Fate of Chemical Warfare Agents and Toxic Industrial Chemicals in Landfills

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One component of preparedness for a chemical attack is planning for the disposal of contaminated debris. To assess the feasibility of contaminated debris disposal in municipal solid waste (MSW) landfills, the fate of selected chemical warfare agents (CWAs) and toxic industrial chemicals (TICs) in MSW landfills was predicted with a mathematical model. Five blister agents [sulfur mustard (HD), nitrogen mustard (HN-2), lewisite (L), ethyldichloroarsine (ED), and phosgene oxime (CX)], eight nerve agents [tabun (GA), sarin (GB), soman (GD), GE, GF, VX, VG, and VM], one riot-control agent [CS], and two TICs [furan and carbon disulfide] were studied. The effects of both infiltration (climate) and contaminant biodegradability on fate predictions were assessed. Model results showed that hydrolysis and gas-phase advection were the principal fate pathways for CWAs and TICs, respectively. Apart from CX and the TICs, none of the investigated compounds was predicted to persist in a landfill for more than 5 years. Climate had little impact on CWA/TIC fate, and biodegradability was only important for compounds with long hydrolysis half-lives. Monte Carlo simulations were performed to assess the influence of uncertainty in model input parameters on CWA/TIC fate predictions. Correlation analyses showed that uncertainty in hydrolysis rate constants was the primary contributor to variance of CWA fate predictions, while uncertainty in the Henry's Law constant and landfill gas-production rate accounted for most of the variance of TIC fate predictions. CWA hydrolysates were more persistent than the parent CWAs, but limited information is available on abiotic or biotic transformation rates for these chemicals.

Introduction

The use of toxic chemicals as weapons of mass destruction began in 1915 with the use of chlorine gas against Allied forces during World War I (*1*). Recently, terrorist organizations have become interested in procuring and using toxic industrial chemicals (TICs) and/or chemical warfare agents (CWAs) for their own sinister purposes. For example, in the mid-1990s, members of the Japanese cult Aum Shinrikyo released sarin gas in five Tokyo subway trains and in Matsumoto (*2, 3*). In light of the potential for a large-scale chemical attack, there is a need to develop a comprehensive plan for the disposal of debris contaminated with CWAs and/or TICs. Based on facility distribution and capacity in the U.S., the disposal of contaminated debris in a landfill permitted for the disposal of nonhazardous solid waste must be considered. Although such debris would likely be decontaminated prior to disposal, application of a decontamination agent to a surface may not completely remove contaminants sorbed to organic debris constituents.

Previous studies on the environmental fate of CWAs have been conducted in aqueous or soil systems as part of decontamination or remediation studies of stockpiled CWAs (*4–9*). However, no information on CWA fate in landfills could be identified. The behavior of organic contaminants in landfills is influenced by the combined effects of biodegradation, sorption, transport in the gas and/or liquid phases (i.e., volatilization and leaching), and abiotic transformation, such as hydrolysis (*10–14*). Many CWAs hydrolyze in aqueous systems with half-lives on the order of minutes to days, and hydrolysis rates are affected by temperature, pH, and water quality (*5, 6, 15–21*). A review of previous research on the behavior of CWAs is presented in the Supporting Information.

A first step in evaluating the suitability of municipal solid waste (MSW) landfills for the disposal of contaminated building debris is to estimate contaminant fate pathways using a mathematical model. Model results can provide initial guidance to decision-makers on disposal options for contaminated debris and can elucidate the most sensitive parameters governing CWA/TIC fate in a landfill.

The objective of this work was to model the distribution and fate of representative CWAs and TICs in MSW landfills. Simulations were performed to assess the impact of climate (infiltration) and biodegradation rate on CWA and TIC fate. An additional objective was to assess the effects of input
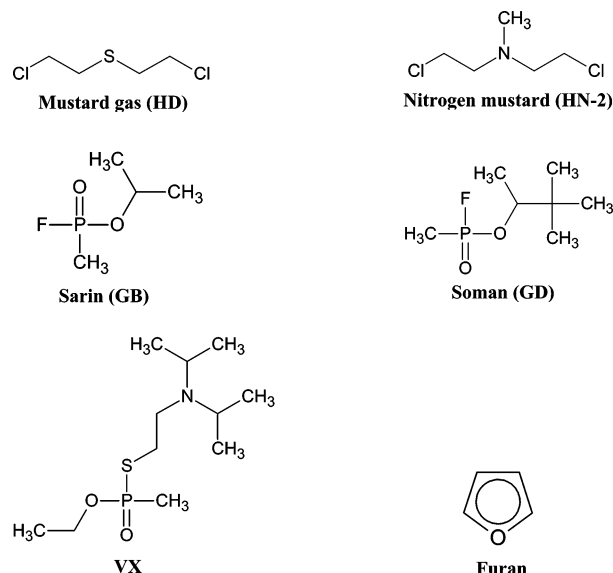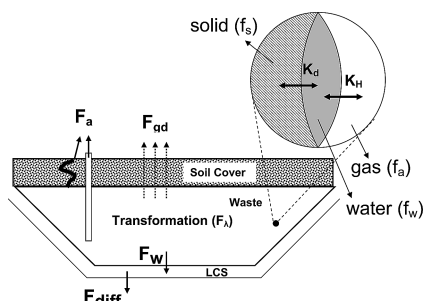
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FIGURE 1. Molecular structures of selected chemical warfare agents and furan.

FIGURE 2. Schematic of MOCLA. Adapted from Kjeldsen and Christensen (23). LCS is leachate collection system. F_λ includes biotic and/or abiotic transformation of aqueous CWAs.

parameter uncertainty on model results by performing Monte Carlo simulations.

Description of Chemicals Studied

The majority of candidate chemical agents for a terrorist attack can be classified as TICs, blister agents, blood agents, and nerve agents (22). TICs include ammonia, carbon disulfide, chlorine, furan, nitric acid, and sulfuric acid. Although furan and carbon disulfide are less toxic than CWAs, they are produced in large quantities and thus readily available. Blister agents include sulfur mustard (HD), nitrogen mustard (HN-2), lewisite (L), ethyldichloroarsine (ED), and phosgene oxime (CX). Arsine (SA), hydrogen cyanide (AC), and cyanogen chloride (CK) are common blood agents. However, because of their volatility, it is unlikely that significant quantities of blood agents would enter a landfill, and blood agents were therefore not studied. Nerve agents include tabun (GA), sarin (GB), soman (GD), GE, cyclohexyl sarin (GF), amiton (VG), VM, and VX. A complete list of CWAs/TICs studied is presented in Table S1 of the Supporting Information, and molecular structures for selected CWAs and furan are presented in Figure 1.

Modeling Approach and Data Development

The fate of CWAs in landfills was evaluated with MOCLA (Model for Organic Chemicals in Landfills) (23), which was modified in this study to include contaminant diffusion through the landfill liner. MOCLA represents a landfill as a fully mixed reactor and describes both the phase distribution of organic chemicals between solid waste, leachate, and landfill gas as well as the chemical fate in terms of landfill gas transport, leachate transport, abiotic transformation, and biodegradation (Figure 2). The distribution of chemicals between the gaseous, liquid, and solid phases is governed by the Henry's Law constant (K_H) for the leachate–gas interface and by the linear partition coefficient (K_{oc}) for the organic waste–leachate interface. The fate pathways considered in the model include: F_a, advective transport of volatilized CWAs into the landfill gas collection system and through the soil cover; F_{gd}, diffusive transport of volatilized CWAs through the soil cover; F_{diff}, diffusive transport of aqueous and volatilized CWAs through the composite liner; F_λ, transformation of aqueous CWAs by biotic and/or abiotic mechanisms; and F_w, transport of aqueous CWAs into the leachate collection system. The modified version of MOCLA is described in the Supporting Information.

To simulate the distribution and fate of chemicals in a landfill, input parameters are required to describe both the landfill and the chemicals. Landfill input parameters are presented in Table 1 with additional detail on the rationale for their selection given in the Supporting Information. The physical-chemical properties of selected compounds are given in Table 2, and data for additional compounds are given in Table S2. For ionizable CWAs, it was assumed that only the neutral species sorbs appreciably; for octanol–water systems, this assumption is valid up to several pH units above the pK_a of organic acids (24). K_H for the TICs and CWAs ranges from 1.2×10^{-8} to 2.2×10^{-1} (Tables 2 and S2). While furan, carbon disulfide, L, and ED are relatively volatile, K_H values for the remaining CWAs indicate that release via a landfill gas pathway should be limited.

Wet conditions (Table 1) were assumed for the base case, and simulations were performed for time periods up to 30 yr. To assess the effect of climate on CWA fate, the net precipitation to the landfill and the gas-production rate were decreased for an arid scenario (Table 1).

Because of the lack of information on anaerobic biodegradation of CWAs, no biological degradation was assumed to occur for base-case simulations. To assess the impact of contaminant biodegradability on fate predictions, results of

TABLE 1. MOCLA Input Parameter Values Describing Landfill Characteristics

parameter	units	base-case	range	source
dry bulk density of waste (ρ_b)	T m^{-3}	0.49	0.34–0.63	calculated from average values of wet bulk density and gravimetric moisture content
waste moisture content	m^3 water m^{-3} LF	0.091	0.042–0.14	calculated from average values of wet bulk density and gravimetric moisture content
waste gas content	m^3 air m^{-3} LF	0.25	0.10–0.40	based on data reported in (27)
organic carbon fraction		0.5	0.40–0.60	based on data reported in (28)
waste height	m	39.7	18.3–61	assumed values
net precipitation (N) arid scenario	m yr^{-1}	0.04	0.02–0.05	based on data reported in (29)
net precipitation (N) wet scenario	m yr^{-1}	0.12	0.04–0.32	based on data reported in (29)
gas-production rate (q_a) arid scenario	m^3 LFG m^{-3} LF yr^{-1}	2.8	1.9–3.7	calculated using gas-production model (30)
gas-production rate (q_a) wet scenario	m^3 LFG m^{-3} LF yr^{-1}	6.75	4.5–9.0	calculated using gas-production model (30)
cover soil thickness (L)	m	0.45		subtitle D regulation (31)
cover soil porosity (ϵ_{sc})		0.4	0.30–0.50	assumed values
cover soil moisture content	% (dry weight basis)	20.0	10.3–30.8	based on data reported in (32)
dry bulk density of cover soil	g cm^{-3}	1.7	1.3–2.0	based on data reported in (32)
liner thickness	m	0.6		subtitle D regulation (31)
liner porosity		0.4	0.3–0.5	assumed values
liner moisture content	% (dry weight basis)	20.0	10.3–30.8	based on data reported in (32)
dry bulk density of liner	g cm^{-3}	1.7	1.3–2.0	based on data reported in (32)

TABLE 2. Physical-Chemical Property Data for Selected CWAs and Furan[a]

chemical	sulfur mustard (HD)	nitrogen mustard (HN-2)	sarin (GB)	soman (GD)	VX	furan
chemical formula	$C_4H_8Cl_2S$	$C_5H_{11}Cl_2N$	$C_4H_{10}FO_2P$	$C_7H_{16}FO_2P$	$C_9H_{26}NO_2PS$	C_4H_4O
CAS number	505-60-2	51-75-2	107-44-8	96-64-0	50782-69-9	110-00-9
molecular weight (g mol^{-1})	159.07	156.05	140.10	182.17	267.37	68.08
boiling point (°C)	218	177	158	198	292	31.4
freezing point (°C)	14.45	−70	−56	−42	<−51	−85.6
vapor pressure (mmHg) at 25 °C	0.11	0.427	2.1	0.4	0.0007	600
Henry's Law constant (dimensionless) at 25 °C[b]	9.8×10^{-4}	3.5×10^{-6}	$3.8 \times 10^{-4\ c}$	1.9×10^{-4}	1.43×10^{-7}	$2.2 \times 10^{-1\ c}$
log K_{ow}	2.41[c]	0.9	0.3	1.78	2.09	1.34
hydrolysis half-life (min)	8.5 (25 °C in distilled water)	660 (25 °C in water/acetone)	2340 (25 °C, pH 7.5)	3600 (25 °C, pH 6)	24 480−60 480 (25 °C, pH 7)	∞
aqueous solubility (mg L^{-1})	684 (25 °C)	13 000 (ambient temp)	$1.0 \times 10^{6\ c}$ (25 °C)	21 000[c] (25 °C)	30 000 (25 °C)	1×10^4 (25 °C)
molecular diffusion coefficient in air (cm^2 s^{-1})[d]	0.074	0.076	0.077	0.064	0.051	0.113
molecular diffusion coefficient in water (cm^2 s^{-1})[e]	8.6×10^{-6}	8.2×10^{-6}	8.6×10^{-6}	7.1×10^{-6}	5.7×10^{-6}	1.2×10^{-5}
pK_a		6.8 (tertiary amine)			9[f] (tertiary amine)	

[a] Data compiled from the following sources: refs 15−18, 33−35. [b] $C_A = K_H C_L$, where C_L (mol/L) represents the aqueous-phase concentration and C_A (mol/L) represents the gas-phase concentration. [c] Estimated with EPI Suite v.3.12; ref 36. K_H values were estimated with the bond contribution method and aqueous solubilities from K_{ow}. [d] Estimated using the Wilke−Lee equation; ref 37. [e] Estimated using the Hayduk−Laudie equation; ref 37. [f] Reported pK_a values for VX range from 8.6 to 9.12; refs 38, 39.

TABLE 3. Predicted Phase Distributions for TICs, CWAs, and CWA Hydrolysates

compound	phase fractions		
	gas (f_a)	water (f_w)	solid (f_s)
furan	0.008	0.013	0.980
carbon disulfide	0.008	0.005	0.988
Chemical Warfare Agents			
HD (sulfur mustard)	0.000	0.002	0.998
HN-2 (nitrogen mustard)	0.000	0.043	0.957
L (lewisite)	0.000	0.002	0.998
ED (ethyldichloroarsine)	0.000	0.003	0.997
CX (phosgene oxime)	0.000	0.056	0.944
GA (tabun)	0.000	0.059	0.941
GB (sarin)	0.000	0.068	0.932
GD (soman)	0.000	0.006	0.994
GE	0.000	0.035	0.965
GF (cyclohexyl sarin)	0.000	0.008	0.992
VX (V-gas)	0.000	0.095	0.905
VG (amiton)	0.000	0.165	0.835
VM	0.000	0.301	0.699
CS (tear gas)	0.000	0.001	0.999
CWA Hydrolysates			
TDG	0.000	0.255	0.745
2-(2-chloroethyl) methylamino ethanol	0.000	0.213	0.787
EA2192	0.000	0.189	0.811

1-year simulations with biotic CWA/TIC half-lives of 1000, 100, and 10 d were compared to those obtained in the absence of biodegradation. These simulations utilized net precipitation and gas-production inputs corresponding to the wet climate scenario (Table 1).

Uncertainty Analysis. Uncertainty is associated with the input parameters shown in Tables 1, 2, and S2; for example, the property data were not always obtained from direct measurements, hydrolysis rates were not measured under conditions representative of a landfill, and no landfill disposal scenario can be exactly represented by the parameter values shown in Table 1. Therefore, Monte Carlo simulations (Crystal Ball v.7) were performed to assess the effects of uncertainty associated with input parameters on CWA/TIC fate. Monte

Carlo simulations were conducted for the 1 year simulation period and resulted in cumulative distribution functions (CDFs) for individual contaminant fate and transport pathways as well as for the contaminant fraction remaining in the landfill at any given time. For the Monte Carlo simulations, a triangular distribution was assigned to each input parameter because the mean or accepted value for each parameter was considered to represent the most likely value and there were not sufficient data to utilize a more sophisticated distribution. To describe the landfill, the maximum and minimum values in each parameter distribution corresponded to the upper and lower ends of the ranges given in Table 1. For K_H and log K_{ow}, only a single value (either an EPI Suite estimate or an experimental data point) was available for many CWAs. Thus, upper and lower bounds of K_H and log K_{ow} needed to be estimated for the uncertainty analysis. To obtain these estimates, the lowest and highest experimental values for K_H and log K_{ow} were identified in the literature (25) for the 37 organic chemicals that were originally modeled in MOCLA (23). These were compared to the value used in MOCLA (23), which was considered to be the "accepted" value. A percent difference was calculated for both the low and the high values (eq 1).

$$\% \text{ difference} = \frac{|\text{high or low} - \text{accepted}|}{\text{accepted}} * 100\% \quad (1)$$

The median percent difference determined from the 37 chemicals was then applied to the accepted value for each CWA/TIC to estimate upper and lower bounds for K_H and log K_{ow}. The accepted value was an experimentally determined value, if available, or an estimate from EPI Suite (Tables 2 and S2). Tables S3 and S4 summarize data representing the upper and lower bounds of K_H and log K_{ow}, respectively, for the 37 chemicals used in MOCLA, while estimated K_H and log K_{ow} ranges for the CWAs/TICs are given in Tables S5 and S6, respectively. The free-air (D_{air}) and free-water (D_{water}) diffusion coefficients and hydrolysis half-lives were increased and decreased by 1 order of magnitude to establish ranges for the uncertainty analysis. In all simulations, latin hypercube

time (yr)	furan fraction remaining	F_a (gas-phase advection)	HD fraction remaining	F_λ (abiotic)	HN-2 fraction remaining	F_λ (abiotic)	GB fraction remaining	F_λ (abiotic)	GD fraction remaining	F_λ (abiotic)	VX fraction remaining	F_λ (abiotic)
0.01	0.998	0.002	0.388	0.612	0.791	0.209	0.899	0.101	0.994	0.006	0.992	0.008
0.05	0.990	0.010	0.009	0.991	0.309	0.691	0.588	0.412	0.969	0.031	0.960	0.040
0.5	0.901	0.099	0.000	1.000	0.000	1.000	0.005	.995	0.729	0.271	0.664	0.336
1	0.812	0.188	0.000	1.000	0.000	1.000	0.000	1.000	0.531	0.468	0.440	0.559
5	0.352	0.647	0.000	1.000	0.000	1.000	0.000	1.000	0.042	0.957	0.017	0.983
10	0.124	0.875	0.000	1.000	0.000	1.000	0.000	1.000	0.002	0.998	0.000	1.000
15	0.043	0.955	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000
20	0.015	0.982	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000
25	0.005	0.993	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000
30	0.002	0.996	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000
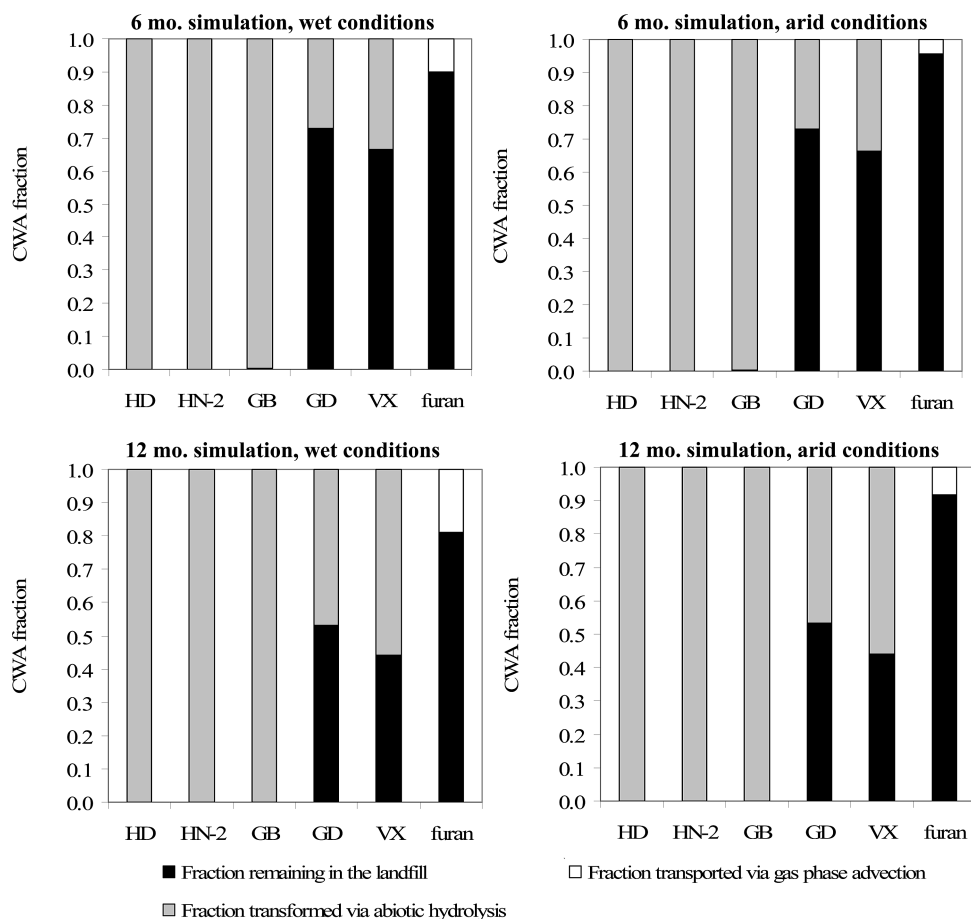
FIGURE 3. Effect of climate on the predicted fate of selected CWAs and furan 6 mo and 1 yr after disposal of contaminated debris.

sampling was used to select parameter values from the distribution, and 1000 realizations were used for each simulation.

Fate of CWA Hydrolysates. Because hydrolysis half-lives for most CWAs are relatively short, abiotic transformation of CWAs was expected to be a significant fate pathway. To illustrate the possible fate of CWA hydrolysis products, physical-chemical property data were identified for three CWA hydrolysates (Table S7). These data were used as MOCLA inputs for 1-year simulations under wet climate conditions to predict hydrolysate behavior. No information was available on abiotic or biotic transformation rates of these chemicals, and transformation was not included as a potential fate pathway.

Results and Discussion

Predicted contaminant distributions among the gas, leachate, and solid phases are presented in Table 3. These results apply at any simulation time because MOCLA assumes that phase distributions are always at equilibrium. Apart from VM and VG, over 90% of the CWAs and TICs resided in the sorbed fraction (Table 3). The remainder was associated with the aqueous fraction, while the fraction in the gas phase was small or negligible. That the sorbed fraction dominated even for polar compounds such as GB (log K_{ow} = 0.3) is principally due to the large sorbent mass and the relatively small water volume in the landfill. Because the selected TICs are more volatile than the CWAs, a small fraction of these chemicals was predicted to be present in the gas phase.

For selected CWAs and furan, Table 4 summarizes the fractional contribution of the principal fate pathway to each compound's mass balance along with compound mass fractions that were predicted to remain in the landfill as a function of time. The primary fate pathway for the CWAs was hydrolysis, while furan was primarily removed from the
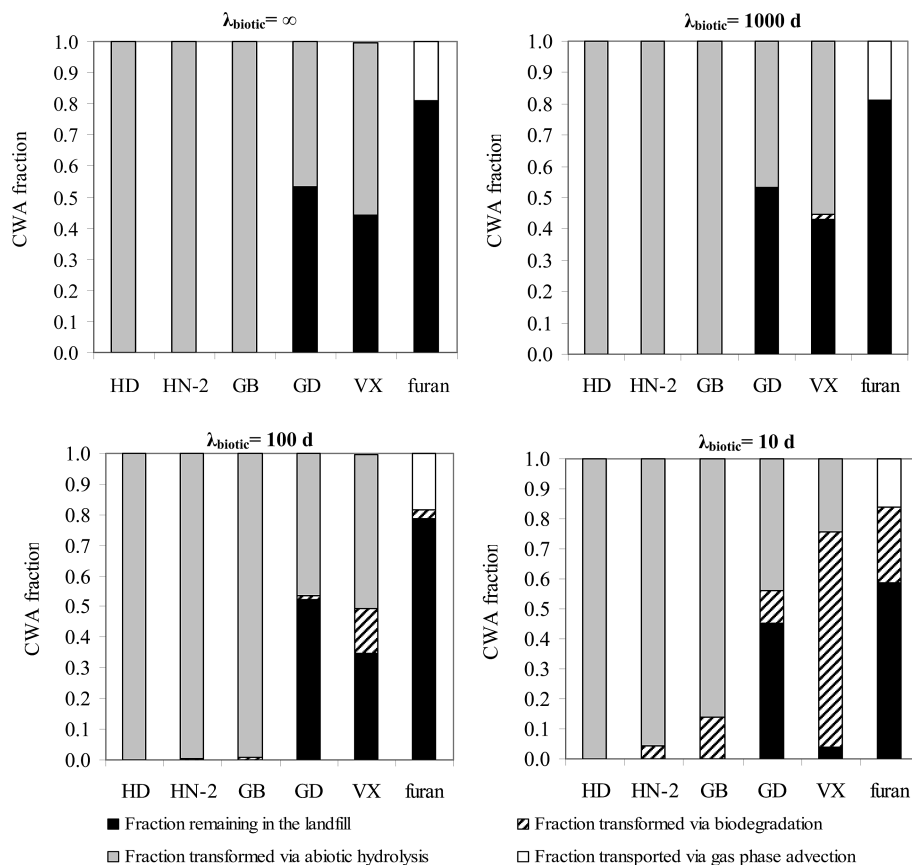
FIGURE 4. Effect of biotic half-life on the predicted fate of selected CWAs and furan 1 yr after disposal of contaminated debris.

landfill via gas-phase advection (Table 4). Hydrolysis of HD, HN-2, and GB was essentially complete within 6 months, while GD and VX hydrolyzed almost completely after 5 years. Over 90% of the furan was transported out of the landfill via gas-phase advection within 15 years (Table 4). MOCLA predicts that some CWAs, primarily those with longer hydrolysis half-lives (e.g., GD, VX), will remain in landfills for several years. This result can be attributed to the model assumption that hydrolysis occurs in the aqueous phase only; however, the fraction of each CWA that was predicted to be in the aqueous phase, and thus available for hydrolysis, was small, with over 90% of CWAs in the sorbed fraction for all but VG and VM (Table 3). It should be noted that CWA fate and transport via all other pathways included in MOCLA was negligible. Complete fate pathways for the base case after 1 yr are presented in Table S8.

The simulation results under wet and arid climate scenarios were the same for most CWAs (Figures 3 and S1-S8), indicating that the magnitude of the gas-production rate and water infiltration had little impact on the fate of most of the blister and all of the nerve agents. An increase in the gas-production rate increased the gas-phase transport for the TICs as these compounds are more volatile.

The effect of biotic half-life on contaminant fate is presented in Figure 4 and Tables S8-S11. CWAs with short abiotic half-lives (e.g., HD, HN-2, and GB) were insensitive to changes in biotic half-life at values greater than 10 d. Many of the blister agents and nerve agents have hydrolysis half-lives that are on the order of hours or minutes; therefore, a decrease in biotic half-life from infinity to 10 d did not appreciably affect the fraction remaining in the landfill 1 yr after disposal of contaminated debris. In contrast, the abiotic half-life of GD is 2.5 d; thus, decreasing the biotic half-life from infinity to 10 d decreased the fraction of the GD remaining in the landfill by ~8% (Figure 4). The magnitude

of the biotic half-life had a greater effect on the fate of V-agents and TICs. The fraction of furan and VX remaining in the landfill after 1 yr decreased by ~22% and ~40%, respectively, when the biotic half-life was decreased from infinity to 10 d (Figure 4). Overall, the results suggest that the magnitude of the biotic half-life is only significant if the abiotic half-life is relatively long. In general, anaerobic biodegradation of organic contaminants occurs slowly; for example, toluene and benzene biodegradation rates are on the order of 0.018 d^{-1} ($\lambda_{1/2} \approx 38.5$ d) and 0.0074 d^{-1} ($\lambda_{1/2} \approx 93$ d), respectively (26).

Uncertainty Analysis. For selected CWAs and furan, CDFs of the fraction remaining in the landfill after 1 year are shown in Figure 5 along with MOCLA point estimates using "accepted" values. The contribution of input parameter uncertainty to the variance in the simulation results is presented in Table 5. For the CWAs in Table 5, the hydrolysis half-life accounted for greater than 80% of the variance in the fraction that was predicted to remain in the landfill after 1 year. The CDF for furan was relatively broad, and uncertainty in the gas-production rate was the largest contributor to the variance in simulations results. The difference in the simulation results under uncertainty for GD as compared to GB (Figure 5) is attributable to the longer hydrolysis half-life of GD combined with its larger log K_{ow} value. For GB, the magnitude of the hydrolysis half-life (~1.6 d) is sufficiently low that uncertainty in log K_{ow} had a negligible effect on model output. The hydrolysis half-life of GD (~2.5 d) is long enough that uncertainty in log K_{ow}, which affects the distribution of the contaminant between the sorbed and aqueous phases, had a greater influence on the predicted fraction of GD transformed via hydrolysis after 1 year (Table 5). The relatively long hydrolysis half-life of VX (~29.5 d) combined with a relatively large log K_{ow} value resulted in a broad CDF for the predicted VX fraction remaining in the
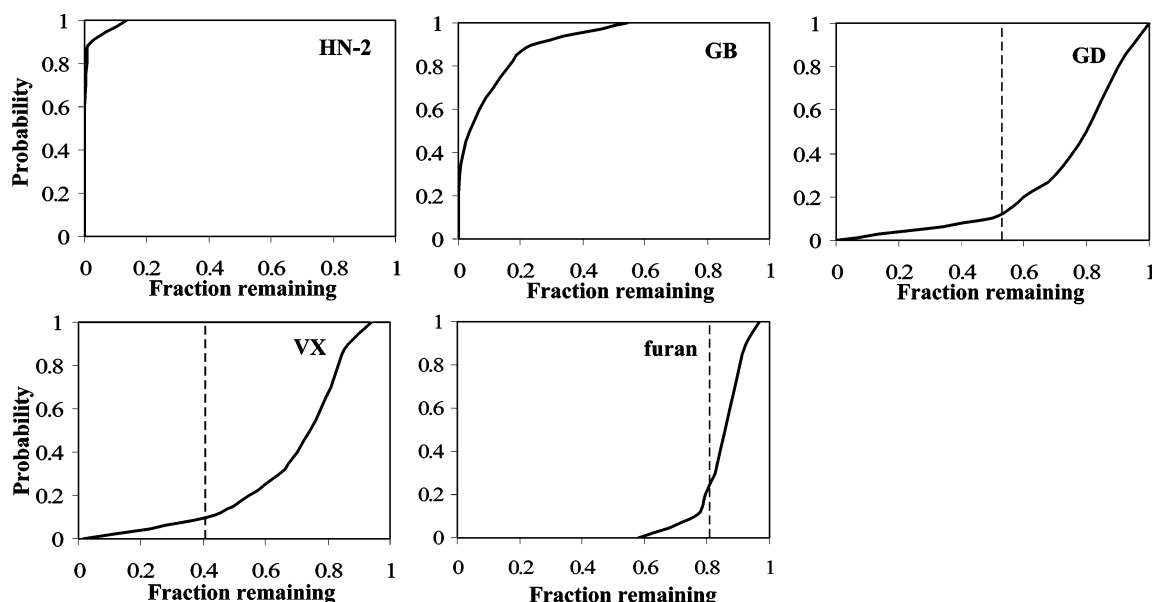
FIGURE 5. Cumulative distribution functions (CDFs) for the predicted CWA/TIC fraction remaining in the landfill 1 yr after disposal of contaminated debris. Dashed vertical lines represent point estimates obtained with MOCLA using accepted values; for HN-2 and GB, point estimates were zero. The CDF for HD is a vertical line at fraction remaining = 0 and is not shown.

TABLE 5. Contribution of Input Parameter Uncertainty to Variance in MOCLA Simulation Results

CWA	MOCLA input parameter	contribution to variance
furan	gas-production rate (q_a)	71.4%
	K_H	16.0%
	waste bulk density (ρ_b)	−6.0%
HD	$\lambda_{abiotic}$	−83.7%
	waste moisture content (ϵ_w)	6.8%
HN-2	$\lambda_{abiotic}$	−84.7%
	waste moisture content (ϵ_w)	7.2%
GB	$\lambda_{abiotic}$	−88.9%
	waste moisture content (ϵ_w)	7.1%
GD	$\lambda_{abiotic}$	−80.4%
	waste moisture content (ϵ_w)	10.3%
	log K_{ow}	−4.9%
VX	$\lambda_{abiotic}$	−87.7%
	waste moisture content (ϵ_w)	8.0%

TABLE 6. Predicted Fate Routes for CWA Hydrolysates under Wet Conditions 1 yr after Disposal of Contaminated Debris

compound	fraction remaining	F_a (gas-phase advection)	F_{gd} (gas-phase diffusion)	F_w (aqueous transport)
thiodiglycol (TDG)	0.991	0.000	0.000	0.008
2-(2-chloroethyl) methylamino ethanol	0.992	0.000	0.000	0.007
EA2192	0.993	0.000	0.000	0.006

landfill. Finally, it should be noted that currently available hydrolysis rate data may not be representative of CWA hydrolysis rates in landfills. To refine model predictions, experimental work is needed to quantify hydrolysis pathways and rates for CWAs under conditions representative of a landfill.

Fate of CWA Hydrolysates. The equilibrium phase fractions and fate routes for CWA hydrolysates are presented in Tables 3 and 6, respectively. In comparison to the CWAs, transport via leachate is more significant for the hydrolysates. This result is partly due to the lower log K_{ow} values of the

hydrolysis products relative to the original agents. Also, the hydrolysates may be more persistent (e.g., slower hydrolysis) than the original agents. Because rate data are not available, the simulation results presented in Table 6 were obtained without considering abiotic or biotic transformations.

Environmental Implications. The results of all simulations indicate the importance of hydrolysis as the primary fate pathway for the examined CWAs. Model results indicate that many CWAs were completely transformed via hydrolysis within 1 yr. Although the results indicate that CWAs may not persist for several years, further information is needed on the fate of hydrolysis products to more completely evaluate risks associated with CWA-contaminated debris disposal. While many hydrolysis products are less toxic than the original agents, HN-2, VX, L, and ED are known to form toxic intermediates that are more persistent than the parent compound (*16*).

Little information is currently available on microbial degradation of CWAs or their hydrolysis products under anaerobic conditions. If CWA-exposed debris is decontaminated prior to disposal, CWA concentrations in the leachate phase may be sufficiently low that some parent compound biodegradation may occur in MSW landfills. Hydrolysis products of many CWAs should be more biodegradable under anaerobic conditions than the corresponding parent compound, but the resulting metabolites may not always be innocuous (e.g., As-containing products of L and ED).

For chemicals for which a significant advective loss to the gas phase was predicted, the results are conservative in that the input values represent gas-production rates at a landfill containing largely MSW. In an actual disposal scenario, contaminated debris would likely be isolated from other waste in the landfill by either a soil barrier or by encasing the debris in plastic containers. Such a barrier would reduce gas production and also limit transport by landfill leachate. In all cases, it is expected that CWA contaminated debris would be disposed of in landfills with leachate and gas collection systems.

It should also be noted that MOCLA does not consider mass transfer limitations between the solid phase and the bulk aqueous phase. Desorption from the solid phase may be a rate-limiting step in CWA hydrolysis, but such a rate limitation would not increase the rate of CWA transport out

of the landfill via gas or liquid pathways beyond the rates predicted here.

Supporting Information Available

Chemical agent classification, environmental fate of chemical agents, physical-chemical property data for additional TICs, CWAs, and their hydrolysates, description of MOCLA and derivation of liner diffusion term, rationale for MOCLA input parameter selection, ranges of K_H and log K_{ow} for uncertainty analyses, and effect of biodegradation and climate on contaminant fate. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Haber, L. F. *The Poisonous Cloud: Chemical Warfare in the First World War*; Oxford University Press: London, 1986.

(2) Morita, H.; Yanagisawa, N.; Nakajima, T.; Shimizu, M.; Hirabayashi, H.; Okudera, H.; Nohara, M.; Midorikawa, Y.; Mimura, S. Sarin poisoning in Matsumoto, Japan. *Lancet* 1995, 346, 290−293.

(3) Suzuki, T.; Morita, H.; Ono, K.; Maekawa, K.; Nagai, R.; Yazaki, Y. Sarin poisoning in Tokyo subway. *Lancet* 1995, 345, 980−981.

(4) Yang, Y.-C.; Baker, J. A.; Ward, J. R. Decontamination of chemical warfare agents. *Chem. Rev.* 1992, 92, 1729−1743.

(5) Kingery, A. F.; Allen, H. E. The environmental fate of organophosphorus nerve agents: A review. *Toxicol. Environ. Chem.* 1995, 47, 155−184.

(6) Harvey, S. P.; Szafraniec, L. L.; Beaudry, W. T.; Earley, J. T.; Irvine, R. L., *Neutralization and biodegradation of sulfur mustard*; ERDEC-TR-388; U.S. Army Munitions Chemical Command: Aberdeen Proving Grounds, MD, 1997.

(7) Wagner, G. W.; MacIver, B. K. Degradation and fate of mustard in soil as determined by ^{13}C MAS NMR. *Langmuir* 1998, 14, 6930−6934.

(8) Skylar, V. I.; Mosolova, T. P.; Kucherenko, I. A.; Degtyarova, N. N.; Varfolomeyev, S. D.; Kalyuzhyi, S. V. Anaerobic toxicity and biodegradability of hydrolysis products of chemical warfare agents. *Appl. Biochem. Biotechnol.* 1999, 81, 107−117.

(9) Raber, E.; McGuire, R. Oxidative decontamination of chemical and biological warfare agents using L-Gel. *J. Hazard. Mater. B* 2002, 93, 339−352.

(10) Reinhart, D. R.; Gould, J. P.; Cross, W. H.; Pohland, F. G. Sorptive behavior of selected organic pollutants codisposed in a municipal landfill. *Emerging Technologies in Hazardous Waste*; ACS Symposium Series; American Chemical Society: Washington, DC, 1990; Vol. 422, pp 292−310.

(11) Ejlertsson, J.; Johansson, E.; Karlson, A.; Meyerson, U.; Svensson, B. H. Anaerobic degradation of xenobiotics by organisms from municipal solid waste landfilling conditions. *Antonie van Leeuwenhoek* 1996, 69, 67−74.

(12) Ejlertsson, J.; Meyerson, U.; Svensson, B. H. Anaerobic degradation of phthalic acid esters during digestion of municipal solid waste under landfilling conditions. *Biodegradation* 1996, 7, 345−352.

(13) Sanin, F.; Knappe, D. R. U.; Barlaz, M. A. Biodegradation and humification of toluene in a simulated landfill. *Water Res.* 2000, 34, 3063−3074.

(14) Wu, B.; Taylor, C. M.; Knappe, D. R. U.; Nanny, M. A.; Barlaz, M. A. Factors controlling alkylbenzene sorption to municipal solid waste. *Environ. Sci. Technol.* 2001, 35, 4569−4576.

(15) Franke, S. *Textbook of Military Chemistry, Vol. 1*; USAMIIA-HT-039-82, AD B062913; Defense Technical Information Center: Alexandria, VA, 1982.

(16) Munro, N. B.; Talmage, S. S.; Griffin, G. D.; Waters, L. C.; Watson, A. P.; King, J. F.; Hauschild, V. The sources, fate and toxicity of chemical warfare agent degradation products. *Environ. Health Perspect.* 1999, 107, 933−974.

(17) Cohen, B. *Chemical Warfare Agents and Related Chemical Problems Parts III−IV*; Summary Technical Report Division 9; NRDC Office of Science Research and Development, 1946.

(18) Morrill, L. G.; Reed, L. W.; Chinn, K. S. K. *Toxic Chemicals in the Soil Environment: Volume 2*; Interactions of some toxic chemicals/chemical warfare agents and soils; TECOM Project 2-CO-210-049; Oklahoma State University, Stillwater, OK, 1985.

(19) Rosenblatt, D. H.; Miller, T. A.; Dacre, J. C.; Muul, I.; Cogley, D. R. *Problem Definition Studies on Potential Environmental Pollutants II*; Physical, Chemical, Toxicological and Biological Properties of 16 Substances; Tech Rpt. 7509; AD A030428; U.S. Army Medical Bioengineering Research and Development Laboratory: Fort Detrick, MD, 1975.

(20) Clark, D. N. *Review of reactions of chemical agents in water*; AD-A213 287; Defense Technical Information Center: Alexandria, VA, 1989.

(21) Epstein, J.; Rosenblatt, D.; Gallacio, A.; McTeague, W. *Summary Report on a Data Base for Predicting Consequences of Chemical Disposal Operations*; EASP 1200-12; Department of the Army Headquarters: Edgewood Arsenal, MD, 1973.

(22) Centers for Disease Control and Prevention. *Chemical Agents*; 2005; http://www.bt.cdc.gov/agent/agentlistchem.asp.

(23) Kjeldsen, P.; Christensen, T. H. A simple model for the distribution and fate of organic chemicals in a landfill: MOCLA. *Waste Manage. Res.* 2001, 19, 201−216.

(24) Escher, B. I.; Schwarzenbach, R. P. Partitioning of substituted phenols in liposome−water, biomembrane−water, and octanol−water systems. *Environ. Sci. Technol.* 1996, 30, 260−270.

(25) Mackay, D.; Shiu, W. Y.; Ma, K. C. *Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals*; Lewis Publishers: Boca Raton, FL, 1992.

(26) Wilson, B. H.; Smith, G. B.; Rees, J. F. Biotransformations of selected alkylbenzenes and halogenated aliphatic hydrocarbons in methanogenic aquifer material: A microcosm study. *Environ. Sci. Technol.* 1986, 20, 997−1002.

(27) Bendz, D.; Singh, V. P.; Rosqvist, H.; Bengtsson, L. Kinematic wave model for water movement in municipal solid waste. *Water Resour. Res.* 1998, 34, 2963−2970.

(28) Barlaz, M. A. Carbon storage during biodegradation of municipal solid waste components in laboratory-scale landfills. *Global Biogeochem. Cycles* 1998, 12, 373−380.

(29) Camobreco, V.; Repa, E.; Ham, R. K.; Barlaz, M. A.; Felker, M.; Rousseau, C.; Clark-Balbo, M.; Rathle, J.; Thorneloe, S. *Life Cycle Inventory of a Modern Municipal Solid Waste Landfill*; Environmental Research and Education Foundation: Washington, DC, 2000.

(30) U.S. Environmental Protection Agency. User's Manual Landfill Gas Emissions Model (Version 2.0); EPA/600/R-98/054; U.S. EPA: Research Triangle Park, NC, 1998.

(31) Code of Federal Regulations; 40 Parts 257 and 258; 1991.

(32) Benson, C. H.; Daniel, D. E.; Boutwell, G. P. Field performance of compacted clay liners. *J. Geotech. Geoenviron. Eng.* 1999, 125, 390−402.

(33) Department of the Army. *Potential Military Chemical/Biological Agents and Compounds*; FM 3-9, NAVFAC P-467, AFR 355-7; Headquarters, Department of the Army, Navy and Air Force: Fort McClellan, AL, 2005.

(34) Opresko, D. M.; Young, R. A.; Faust, R. A.; Talmage, S. S.; Watson, A. P.; Ross, R. H.; Davidson, K. A.; King, J. Chemical warfare agents: Estimating Oral Reference Doses. *Rev. Environ. Contam. Toxicol.* 1998, 156, 1−183.

(35) Benschop, H. P.; Wesselman, H. C. Pharmacokinetics of the soman simulant 1,2,2-trimethlpropyl dimethylphosphinate (PDP) in rats. *Arch. Toxicol.* 1989, 63, 238−243.

(36) U.S. Environmental Protection Agency. *Estimation Program Interface (EPI) Suite*, August 17, 2004; http://www.epa.gov/opptintr/exposure/docs/episuite.htm.

(37) Lyman, W. J.; Reehl, W. F.; Rosenblatt, D. H. *Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds*; American Chemical Society: Washington, DC, 1990.

(38) Small, M. J. *Compounds formed from the chemical decontamination of HD, GB, VX and their environmental fate*; Technical Report 8304; U.S. Army Medical Bioengineering Research and Development Laboratory: Fort Detrick, MD, 1984.

(39) Yang, Y.-C.; Szafraniec, L. L.; Beaudry, W. T.; Rohrbaugh, D. K.; Procell, L. R.; Samuel, J. B. Autocatalytic hydrolysis of V-type nerve agents. *J. Org. Chem.* 1996, 61, 8407−8413.