bacteria and that do not equilibrate readily with bulk air or liquid phases. Although the high activation enthalpy (66 ± 11 kJ/mol) may be consistent with desorption from a chemisorbed state, this is unlikely because EDB has no strongly interacting functional groups and, in any case, can be ruled out on the basis of the pulverization experiments.

The great difference in apparent 24-h K_p between added and native EDB is likely due to kinetics rather than thermodynamics. From either a sorptive or desorptive direction, K_p is by definition only valid when true equilibrium has been reached. Karickhoff (*9*) showed that sediments continue to sorb hydrophobic compounds from water indefinitely at a slow rate after the initial rapid uptake. Presumably, the native EDB is material from the original fumigations that sorbed at the slow rate, and which we now demonstrate is highly resistant to mobilization.

The nature of the soil micropores is at present obscure. Organic compounds, particularly organocations, are known to penetrate and bind at the expandable interlayer regions of 2:1 layer silicate clays of the smectite–vermiculite group (*24*). Sorption isotherms of EDB on Ca^{2+}-saturated montmorillonite clay as a function of relative humidity suggest that EDB enters interlayer regions at low, nonzero humidities (*25*). Water appeared to displace EDB from these regions. The dominant clay in the soils of this study is illite, which does not have expandable interlayers. Nevertheless, even a trace of expandable clay conceivably could be responsible for EDB occulsion in our samples. Table III, however, shows that the clay fraction (<2-μm effective particle diameter) contained the lowest amounts of EDB by far. These results demonstrate that clay interlayer regions do not play a major role in entrapment of EDB.

Entrapment of EDB in micropores suggests that release into bulk solution is diffusion-controlled. By use of a radial diffusion model, the calculated effective diffusivity D_{eff} of EDB within particles is (2–8) × 10^{-17} cm^2/s (Table II, Figure 4) on the basis of data for the 2–53-μm particle size

fraction and assuming initial uniform distribution within individual particles. By comparison, molecular diffusion coefficients of small organic nonelectrolytes in water are in the range 10^{-6}–10^{-5} cm^2/s.

To understand these low diffusivities, we consider the model of Wu and Gschwend (*12*) for diffusion of hydrophobic organic compounds from soil/sediment particles. This model assumes that individual stable particles are aggregates of fine mineral grains and natural organic matter. A compound diffuses in or out of pore spaces between the grains, and this diffusion is retarded by microscale partitioning of the compound between pore fluids and pore solid surfaces or organic phases. The derived equation relates D_{eff} to K_p:

$$D_{eff} = \frac{D_m n f(n,\tau)}{(1-n)\rho_s K_p + n} \quad (7)$$

where D_m is the pore fluid diffusivity (cm^2/s), n is the porosity of the sorbent particles, ρ_s is the specific gravity of the sorbent, K_p is the equilibrium partion coefficient, and $f(n,\tau)$ is an undefined function of n and the tortuosity of diffusion paths τ.

A correlation of D_{eff} with K_p using data from several systems (sorption/desorption of various chlorobenzenes in sediments and soil, sorption of kepone on sediments; Figure 11 of ref 12) predicts a D_{eff} for a compound with $K_p = 1$ (approximately equal to the K_p for EDB determined from sorption isotherms, Table I) of about 10^{-7} cm^2/s. This is at least 9 orders of magnitude greater than the experimentally determined values (Table II), which are based on the release of EDB from the 2–53-μm size fraction. Conversely, the model would require K_p for EDB of about 10^9 mL/g. The finding here that release is relatively insensitive to particle radius (Figure 5) may indicate that release is mostly controlled by diffusion from micropores of substructures within the particles that are common to all size fractions. Therefore, the determined values of D_{eff} may be upper limits, making the discrepancy with the predicted values even more pronounced.

To further illustrate the contrasts, consider the desorption time of <2 days for 1,2,3,4-tetrachlorobenzene from sediments (*12*) to that of decades for EDB, despite the fact that tetrachlorobenzene is much more hydrophobic than EDB. (The K_{ow} for tetrachlorobenzene is about 10^3 times greater than that of EDB.) Furthermore, EDB release is strongly temperature dependent compared to slight, if any, temperature dependence of 1,2,3,4-tetrachlorobenzene sorption rates to sediment (*12*). The extremely small diffusivities and the large temperature dependence, reflected in the high apparent ΔH^*, indicate extremely tortuous or sterically hindered diffusion paths through microporous structures. It is known that diffusion of solutes within porous adsorbents can be accompanied by appreciable apparent activation energies (*26*).

An important implication of the diffusion model is that the time needed to reach sorptive equilibrium for a given compound and soil will depend on the steric and tortuosity factors associated with the micropores. This was pointed out by Wu and Gschwend (*12*). Presumably, soils possess a gradation of pore sizes and associated tortuosities. Increasingly "remote" sites will become populated with time. Higher initial concentrations of chemical in bulk solution will result in more chemical diffusing to a particular pore in a given period of time. Consequently, subsequent desorption will reflect the sorptive history of the system. Also, the observed D_{eff} will become smaller with increasing extent of desorption, as the more available sites empty and as the release of compound from the more remote sites becomes observable. The more remote sites also can be expected to give rise to a greater temperature dependence of release. It follows from this that the rapid rates and weak temperature dependence observed by Wu and Gschwend (*12*) may be representative of relatively labile sites, since these investigators used short sorption periods and monitored the bulk of added chemical.

The residue of EDB in the fumigated soils that we find may be a small fraction of the added chemical that diffuses to remote micropore sites as a consequence of long exposure times, high initial field-applied concentrations, or effective penetration in the vapor state. The bulk of the initially sorbed material most likely conformed to prediction and, consequently, evaporated, degraded, or leached to groundwater relatively quickly. The remainder assumes importance because it can slowly leach out over years to supply groundwater with concentrations that may be considered significant to human health (0.1 ppb or less).

These findings show that direct application of a volatile, soluble, and weakly interacting molecule like EDB can result in its tenacious binding to soil particles. Other compounds that come into direct contact with soils need to be investigated to see if they behave similarly. Clearly, mathematical models describing the fate and transport of organic compounds in the environment would fail to predict the behavior of EDB described here. Standard biodegradation tests are also inadequate. Persistence in the field despite ready microbial transformation in the laboratory has been noted for a number of pesticides (*27*). Finally, these results may have bearing on the availability of toxic chemicals in soil during human ingestion or skin contact, and in regard to soil remediation efforts.

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Abiotic and Biotic Transformations of 1,1,1-Trichloroethane under Methanogenic Conditions

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■ A common industrial solvent, 1,1,1-trichloroethane (TCA), is one of the most frequently found contaminants in groundwater. The fate of TCA in groundwater is complicated by the different possible abiotic and biotic transformations that it may undergo. Abiotic transformation of TCA can result in a mixture of 1,1-dichloroethylene (1,1-DCE) and acetic acid, as shown by others. This study confirms that TCA can be biotransformed by reductive dehalogenation to 1,1-dichloroethane (1,1-DCA) and chloroethane (CA) under methanogenic conditions. Also, reductive dehalogenation of 1,1-DCE to vinyl chloride (VC) is confirmed. This study demonstrates that these transformations can occur stoichiometrically. In addition, [^{14}C]TCA, [^{14}C]-1,1-DCA, [^{14}C]-1,1-DCE, [^{14}C]CA, and [^{14}C]VC were at least partially mineralized to $^{14}CO_2$ under similar methanogenic conditions.

Introduction

Contamination of groundwater by halogenated aliphatic compounds, including 1,1,1-trichloroethane (TCA) (*1*), has led to investigations to determine their fate in the environment. Previous studies have illustrated that a potential exists for biotransformation of halogenated aliphatic compounds under anaerobic conditions that are conducive to methanogenesis (*2–4*).

The fate of TCA in groundwater is partially governed by both abiotic and biotic transformations. The biotransformation of TCA by a mixed methanogenic culture supported through continuous feed of acetate as the primary source of organic carbon was demonstrated by Bouwer and McCarty (*2*). The reductive dehalogenation of TCA to 1,1-dichloroethane (1,1-DCA) (*5*, *6*) and then to chloroethane (CA) (*7*) under anaerobic conditions has also been described. In addition, traces of chloroethane (CA) were observed in anaerobic mucks following the disappearance of TCA (*5*).

TCA has also been reported to undergo abiotic transformation to 1,1-dichloroethylene (1,1-DCE) (*8–10*) and to acetic acid (*11–13*). Probably both 1,1-DCE and acetic acid are produced simultaneously: 1,1-DCE as a result of elimination and acetic acid as a result of hydrolysis (*10*). The pseudo-first-order rate constant for 1,1-DCE formation from TCA was reported as 0.04 yr^{-1} at 20 °C (*9*). While no rate constant for the formation of acetic acid from TCA has yet been documented, Haag et al. (*10*) have shown that acetic acid is produced 5 times as fast as 1,1-DCE at 40 °C. Therefore, the pseudo-first-order rate constant for the disappearance of TCA at 20 °C could be as high as 0.25 yr^{-1} (*9*). These values are consistent with a TCA hydrolysis (to acetic acid) rate of about 0.2 yr^{-1}.

Both acetic acid and 1,1-DCE can be further biotransformed under methanogenic conditions. Acetic acid can be mineralized to CO_2 and CH_4 (*14*). Traces of vinyl chloride (VC) were observed after addition of 1,1-DCE to microcosms (*3*).

On the basis of the above, a possible scheme for the fate of TCA and its abiotic and biotic transformation products, including that of 1,1-DCE, 1,1-DCA, and CA, is shown in Figure 1. Research to date has not clearly demonstrated whether the indicated bioconversion of TCA to 1,1-DCA and CA and of 1,1-DCE to VC occurs stoichiometrically nor whether any processes can lead to the mineralization of these compounds. Such information was sought in this study.

Materials and Methods

Chemicals and Radioisotopes. GC-grade TCA and 1,1-DCA (Supelco Inc., Bellefonte, PA) were used. CA was obtained diluted 0.1 mg/mL of methanol (MeOH) (Supelco Inc., Bellefonte, PA). Other organics used were MeOH, acetone (99.9%; J. T. Baker Chemical Co., Phillipsburg, NJ), and 2-propanol (99+%; Aldrich Chemical Co., Milwaukee, WI). [^{14}C]TCA, [^{14}C]-1,1-DCA, [^{14}C]-1,1-DCE, and [^{14}C]VC (New England Nuclear, Boston, MA) were diluted initially in methanol (absolute; J. T. Baker Chemical Co., Phillipsburg, NJ) to 5.1×10^6 dpm/μL (74.8 mg of TCA/mL of MeOH), 2.9×10^6 dpm/μL (57.6 mg of 1,1-DCA/mL of MeOH), 4.2×10^6 dpm/μL (680 mg of 1,1-DCE/mL of MeOH), and 1.1×10^6 dpm/μL (110 mg of VC/mL of MeOH), respectively. [^{14}C]CA (Amersham Corp., Grover Heights, IL) was diluted

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