A REVIEW OF THE POTENTIAL FOR PHYTOVOLATILIZATION OF THE VOLATILE CONTAMINANTS ETHYLENE DIBROMIDE, ETHYLENE DICHLORIDE, AND CARBON TETRACHLORIDE

[1]L.C. Davis and [2]L.E. Erickson

[1]*Department of Biochemistry, Chemistry and Biochemistry Hall, Kansas State University, Manhattan, KS 66506; Phone: (785)532-6121; Fax: (785)532-7278.*
[2]*Department of Chemical Engineering, Durland Hall, Kansas State University, Manhattan, KS 66506; Phone: (785)532-4313; Fax: (785)532-7372.*

ABSTRACT

Plants may serve as effective pump-and-treat systems for mobile contaminants including volatiles such as carbon tetrachloride (CCl_4) and ethylene dibromide (EDB). There is considerable interest in finding economical remediation processes for residuals of these compounds from grain fumigations. Experimental investigations with other volatiles have shown that trichloroethylene (TCE) and methyl *tert*-butyl ether (MTBE) move freely through plants and are released to the atmosphere at very low atmospheric concentrations, even while a significant fraction of the input contaminant is removed from the contaminated soil. Such compounds are photo-reactive and readily degrade in the atmosphere. Metabolic processes within the plants and associated microorganisms also convert a portion of the input compounds to less volatile materials. Removal of tightly sorbed EDB and CCl_4 from micropores within the soil may be the rate-limiting step for their remediation. Dewatering promoted by vegetation may enhance this process, increasing the potential for gas-phase diffusion within the soil. Plant root exudations also increase microbial populations, which may facilitate co-metabolism of EDB and CCl_4. Here we provide an extensive review of the published literature for ethylene dibromide, ethylene dichloride and carbon tetrachloride.

Key words: phytovolatilization, phytoremediation, ethylene dibromide, and carbon tetrachloride

INTRODUCTION

For some years, combinations of fumigants ethylene dibromide (EDB), ethylene dichloride, also called 1,2-dichloroethane (DCA), and carbon tetrachloride (CT), were used to control insect activity in grain bins (Berck, 1965). These compounds are toxic to other life forms, and EDB in particular was banned for further use in such applications nearly 20 years ago (USEPA, 1983; ATSDR, 1992). Steinberg et al. (1987) showed that significant levels of EDB could persist in soils for 20 years, potentially contributing to low-level contamination of groundwater. Pignatello and Cohen (1990) reviewed the environmental chemistry of EDB, while Alexeeff et al (1990) reviewed the toxicology and risks. Despite a 20-year ban on agricultural use, problems with EDB in water and soil still occur. Because EDB is a potent carcinogen in animals, even low levels in water and food present a potential risk to exposed populations (Alexeeff et al., 1990). Site remediation is necessary.

All three fumigants are dense liquids which settle through grain, soil, and water until they strike a solid surface. Thus some sites may contain dense, non aqueous-phase liquid pools of one or more of these fumigants. This may be uncommon except at sites used for distribution where spills could have occurred. However, traces of CT remain in many locations, including 25 wells in Kansas (Manning, 2002), while EDB and DCA have been found in recent water surveys (Idaho, 1999). Some state regulatory limits for EDB are 0.02 µg/L for drinking water, while some aquifers have plumes containing >100 µg/L (Hartzell et al. 2001; MESL, 2001). Because all three solvents had much wider applications than just fumigation, a contaminated plume may need to be characterized for other materials to determine its source. For instance, in the Idaho survey, EDB and DCA were associated with gasoline and diesel fuel spills. They were used as lead scavengers in leaded gasoline and jet fuel from the 1920s until the phase-out of lead (Alexeeff et al., 1990). In Massachusetts, recent EDB contamination of water, and potentially of cranberries grown with that water (Xia and Rice, 2001), has been attributed to fuel spills (MESL, 2001). Historically, CT was used as a cleaning solvent, so it may be found in association with trichloroethylene (TCE) and trichloroethane (TCA), instead of EDB and DCA. The nature and quantity of co-contaminants may affect the remediation strategy that is to be applied.

PHYSICAL PROPERTIES AND REACTIVITY

The fully chlorinated tetrachloromethane, CT, is amenable to reductive dehalogenation (biotic or abiotic) under strongly anoxic conditions, including sulfate-reducing conditions. The less extensively halogenated EDB and DCA can be dehalogenated oxidatively as well as reductively (Jafvert and Wolfe, 1987; Freitas dos Santos et al., 1996; Cox et al., 1998). Reactivities of all three compounds are summarized in Vogel et al. (1987). All are moderately sorbed to organic matter and are relatively volatile. They have slight to moderate solubility in water. Table 1 summarizes pertinent properties of the three compounds.

Carbon tetrachloride partitions mainly to the gas phase, while EDB and DCA partition relatively strongly to the aqueous phase. The combination of the characteristic boiling points and water solubilities results in rather different tendencies to partition to gas vs aqueous phase in dilute solution, as reflected in the Henry constant (H) value. Washington (1996) provided a thorough review of such properties and their implications for remediation of many halogenated ethanes and methanes. Unfortunately EDB was not one of them, though he listed several other compounds having very similar H constant values at 20ºC. Of the

compounds he listed, the tetrachloroethanes, are most like EDB in boiling point and H constant value. Carbon tetrachloride, with the H constant value of 1 at 20º, has a stronger tendency to partition to gas phase than TCA (H~0.70), TCE (H~0.4), or chloroform (H~0.15), which are more polar and less halogenated (Staudinger and Roberts, 1996). The other two fumigants, EDB and DCA, tend to remain with the water phase, about the same as the gasoline additive MTBE (H~0.03), which we have studied extensively (Davis et al., 2001; Zhang et al., 2001a,b). Both EDB and DCA are less halogenated than TCE, TCA, or chloroform. They are several-fold more water soluble than TCE or TCA, but less soluble than chloroform, which is a smaller molecule.

Partitioning between gas and liquid phases, as indicated by the H constant, is temperature-dependent, responding to both the change of water solubility with temperature and the boiling point of the compound (Washington, 1996). Temperature extremes in a continental climate result in dramatic annual differences in the partitioning behavior of the low-boiling compounds CT and DCA. The difference is even more

Table 1. Properties of halogenated grain fumigants.			
Common Name	Carbon Tectrachloride	Ethylene Dibromide	Ethylene Dichloride
Formal Name	Tetrachloro-methane	1,2-dibromo-ethane	1,2-dichloro-ethane
Formula	CCl_4	$C_2H_2Br_2$	$C_2H_2Cl_2$
Molar Mass	153.8	187.88	98.96
Boiling Point (ºC)	76.5	131	83.5
Vapor Pressure (mm Hg, 20º)	91	8.1	62
Henry's Constant (20º), dimensionless	1	0.02	0.04
Water Solubility (g/L)	0.8	4.2	8.7
Octanol: Water Partition (K_{ow})	500	44-100	22-30
Estimated log K_{ow}	2.7	1.6-2.0	1.3-1.5

*Calculated using data and equations in Yaws (1992), and critical review by Staudinger and Roberts (1996). Values for K_{ow} reported by Jury et al. (1990) and Walton et al. (1992).

striking for 1,1,1,2-tetrachloroethane, which may serve as a surrogate for EDB. Overall partitioning also changes when the relative water-filled porosity of the soil varies. At low temperatures ($<10^{\circ}$ C) and high saturation (>0.8), 95% of the compound 1,1,1,2-tetrachloroethane is found in the aqueous phase, while at higher temperatures ($>20^{\circ}$ C) and low saturation (<0.2), 30% of the compound is in the air phase. This six-fold difference in equilibrium partitioning may result in greatly altered transfer behavior in soil.

TRANSPORT CHARACTERISTICS

In previously published work, we have shown that the movement of contaminants upward through moist soil depends critically on their water solubility and H constant value (Narayanan et al., 1999a; Davis et al., 2001). Plants can facilitate the upward movement of solubilized contaminants by transpiration (Davis et al., 1998a,b), withdrawing water from the capillary fringe which may overlie a DNAPL. As water flows, the DNAPL, for instance TCE, dissolves within it and is drawn to the surface (Zhang et al., 1998). The evapotranspiration rate and rate of transport of contaminant are both greater when plants are present to transpire water and volatile contaminant to the atmosphere (Zhang et al., 1998; Zhang et al., 2001b). A fraction of the dissolved contaminant may pass into the plant and be released to the atmosphere by transpiration. Much more will volatilize from the water when it reaches the vadose zone, and relatively little will remain in the plant to reach the leaves (Hu et al., 1998, Davis et al., 1999). Instead, it may diffuse out through roots, stems, and petioles. This property for CT is more extreme than that of TCE or TCA; that is, it will less likely remain with the transpiration stream to reach the leaves.

For a more soluble, volatile contaminant such as methyl *t*-butyl ether (MTBE), the contaminant moves readily with water, and a larger fraction is transpired. The key to what fraction remains with the transpiration stream water up to the leaves is found in the dimensionless H constant value. Zhang et al. (2001a,b) demonstrated the movement of MTBE into and through alfalfa, and Davis et al. (2001) characterized its distribution within soil under various evapotranspiration conditions. The associated modeling studies with MTBE showed the predicted soil profiles, assuming the H constant value to be between 0.02 and 0.04, varying as a function of temperature. These values are in exactly the same range as the halogenated ethanes, EDB and DCA, considered here. Some results are shown for a sandy soil that is relatively low in organic matter and is supplied water from below. Figure 1 shows the large impact of H constant, with varying water velocity, on the observed profiles in the vadose zone of soil (Davis et al., 2001).
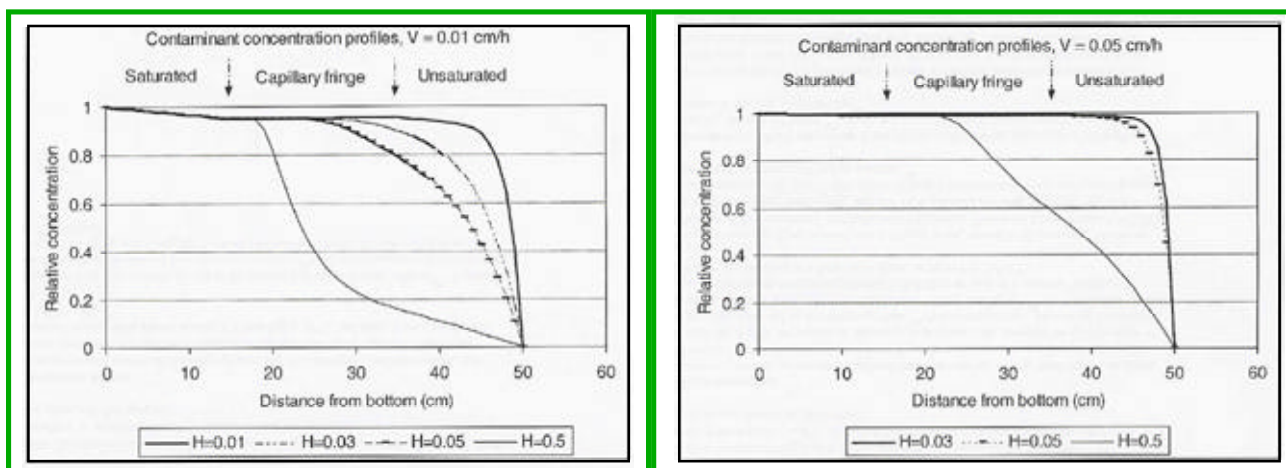
Figure 1. Steady state aqueous phase concentration profiles for a contaminant with variation in water velocity driven by evapotranspiration and different Henry's law constants. Details are provided in the work of Narayanan et al. (1999a). In the figure, distance is measured from the bottom of a chamber with the position of the water table and the capillary fringe indicated by arrows. The surface from which evaporation occurs is found at 50 cm. Vertical Darcy velocities are expressed in units of cm/h for evaporation rates of 0.24 and 1.2 cm/d, which are reasonable for unplanted and planted soils during summer in a moderate climate. Henry's law constants are chosen to approximate those of the volatiles of interest, as indicated in Table 1.

SORPTION BEHAVIOR

Hydrophobic compounds sorb to organic matter in soil and the plant. The most important measure of this tendency is the octanol/water partition coefficient. Values are approximately: 500 for CT, 22-30 for DCA, and 44-100 for EDB (Jury et al., 1990; Walton et al., 1992). The values for the doubly halogenated ethanes are similar to or somewhat lower than for the triply halogenated TCA (113), TCE (138), or chloroform (60-100). Thus, the sorption effects will be somewhat less obvious for EDB and DCA, while they will be stronger for CT, compared to TCE, which is well studied (Burken and Schnoor, 1998; Narayanan et al., 1999a). Washington (1996) showed that the relative equilibrium fraction of DCA in water, air, and solid phase of soil depended strongly on the organic matter content of the soil. For a soil with 1 % organic matter, most of the contaminant was in the water phase for saturations >0.3, while when the organic matter was 10 %, 50-90 % of the contaminant was associated with the organic matter, decreasing with increasing soil saturation. For EDB, the sorption effect would be several-fold stronger.

The ease with which compounds pass into and through plants depends on the same polarity property, reflected in the log K_{ow}, in a complex way. Measured results for mobility vs log K_{ow} are usually fitted with a Gaussian curve that has a peak in the range of log K_{ow} of 2-3. Very polar and very nonpolar compounds are poorly transferred into the transpiration stream. The three fumigants of interest have

octanol/water partition coefficients in the optimum range for uptake and transfer through plants such that the expected concentration in the transpiration stream water is about three-fourths of the concentration in the water surrounding the roots of the plant (Briggs et al., 1982; Burken and Schnoor, 1998).

LOSSES AND ABIOTIC REMOVAL OF THE HALOGENATED FUMIGANTS

Jury et al. (1990) compared the hypothetical effect of sandy and clayey soil to bury contaminants, considering the potential loss by volatilization while biodegradation occurred. For EDB placed 1 m below ground in sandy soil, the predicted loss in a year is 53 %, while in clayey soil the predicted loss is only 3.6 %. For DCA, predicted losses are about 30 % and 2 % in the two soil types. These are only relative values because they are sensitive to the chosen H constant value, the log K_{ow}, and the soil porosity. Losses of CT would be expected to be considerably greater under similar conditions because the H constant value for that compound is more than 25 times greater than for the dihaloethanes, and the octanol/water partition coefficient is only a few-fold greater. Hence, it will be sorbed to the soil a bit more but move much more freely into the gas phase.

The chief difference between sandy and clayey soils is in the air-filled porosity, which in turn has an approximately cubic relationship to the ease of diffusion of contaminants through the soil. Soil moisture alters the air-filled porosity. Immediately after a rain, the soil may be saturated so that there is essentially no gas-phase movement of contaminants. During dry spells, as much as one-third of the soil volume may be air spaces. As discussed by Washington (1996), the relative water saturation alters the fraction of contaminants partitioning to the available gas phase. Plants will facilitate dewatering of a soil and thereby increase the gas-phase movement of contaminants.

Fumigants may remain for long periods of time when covered by an impermeable barrier such as asphalt or compacted soil. Current practice for fumigation with methyl bromide (which is not yet banned) includes covering the soil with plastic sheeting and/or irrigation (Jury et al., 1996). Submersion beneath water allows volatiles to remain in place unless there is a population of dehalogenating bacteria, and a carbon, metallic, or other substrate to supply reducing power. Diffusion through the aqueous phase is about 10,000 times slower than through the gas phase, which is why the water-filled porosity of soil has such a dramatic effect on diffusive movement through soil.

Further complexity is added in the case of EDB by the observations of Steinberg et al (1987). They showed persistence of EDB in topsoils where the last known application had occurred up to 19 years prior

to the study. Extremely low rates of diffusion from the soil were observed. Pulverizing the soil markedly enhanced release, indicating that tortuous micropores within the usual soil particles were responsible for the slow desorption. Elevated temperatures increased the release rate also, and 24 h extraction with methanol at 75º C gave apparently quantitative release of the tightly sorbed material. The amounts of EDB present were significant, on the order of 100 ppb μg/kg soil), and sufficient to contaminate a large amount of water to the maximum contaminant limit (MCL) of 0.05 μg/L. Degradation of added spikes of EDB was rapid in aqueous suspensions, indicating that bioremediation could occur once the EDB was released from the micropores. Thus, the likelihood of significant groundwater contamination might be low despite the presence of residual EDB, but making reliable predictions is difficult. Pignatello et al., (1990) found EDB in an aquifer after two decades, despite previous studies showing the presence of aquifer organisms potentially able to degrade EDB (Pignatello, 1986b).

The extent to which this unusual persistence occurs for the other fumigants is unknown. Similar slow desorption behavior has been reported for other more hydrophobic compounds such as PCBs (DiToro and Horzempa, 1982) but also disputed as an artifact by others (Geschwend and Wu, 1985). Most laboratory experiments are not conducted over sufficient time to observe slow sorption or desorption profiles, and field studies usually have several uncontrolled variables.

POTENTIAL FOR BIODEGRADATION

Estimated half-lives of DCA, EDB, and CT in typical soils are relatively long, months to years. There generally are not many bacteria available to use the fumigants upon initial exposure (Witt et al., 1999). High concentrations kill bacteria, so biodegradation depends on several conditions, including the concentration of fumigants, availability of necessary energy sources, other nutrients, and presence of suitable bacteria. Supplementation of contaminated waters with carbon substrates such as vegetable oil has proven effective for stimulating reductive dehalogenation of TCE and TCA (Wiedemeier et a.,l 2001).

Witt et al. (1999) showed in model columns that supplementation with acetate could enhance the removal of CT by the indigenous bacterial population, but better results were obtained when specific inoculant was added. Gregory et al (2000) successfully used Fe(0) and methanogenic organisms to dehalogenate CT in laboratory experiments. Denitrifying strain *Pseudomonas stutzeri* KC was able to remove 50-80% of CT in field conditions (Dybas et al., 1998). McQuillan et al. (1998) described intrinsic remediation of CT driven by spilled gasoline, whereby the CT levels dropped 100-fold within two years.

The rates of degradation under these various stimulated conditions are much more rapid than the generally estimated half-life, suggesting that with appropriate conditions, degradation can occur relatively fast.

For DCA, a complete review of potential degradation was done for soils and waters (Chiao, 1994). More recent work would allow an effective update of those published estimates. For instance Cox et al. (1998) documented natural attenuation of DCA and chloroform by a combination of anaerobic and aerobic processes. Bradley et al. (2000) showed that Mn(IV)-reducing conditions promoted mineralization of DCA.

Remediation of DCA has been successful in a groundwater treatment system, removing ~400 kg/yr from water contaminated with 2-15 μg/mL of DCA by use of a culture of DCA-degrading organisms (Stucki and Thueer, 1995). A number of pure cultures have been shown to degrade the compound with high efficiency in the laboratory, and a pathway for full dehalogenation to glycolic acid has been demonstrated (Janssen et al., 1994). Riebeth et al. (1992) found a $t_{1/2}$ of 2.6 h with a high density suspension of resting cells from a culture of *Methylosinus*. Of course, this rate translates to a much longer half-life at field concentrations of the bacteria.

There is a limited amount of literature on the biological degradation of EDB. Most recently, Hartzell et al. (2001) showed that cometabolism in the presence of propane, methane, or natural gas was highly efficient when a consortium of organisms was added in lab-scale batch reactors. Earlier a group in the Netherlands had shown that several bacterial species contain a haloalkane-dehalogenase gene carried on a plasmid, with much similarity of the enzyme in different species (Poelarends et al., 2000). The aerobic degradation is attributed to attack by a cytochrome P-450 (Castro et al., 1989), which serves as a hydroxylating-dehalogenase yielding a halogenated alcohol which is further metabolized.

Species able to mineralize EDB have been found in several locations, and aerobic reaction is more rapid than anaerobic (Pignatello, 1986a,b; Castro, 1993). In soil containing the appropriate organisms, starting levels of 6-8 μg/L EDB dropped to below detection (0.02 μg/L) within a few days, while at mg/L starting concentrations, degradation was considerably slower.

PLANT INTERACTIONS WITH EDB

Some years ago, Isaacson and Gent (1986) showed that tobacco and radish leaves readily sorbed EDB into the leaf. For radish, they showed that it could be translocated from petiole to leaf with a transpiration stream concentration factor of 0.86, but the concentration measured in the leaf never was more than

about one-tenth that in the petiole. This shows the high fugacity of EDB, that is its tendency to partition to and diffuse through the gas phase of the leaves. When an intact radish plant was treated similarly by feeding contaminant to the roots for two hours, the concentration found in the root ("tuber") was about 54% that of the input water, while the petiole level was only 12% of input and the leaves showed less than 1%. Unfortunately, without knowing the fresh and dry mass of the plant, it is impossible to calculate whether sufficient time elapsed to allow sorption equilibrium within the various tissues. The large difference between root and petiole indicates that it may not have been, and the authors indicated that a steady state transfer from solution to air was not attained. One would expect that with a log K_{ow} near 2 and a dry weight fraction of 10% or more, the root ought to have a higher concentration than the input solution at steady state. For most nonpolar compounds, the root concentration factor is >1 (Briggs et al., 1982; Burken and Schnoor, 1998).

Although the work of Isaacson and Gent (1986) allows no quantitative measure of the transfer of EDB through plants, it makes clear that it is readily transported. It would also likely be metabolized to some extent, depending on the level of expression of endogenous cytochromes P450. Plants have the ability to degrade a wide range of compounds in much the same way that the mammalian liver does. Indeed, a "green liver" model has been used to describe the pathways. Many herbicides and pesticides are modified and usually detoxified by plants via cytochrome P450-dependent pathways.

Frink and Bugbee (1989) examined the impact of soil fumigation with EDB on concentrations detectable in radishes and rye grass planted just one week after the fumigation event. During the first growing season, there was measurable EDB within the plants, but in the second season there was not, despite the presence of methanol-extractable EDB at a level of about 100 μg/kg in the soil. During the first growing season, the hexane-extractable EDB decreased more than 100-fold from an initial level of above 10 mg/kg, while the methanol extractable level declined only 10-15 fold. The authors suggest that the hexane-extractable level may better reflect the amount available to the plants. During half a dozen sampling events for batches of radish (planted at intervals and harvested at the same age), in the first year after fumigation, the roots initially had an EDB level above that of the soil, while the shoots always had less than the soil. The root concentration fell more rapidly than that of the shoots, becoming identical with it at two months after fumigation. Both were about five-fold below the soil level by four months. Concentrations found in grass foliage were 10-fold lower than in soil at the first sampling and about 100-fold lower by 4.5 months. The

large change of observed EDB within the grass suggests that the fraction available to plants had decreased 100-fold over this time period, as for the hexane-extractable fraction.

A recent laboratory study by Koch (2002) showed low levels of EDB in cranberry plants exposed to irrigation water contaminated with EDB during one season, with no detectable level appearing during the second year when EDB was not introduced to the water. Given a Henry's constant similar to that of MTBE and a log K_{ow} similar to TCE, one would expect relatively low EDB concentrations in the above-ground tissues, at steady state. As described by Zhang et al. (2001b), in the case of alfalfa, the concentration within the stem fell by a factor of two for each 10-15 cm along the stem. For larger diameter stems, the decline is proportionally longer, depending on the radius across which the compound must diffuse out of the stem.

Non-polar compounds such as EDB are expected to move freely through lipid membranes and cuticular waxes, accumulating within them to a concentration above that of the bulk water of the plant. Lipids and waxes are a small fraction of most plants. Sorption to cellulose is negligible for TCE and TCA, and sorption to lignin has not been determined. Overall the alfalfa: water sorption ratio is 10 for TCE and 5 for TCA, on a dry weight basis (Davis et al., 1998c). The sorption ratio of EDB will be in this range also. Thus, observed concentrations in above-ground plant parts will depend on the concentration of input water, the average residence time of the water in the stem, dry weight, tissue composition, and the portion of the plant being sampled. Because the fruit of the cranberry grows slowly, it is unlikely to be contaminated via the transpiration stream, given the free diffusion of EDB as it moves up through the plant and then down through the very fine stem into the fruit. Contamination could occur by direct transfer from water to cuticular wax during bog flooding at harvest (Xia and Rice, 2001).

ENGINEERING PLANTS TO DEGRADE CONTAMINANTS

A specific cytochrome, P-450 (2E1), from humans has been engineered (transformed) into tobacco plants in an effort to enhance metabolism of various halogenated contaminants (Doty et al., 2000). When hydroponically grown cuttings were exposed to 2 μg/mL of EDB, the compound was removed to a significant extent. Up to 0.24 μg/mL Br$^-$ was left in the water surrounding the roots, while 98% of the EDB disappeared. For untransformed plants, nearly two-thirds of the EDB disappeared from solution, but only traces of Br$^-$ were found in the culture solution. The observation of Br$^-$ in the culture suggests that some of

the P450 must be close to the exterior of the plant roots, because it was claimed by Doty et al. (2000) that Br⁻ ion was not significantly taken up by plants.

PRACTICAL IMPLICATIONS

Although EDB in particular has been used as a fumigant to kill plant tissues remaining in the field following harvest, at low concentrations, plants are likely able to detoxify it effectively. In addition, plants harbor high populations of microbes in, on, and around their roots. Some of these may have the capacity to fully mineralize the fumigants, starting from relatively low, non-toxic concentrations. Through their ability to dewater soil and to supply nutrients to sustain microbial populations, trees or other deep-rooted plants such as alfalfa are likely to make a significant contribution to removal of EDB or other contaminants in shallow aquifers, particularly in relatively dry climates where potential evapotranspiration exceeds rainfall.

Treatment of EDB, CT, TCE, tetrachloroethylene, and TCA has successfully been done using sprinkler irrigation (Richardson and Sahle-Demessie, 1998). In this instance, the primary loss mode was volatilization to the atmosphere while the plants used up the water that remained. The authors documented that the risk via atmospheric contamination was well within acceptable limits, and for an agricultural area, the economics were favorable. Overall losses were 20 to 40-fold during irrigation. Removal of EDB was >95% in the collected spray stream from the irrigation system, but this extent of loss would not suffice to lower the concentration to the MCL if the starting level in water was above 1 μg/L. Further reduction of contaminant levels might be attained in the soil or plant, but this was not monitored. The cited publication is important because it indicates that intermedia transfer of the contaminants does not present an unacceptable risk. It may be feasible to use commercial row crops under irrigation to provide an efficient pump-and-treat remediation of the volatile contaminants.

The limiting step in remediation may well be the slow desorption of EDB or other non-polar contaminants out of soil micropores (Pignatello and Cohen, 1990). It is expected that desorption and out-diffusion will be faster in dry than moist soil, so the dewatering ability of plants will prove beneficial. When contaminant levels in soil are low, crop plants may provide the most economical means to remediate the residual traces, assuring that they do not move to groundwater.

REFERENCES

Alexeeff, G.V., Kilgore, W.W., and Li, M.-Y. (1990) Ethylene dibromide: toxicology and risk management. *Rev. Environ. Contam. Toxicol.* 112:49-122.

ATSDR (1992) Toxicological profile for 1,2-dibromoethane (cited by http://www.lakes-environmental.com/toxic/ETHYLENE_DIBROMIDE.HTML).

Berck, B. (1965) Sorption of ethylene dibromide, ethylene dichloride and carbon tetrachloride by cereal products, *J. Agr. Food Chem.* 13:248-254

Bradley, P.M., Dinicola, R.S., and Landmeyer, J.E. (2000) Natural attentuation of 1,2-dichloroethane by aquifer microorganisms under Mn(IV)-reducing conditions. in *Second Int. Conf. Rem. Chlorinated and Recalcitrant Compds., Natural Attenuation Considerations and Case Studies*. Wickramanayake, G.B., Gavaskar, A.R., and Kelley, M.E., Editors, Battelle Press, Columbus, OH pp 169-173

Briggs, G.G., Bromilow, R.H., and Evans, A.A. (1982) Relationships between lipophilicity and root uptake and translocation of non-ionized chemicals by barley. *Pestic. Sci.* 13:495-504.

Burken, J.R., and Schnoor, J.L. (1998) Predictive relationships for uptake of organic contaminants by hybrid poplar trees. *Environ. Sci. Technol.* 32:3379-3385.

Castro, C.E. (1993) Biodehalogenation: the kinetics and rates of microbial cleavage of carbon-halogen bonds. *Environ. Toxicol. Chem.* 12:1609-1618.

Castro, C.E., Yokoyama, W., and Belser, N.O. (1989) Biodehalogenation: active site vs enzymatic and whole cell rates with cytochrome P-450. *Environ. Toxicol. Chem.* 8:13-18.

Chiao, F.F. [Risk Science Program] (1994) *Intermedia transfer factors for contaminants found at hazardous waste sites. 1,2-dichloroethane (DCA)*., prepared for OSA, DTSC, California EPA in support of the CalTOX model. http://www.cwo.com/~herd1/.

Cox, E.C., McMaster, M., and Major, D.W. (1998) Natural attenuation of 1,2-dichloroethane and chloroform in groundwater at a superfund site. in *Int. Conf. Rem. Chlorinated Recalcitrant Compd., Natural Attenuation*, Wickramanayake, G.B., and Hinchee, R.E., Eds. Battelle Press, Columbus, OH pp 309-314.

Davis, L.C., Banks, M.K., Schwab, A.P., Muralidharan, N., Erickson, L.E. and Tracy, J.C. (1998a) Plant-based bioremediation in *Principles and Practice of Bioremediation, vol. 2. Biodegradation technology developments*, R.L. Irvine and S.K. Sikdar, eds. Technomics Publ Co., Lancaster, PA. pp 183-219.

Davis, L.C., Vanderhoof, S., Dana, J., Selk, K., Smith, K., Goplen, B., and Erickson, L.E. (1998b) Movement of chlorinated solvents and other volatile organic compounds through plants monitored by Fourier Transform Infrared (FT-IR) Spectrometry (1998b) *Journal of Hazardous Substance Research* Vol 1, #4, pp 1-26.

Davis, L.C., Vanderhoof, S.L., and Lupher, D. (1998c) Sorption of trichloroethylene (TCE) and other halogenated aliphatics on plant materials. *Proceedings of the 1998 Conference on Hazardous Waste Research*, Erickson, L.E., and Rankin, M., Eds. Kansas State University, Manhattan, KS pp 319-325. http://www.engg.ksu.edu/HSRC/.

Davis, L.C., Lupher, D., Hu, J., and Erickson, L.E. (1999) Transport of trichloroethylene through living plant tissues. *Proceedings of the 1999 Conference on Hazardous Waste Research*, Erickson, L.E., and Rankin, M., Eds. Kansas State University, Manhattan, KS pp 205-209. http://www.engg.ksu.edu/HSRC/.

Davis, L.C., Pitzer, C., Castro, S., and Erickson, L.E. (2001) Henry's constant, Darcy's law, and contaminant loss. *Proceedings of the 2001 Conference on Environmental Research*. pp 2-15. Erickson, L.E. and Rankin, M.M., Eds. Kansas State University, Manhattan, KS. http://www.engg.ksu.edu/HSRC.

DiToro, D.M., and Horzempa, L.M. (1982) Reversible and resistant components of PCB adsorption-desorption isotherm. *Environ. Sci. Technol.* 16:594-602.

Doty, S.L., Shang, T.Q., Wilson, A.M., Tangen, J., Westergreen, A.D., Newman, L.A., Strand, S.E., and Gordon, M.P. (2000) Enhanced metabolism of halogenated hydrocarbons in transgenic plants containing mammalian cytochrome P450 2E1. *Proc. Nat. Acad. Sci. U.S.A.* 97:6287-6291.

Dybas, M.J., Barcelona, M., and 14 others (1998) Pilot-scale evaluation of bioaugmentation for *in situ* remediation of a carbon tetrachloride-contaminated aquifer. *Environ. Sci. Technol.* 32:3598-3611.

Freitas dos Santos, L.M., Leak, D.J., and Livingston, A.G. (1996) Enrichment of mixed cultures capable of aerobic degradation of 1,2-dibromoethane. *Appl. Environ. Microbiol.* 62:4675-4677.

Frink, C.R., and Bugbee, G.J. (1989) Ethylene dibromide persistence in soil and uptake by plants. *Soil Science* 148:303-307.

Geschwend, P.M., and Wu, S. (1985) On the constancy of sediment-water partition coefficients of hydrophobic organic pollutants. *Environ. Sci. Technol.* 19:90-96.

Gregory, K.B., Mason, M.G., Picken, H.D., Weathers, L.J., and Parkin, G.F. (2000) Bioaugmentation of Fe(0) for the remediation of chlorinated aliphatic hydrocarbons. *Environ. Engg. Science* 17:169-181.

Hartzell, K.E., Burton, C.D., and Leeson, A. (2001) Biodegradation of ethylene dibromide through cometabolic mechanisms. in *In situ Aeration and Aerobic Remediation: Sixth International In Situ and On-Site Bioremediation Symposium, vol 10*, Leeson, A., Johnson, P.C., Hinchee, R.E., Semprini, L., and Magar, V.S. Eds. Battelle Press, Columbus Ohio pp 193-199.

Hu, J., Davis, L.C., and Erickson, L.E. (1998) Modeling contaminants transport in plants. *Proceedings of the 1998 Conference on Hazardous Waste Research*, Erickson, L.E., and Rankin, M., Eds. Kansas State University, Manhattan, KS pp 285-295. http://www.engg.ksu.edu/HSRC/.

Idaho Division of Environmental Quality Watershed and Aquifer Protection Bureau (1999) An evaluation of methyl tert-butyl ether (MTBE) in groundwater at leaking underground storage tank sites. http://www2.state.id.us/deq/waste/waste1.htm.

Isaacson, P.J., and Gent, M.P.N. (1986) Uptake and transpiration of 1,2-dibromoethane by leaves. *Plant and Soil* 95:431-434.

Janssen, D.B., van der Ploeg, J.R., and Pries, F. (1994) Genetics and biochemistry of 1,2-dichloroethane degradation. *Biodegradation* 5:249-257.

Jafvert, C.T., and Wolfe, N.L. (1987) Degradation of selected halogenated ethanes in anoxic sediment-water systems. *Environ. Toxicol. Chem.* 6:827-837.

Jury, W.A., Russo, D., Streile, G., and El Abd, H. (1990) Evaluation of volatilization by organic chemicals residing below the soil surface. *Water Resour. Res.* 26:13-20.

Jury, W.A., Jin, Y., Gan, J., and Gimmi, T. (1996) Strategies for reducing fumigant loss to the atmosphere. in *Fumigants. Environmental Fate, Exposure, and Analysis*, Seiber, J.N., Knuteson, J.A., Woodrow, J.E., Wolfe, N.L., Yates, M.V., and Yates, S.R., ACS Symposium Series # 652, American Chemical Society, Washington, DC. pp 104-115.

Koch, D.E. (2002) The uptake of ethylene dibromide by cranberry (*Vaccinum macrocarpon*) plants via exposure through the air and soil. M.S. Thesis, Dept. of Agronomy, Kansas State University.

Manning, C. (2002) Bad water, U.S. inaction irk town. *Wichita Eagle* Sunday May 19, 2002.

McQuillan, D.M., Faris, B.H., and Swanson, B.H. (1998) Intrinsic cometabolism of carbon tetrachloride with gasoline: regulatory site closure. in *Int. Conf. Rem. Chlorinated Recalcitrant Compd., Natural Attenuation*, Wickramanayake, G.B., and Hinchee, R.E., Eds. Battelle Press, Columbus, OH pp 263-268.

MESL (2001) Multimedia environmental simulation laboratory site studies: Hatchville, MA http://groups.ce.gatech.edu/Research/MESL/site_studies/MMR/index.htm.

Narayanan, M., Russell, N.K., Davis, L.C., and Erickson, L.E. (1999a) Fate and transport of trichloroethylene in a chamber with alfalfa plants, *Internat. J. Phytorem.* 1:387-411.

Narayanan, M., Erickson, L.E., and Davis, L.C. (1999b) Simple plant-based design strategies for volatile organic pollutants, *Environ. Prog.* 18:231-242.

Pignatello, J.J. (1986a) Ethylene dibromide mineralization in soils under aerobic conditions. *Appl. Environ. Microbiol.* 86:588-592.

Pignatello, J.J. (1986b) Microbial degradation of ethylene dibromide in shallow aquifer materials. *J. Environ. Qual.* 16:307-312.

Pignatello, J.J., and Cohen, S.Z. (1990) Environmental chemistry of ethylene dibromide in soil and groundwater. *Rev. Environ. COntam. Toxicol.* 112:1-48.

Pignatello, J.J., Frink, C.R., Marin, P.A., and Droste, E.X. (1990) Field-observed ethylene dibromide in an aquifer after two decades. *J. Contam. Hydrol.* 5:195-214.

Poelerends, G.J., Kulakov, L.A., Larkin, M.J., van Hylkama, V., Johan, E.T., and Janssen, D.B. (2000) Role of horizontal gene transfer and gene integration in evolution of 1,3-dichloropropene- and 1,2-dibromoethane-degradative pathways. *J. Bacteriol.* 182:2191-2199.

Report on Carcinogens: http://ehis.niehs.gov/roc/ninth/rahc/.

Richardson, T.L., and Sahle-Demesse, E. (1998) Sprinkler irrigation for the removal of VOCs from groundwater. *Environ. Technol.* 19:1049-1054.

Riebeth, D.M., Belser, N.O., and Castro, C.E. (1992) Partial rapid metabolism of 1.2-dichloroethane by *Methylosinus trichosporium* OB-3b. *Environ. Toxicol. Chem.* 11:497-501.

Staudinger, J., and Roberts P.V. (1996) A critical review of Henry's law constants for environmental applications. *Crit. Rev. in Env. Sci. Technol.* 26:205-297.

Steinberg, S.M., Pignatello, J.J., and Sawhney, B.L. (1987) Persistence of 1,2-dibromoethane in soils: entrapment in intraparticle micropores. *Environ. Sci. Technol.* 21:1201-1208.

Stucki, G., and Thueer, M. (1995) Experiences of a large-scale application of 1,2-dichloroethane degradation microorganisms for groundwater treatment. *Environ. Sci. Technol.* 29:2339-2345.

USEPA (1983) Ethylene dibromide: decision and emergency order suspending registration of pesticide products containing ethylene dibromide for use as a soil fumigant. *Fed. Regist.* 48(197): 46228-46248.

Vogel, T.M., Criddle, C.S., and McCarty, P.L. (1987) Transformation of halogenated aliphatic compounds. *Environ. Sci. Technol.* 21:722-736.

Walton, B.T., Hendricks, M.S., Anderson, T.A., Griest, W.H., Merriweather, R., Beauchamp, J.J., and Francis, C.W. (1992) Soil sorption of volatile and semi-volatile organic compounds in a mixture. *J. Environ. Qual.* 21:552-558.

Washington, J.W. (1996) Gas partitioning of dissolved volatile organic compounds in the vadose zone: principles, temperature effects, and literature review. *Ground Water* 34:709-718.

Wiedemeier, T.H., Henry, B.M., and Haas, P.E. (2001) Technical protocol for enhanced reductive dechlorination via vegetable oil injection in *Anaerobic Degradation of Chlorinated Solvents*, V.S. Magar, V.S., Fennell, D.E., Morse, J.J., Alleman, B.C., and Leeson, A., Eds, Battelle Press, Columbus, pp 241-248.

Witt, M.E., Dybas, M.J., Wiggert, D.G., and Criddle, C.S. (1999) Use of bioaugmentation for continuous removal of carbon tetrachloride in model aquifer columns, *Environ. Eng. Sci.* 16:475-485.

Xia, K., and Rice, C.W. (2001) Association of ethylene dibromide (EDB) with mature cranberry (*Vaccinium macrocarpon)* fruit, *J. Agric. Food Chem.* 49:1246-1252

Yaws, C.L. (1992) *Thermodynamic and physical property data*, Gulf Publ. Co., Houston, TX.

Zhang, Q., Davis, L.C., and Erickson, L.E. (1998) Effect of vegetation on transport of groundwater and nonaqueous-phase liquid contaminants. *Journal of Hazardous Substance Research,* Vol 1, #8. pp 1-20 www.engg.ksu.edu/HSRC/.

Zhang, Q., Davis, L.C., and Erickson, L.E. (2001a) Transport of methyl tert-butyl ether (MTBE) through alfalfa plants. *Environ. Sci. Technol*. 35:725-731.

Zhang, Q., Davis, L.C., and Erickson, L.E. (2001b) Plant uptake of methyl-tert-butyl ether (MTBE) from groundwater. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management* 5:136-140.