

SIMULATION AND MODELLING OF THE FATE AND TRANSPORT OF CHEMICAL WARFARE AGENTS IN LABORATORY-SCALE LANDFILLS

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SUMMARY: A terrorist attack could result in the generation of large quantities of contaminated building debris that requires disposal. This debris could be contaminated with chemical and/or biological contaminants. The development of plans for the safe disposal of large quantities of contaminated debris requires information on the behavior of such debris in landfills. The overall objective of this research is to develop and experimentally validate a model to describe the transport of chemical warfare agents in a simulated landfill. The fate and transport of organic chemicals in landfills is governed by several processes including volatilization, sorption/desorption, biodegradation, abiotic hydrolysis and the association of chemicals with humic matter. Initial work will be conducted in batch systems to study each fate process in isolation. Thereafter, work will be conducted in columns in which all fate processes, landfill gas production, and water flux are influencing contaminant behavior concurrently.

1. INTRODUCTION

A terrorist attack could result in the generation of large quantities of contaminated building debris that requires disposal. This debris could be contaminated with chemical and/or biological contaminants. The development of plans for the safe disposal of large quantities of contaminated debris requires information on the behavior of such debris in landfills. This information is required to insure that the cleanup from a catastrophic event can proceed without delays attributable to concerns over the safety of a disposal alternative.

The overall objective of this research is to develop and experimentally validate a model to describe the transport of chemical warfare agents in a simulated landfill. This research builds on previous work to evaluate the behavior of chemical warfare agents in landfills using an equilibrium model (Bartelt-Hunt et al., 2006).

2. EXPERIMENTAL PROGRAM

2.1 Experimental design for fate and transport of chemical agents

The fate and transport of organic chemicals in landfills is governed by several processes including volatilization, sorption/desorption, biodegradation, abiotic hydrolysis and the

association of chemicals with humic matter. Initial work will be conducted in batch systems to study each fate process in isolation. Thereafter, work will be conducted in columns filled with synthetic building debris (SBD) in which all fate processes, landfill gas production, and water flux are influencing contaminant behavior concurrently.

Due to the hazardous nature of chemical warfare agents and restrictions on their use outside of secured areas, experimental work will be performed with a surrogate chemical that exhibits all of the fate processes listed above. A review of appropriate surrogates for a variety of chemical warfare agents has been published (Bartelt-Hunt et al., accepted for publication). Malathion has been chosen as the surrogate compound. One advantage of malathion is that it is available in ^{14}C -labeled form, which allows analyses to be conducted by scintillation counting as well as GC/HPLC. The chemical processes influencing the fate of malathion are the same processes affecting chemical agents, namely hydrolysis, sorption, biodegradation, volatilization and leaching. Using malathion as a surrogate chemical in batch and column studies will allow for the development and validation of a mathematical model that can be used to describe the fate of organic chemicals in a landfill. This model can then be used to predict the behavior of a range of chemical warfare agents for which experimental work would be difficult, dangerous and expensive.

Experiments to quantify abiotic hydrolysis will be conducted in deionized water, methanogenic leachate and acidogenic leachate at a range of temperatures and ionic strengths representative of what can be expected in landfill leachate. Sorption and desorption tests will be conducted with both fresh and decomposed building debris. The reason for testing both fresh and decomposed building debris is that as the debris decomposes, the cellulose and hemicellulose concentrations decrease, while the concentrations of lignin and other hydrophobic organic matter (humic and cellular material) increase. This change in composition could change the sorptive properties of the building debris (Wu et al. 2001). To understand the behavior of contaminants in landfills over long periods of time, it is important to understand how the nature of the sorbent (building debris) changes with time.

The anaerobic biodegradability of malathion will be measured in batch tests analogous to a biochemical methane potential test. Experiments will be designed to measure disappearance of the parent compound (malathion) in both live and killed controls, and the association of malathion and daughter products with humic matter will be quantified. The effect of fresh refuse as an additional carbon source will also be assessed, as will the potential for malathion to inhibit refuse decomposition. Abiotic controls will be used to identify results that can be attributed to biological activity as malathion forms multiple hydrolysis products under abiotic conditions at neutral pH. The biodegradability test will measure malathion disappearance, as well as the conversion of malathion to methane. ^{14}C -labeled malathion will be utilized to increase the sensitivity of the assay.

At the conclusion of the biodegradation assay, the residual solids will be sequentially extracted with a solvent to remove the sorbed fraction, followed by base to measure the fraction associated with humic matter. After solvent and base extraction, the residual solid will be combusted to determine the fraction of the chemical that is associated with the humin fraction. A complete description of the extraction procedure used to separate the water soluble, solvent extractable, humic acid, fulvic acid and humin fractions has been published (Chen et al., 2004).

Finally, a mathematical model describing organic contaminant fate and transport in landfills will be developed. This model will simulate organic contaminant partitioning among solid, aqueous, and gaseous phases. In addition, effects of landfill gas production and water flux on contaminant fate and transport will be described. Process parameters determined from bench-scale studies will be used to predict the fate and transport of malathion in a column containing SBD. Model predictions will be verified with column experiments, in which all fate processes

Table 1. Composition of Synthetic Building Debris.

Waste Component	Initial Composition of Synthetic Building Debris (%)	Synthetic Building Debris without Wallboard (%)	Assigned Model Waste Component for K_p Estimate
Drywall (gypsum wallboard)	22	0	
Ceiling Tiles	10	12.8	Newsprint
Carpet (<i>Nylon 6</i>)	3.5	4.5	Glassy polymer (PVC)
Vinyl (flooring tiles)	0.6	0.8	Glassy polymer (PVC)
Electronics (plastic component)	4.3	5.5	Glassy polymer (PVC)
Folders/Cardboard	3.3	4.2	Newsprint
White paper	26.7	34.2	Office Paper
Mixed Office Paper	3.3	4.2	Office Paper
Furniture	26.3 ^a	33.7 ^a	
<i>polyurethane foam</i>	1.3	1.7	Rubbery polymer (HDPE)
<i>formica sheets</i>	0.2	0.3	Glassy polymer (PVC)
<i>medium density fiberboard</i>	24.7	31.7	Newsprint

^a This value represents total furniture. Furniture was simulated by foam, formica and fiberboard as listed in the table.

occur concurrently. Ultimately, the model will be used to predict the behavior of a range of chemical warfare agents in typical landfill environments.

2.2 Preparation of Synthetic Building Debris (SBD)

The composition of SBD is presented in Table 1 and is based on a US EPA Decision Support Tool for management of building debris (Thorneloe et al., 2007; Lemieux et al., 2006). To simulate commercial carpet, a 100% nylon carpet with a latex backing was utilized. No carpet padding was included as padding is not typically used in office environments. Materials such as restroom equipment, doors, and window coverings were not included because their overall concentration is small, and the materials are not expected to contribute significantly to organic contaminant sorption. Electronic equipment was simulated by personal computers and monitors. Because certain metals such as iron interfere with nuclear magnetic resonance (NMR) analyses, only the cases and plastic components from the computers were used. To simulate furniture, representative components that were expected to contribute to sorption (polyurethane foam, formica, and wood) were included. All three components were purchased in pure form. This simulation of furniture is more reproducible than if actual office furniture would have been shredded. The fiber category was simulated by assuming that 80% of this category is white office paper, 10% is cardboard and manila folders, and 10% is mixed office paper.

All materials were shredded or cut and then mixed in the proportions given in Table 1. The physical-chemical characteristics of this material have the potential to change during biodegradation. Thus, to study the transport of both chemical and biological surrogate agents, it was desirable to have SBD available in both fresh and decomposed form. To prepare decomposed SBD, the fresh material was decomposed in a 208-L drum that was inoculated with leachate from actively decomposing refuse. The drum was operated with leachate neutralization and recirculation and incubated in a room maintained at 38°C to accelerate the rate of decomposition.

3. RESULTS AND DISCUSSION

3.1 Decomposition of Synthetic Building Debris

After approximately 200 days of incubation, the SBD did not exhibit any indication of methanogenesis despite two reinoculations. The most likely explanation for this is that the high wallboard (CaSO_4) content resulted in an inhibitory accumulation of sulfide. As a result, the wallboard was eliminated from the synthetic SBD and the remaining components normalized to 100%. The exclusion of wallboard (calcium sulfate) from the building debris is insignificant from a sorption perspective as its sorption capacity for organic compounds is expected to be negligible. The revised SBD composition is presented in Table 1. As the plastics, and not the cellulosic components of the SBD, are expected to dominate the sorbent characteristics of the material, we do not expect to see a measurable difference in sorption between fresh and decomposed building debris.

The SBD without wallboard was inoculated with methanogenic leachate in a 8-L reactor and again incubated at 38°C with leachate neutralization and recirculation. The methane production rate is illustrated in Figure 1. After 410 days, the measured yield is $90 \text{ mL CH}_4/\text{dry gm SBD}$ which suggests that 37% of the initial cellulose has been degraded based on the measured methane yield and the assumption that all of the methane resulted from cellulose.

3.2 Abiotic Hydrolysis

Abiotic hydrolysis experiments are required to understand the rate of malathion disappearance in nonezymatic systems. Work with malathion must be conducted in consideration of the fact that it hydrolyzes fairly rapidly at pH 7. Major hydrolysis products include malathion monocarboxylic acid, O,O-dimethyl phosphorodithioic acid, diethyl fumarate, and ethyl hydrogen fumarate.

The initial objective of the abiotic hydrolysis work is to obtain k_h (eqn. 1) in phosphate buffer at pH 2.2 and 7.8, at 5 different temperatures, where ionic strength and redox potential will be adjusted to match landfill conditions. The influence of pH on the hydrolysis rate constant is represented by Equation 1 (Wolfe, *et al.*, 1977):

$$k_h = k_A[H^+] + k_N + k_B[OH^-] \quad (1)$$

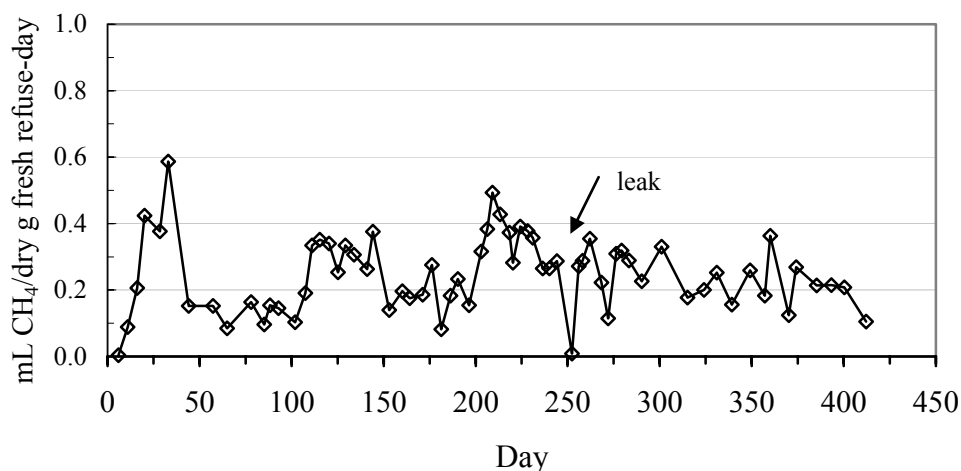


Figure 1. Methane Production from Synthetic Building Debris.

Table 2. Comparison of k_h obtained experimentally with k_h from Wolfe's prediction.

Buffer type	Concentration [M]	Ionic strength [M]	T [°C]	pH	k_h , experimental [h ⁻¹]	k_h , from Wolfe [h ⁻¹]	ratio ($k_h/k_{h,Wolfe}$)
phosphate	5.00E-03	4.00E-02 *	52	7.00	1.07E-01	1.18E-01	0.91
phosphate	5.00E-03	4.00E-02 *	52	6.85	9.25E-02	8.33E-02	1.11
phosphate	3.00E-01	7.80E-01	52	7.77	3.46E-01	6.93E-01	0.50
phosphate	1.20E-01	3.00E-01	52	7.78	2.88E-01	7.09E-01	0.41
phosphate	5.00E-03	1.30E-02	52	7.84	3.11E-01	8.14E-01	0.38
bicarbonate	3.00E-01	3.00E-01	46	8.62	9.74E-01	1.12E+00	0.87
bicarbonate	3.00E-01	4.00E-01 *	46	8.68	1.03E+00	1.28E+00	0.80

* Ionic strength adjusted with sodium chloride.

By working at different pHs and temperatures, k_A (2nd order acid-catalyzed hydrolysis constant), k_B (2nd order base-catalyzed hydrolysis constant) and E_a (activation energy of the malathion hydrolysis reaction), can be determined so that k_h can be obtained at any temperature and pH observed in a landfill. Wolfe et al. (1977) demonstrated that the hydrolysis rate constant of malathion at a given temperature as a function of solution pH is only influenced by the contribution of the acid-catalyzed, (slope +1 in the half-life vs. pH plot) and base-catalyzed (slope -1 in the half-life vs. pH plot) mechanisms, such that k_N , the neutral hydrolysis rate constant, has no influence on the overall k_h at any pH. Therefore, k_A can be obtained from experiments performed at low pHs, where k_B can be neglected, and k_B can be obtained from experiments performed at high pHs, where k_A can be neglected. The activation energy, E_a , can be obtained from the Arrhenius relationship (Equation 2), where k_h is obtained at different temperatures and under the same experimental conditions (pH, buffer type, buffer concentration, ionic strength concentration).

$$\ln k_h = \ln A - \frac{E_a}{RT} \quad (2)$$

A represents the frequency factor,

R is the ideal gas constant [J mol⁻¹ K⁻¹] and

T is the absolute temperature [K].

Finally, the k_h of malathion will be measured in leachate (acidogenic and methanogenic) to observe the influence of dissolved organic matter on k_h .

To date, malathion hydrolysis experiments have been conducted in deionized water under five different conditions using phosphate buffer and under two different conditions using bicarbonate buffer. The experimental conditions are summarized in Table 2 along with the measured k_h and the k_h predicted with a model published by Wolfe et al. (1977).

The results in Table 2 show that the hydrolysis rate constants obtained in phosphate buffer ($C = 5\text{mM}$, ionic strength = 40mM) are within 20% of the prediction by Wolfe's model. However, the hydrolysis rate constants obtained in phosphate buffer at 300 mM, 120 mM and 5mM (without the addition of sodium chloride) show a much larger deviation from Wolfe's predictions. Although the addition of sodium chloride, as a means to increase the ionic strength of the solution, does not seem to influence the hydrolysis rate constant of malathion obtained in 300 mM bicarbonate, the same is not true for the experiments conducted with phosphate buffer, where the ratio of the experimental k_h to that predicted from Wolfe's model varied from 0.50 to 0.38.

3.3 Sorption/Desorption

The sorption and desorption of malathion to SBD will be measured in ultrapure water as well as in acidogenic and methanogenic leachate. Leachates will be generated in laboratory-scale reactors containing decomposing SBD. All work will be conducted at pH 4 to prevent malathion hydrolysis. For sorption isotherms, preliminary work will be conducted to obtain estimates of K_p [$(\mu\text{g}/\text{kg})(\text{L}/\mu\text{g})$] and the time required for equilibration to more precisely define the isotherm tests.

To study desorption, malathion will be sorbed to SBD for various aging times. Thereafter, fresh, malathion-free, liquid will be added to the system and malathion release measured. The study of desorption requires that the dissolved concentration of the malathion approach zero, thus maximizing the concentration gradient between the sorbent and solution. Tenax beads contained in a mesh bag will be added to the system containing malathion sorbed to SBD. As malathion desorbs, it will be removed from solution by the tenax beads. Preliminary work has been conducted to develop a method to maintain the lowest possible aqueous malathion concentration. The initial objective was to demonstrate that over 95% of the sorbate can be removed from solution in less than 7 minutes. However, results to date suggest that this is not attainable given other constraints on the system. The surface area of the bag holding the tenax beads, as well as the manner in which the system is mixed are both important. The use of a short but wide mouth 60 mL bottle, 55 μm mesh bags for the tenax beads, and an orbital shaker resulted in the highest malathion uptake. Uptake was 68% in 7 min and increased to 84, 92 and 95% after 15, 30 and 60 min, respectively.

The infiltration of SBD into the bag holding the tenax was also evaluated. After 17 hr of mixing empty bags with SBD, 2.4% of SBD penetrated the 55 μm mesh empty bags while 3.7% of SBD was trapped in 104 μm empty bags. The malathion adsorption capacity of these trapped solids was 5% of the initial malathion concentration after 1 week of aging. Additional tests will be conducted to determine the amount of solids trapped during desorption experiments. The results will be used to correct the presence of malathion on the tenax for the amount attributable to SBD that penetrated the 55 μm bag. It is expected that less solids will penetrate the tenax bag in the actual desorption test because the tenax beads tend to stick to the mesh surface.

Initial tests using methylene chloride as the solvent to extract malathion from tenax beads obtained 87 to 92% recovery after 2 to 3 sequential extractions over a period of 8 days. Acetone and methanol are other common organic solvents used to extract malathion from various sorbents (i.e. soil, plants, resins). Since GC-MS analysis will be used to check for hydrolysis products during the desorption experiment, standardization of the solvent extraction protocol will consider methylene chloride (39.8°C) and acetone (56.2°C) which have lower boiling points than methanol (64.7°C).

4. CONCLUSIONS

In work with malathion, careful control of environmental conditions (pH, temperature, ionic strength, water chemistry) is essential to separate biological and abiotic processes. Abiotic hydrolysis is highly sensitive to pH and temperature.

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