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## Occurrence and Fate of Organic Solvent Residues in Anoxic Groundwater at the Gloucester Landfill, Canada

Suzanne Lesage,\* Richard E. Jackson, Mark W. Priddle, and Peter G. Riemann

National Water Research Institute, Canada Centre for Inland Waters, Burlington, Ontario, Canada L7R 4A6

■ The disposal of organic chemicals in trenches at a waste disposal site near Ottawa, Ontario, Canada, has resulted in the contamination of the underlying aquifer. The organic residues measured in groundwater samples are reported and the mechanisms of contaminant transport in the aquifer discussed. Groundwater samples from monitoring wells and multilevel samplers were analysed by gas chromatography-mass spectrometry. Ultratrace quantities of chlorinated dibenzodioxins and furans were found in groundwaters directly beneath the trenches. A wide variety of volatile compounds were identified and quantitated in samples from the aquifer. The compound of greatest concern was 1,4-dioxane, because of its toxicity and mobility, while that present in greatest concentration was a Freon, F113, which appeared to be very persistent, although three transformation products were identified.

### Introduction

During the 1980s, the contamination of groundwater by toxic organic chemicals became a major environmental concern in North America and Europe. Not only does this contamination directly threaten groundwater supplies used by municipal and rural populations for drinking water, but also the subsurface transport of contaminants threatens surface water supplies, such as the Great Lakes system, which are used by millions of North Americans as their potable water supply.

The danger posed by such chemicals to drinking water supplies has brought about the rapid growth in contaminant hydrogeology, the passing into law of much regulatory legislation, and the creation of numerous consulting and analytical businesses. Despite all this activity, few substantial descriptions of the occurrence and distribution of toxic organic contaminants in groundwater flow systems have appeared in print (1-9). Only a handful of these provide a detailed account of the analytical organic chemistry of the groundwater. It is questionable whether the U.S. EPA priority chemicals list (10) actually defines those chemicals of greatest concern in groundwater contamination studies; furthermore, it is noteworthy that much of the unpublished information on nonpriority pollutants is thought to be flawed (11).

This paper is concerned with the organic contamination of groundwater following incineration of laboratory organic solvents and wood preservatives in trenches at the Gloucester Landfill, near Ottawa, Ontario, Canada, during the period 1969-1980. This site is unique in that the hydrogeological and geochemical properties of the groundwater flow system are well-known (3, 5), the wastes that were

disposed in the trenches are relatively well defined, and the toxic organic chemicals of concern have been monitored intermittently over a period of 8 years by use of a dense network of hydrogeological monitoring devices concentrated in a single aquifer.

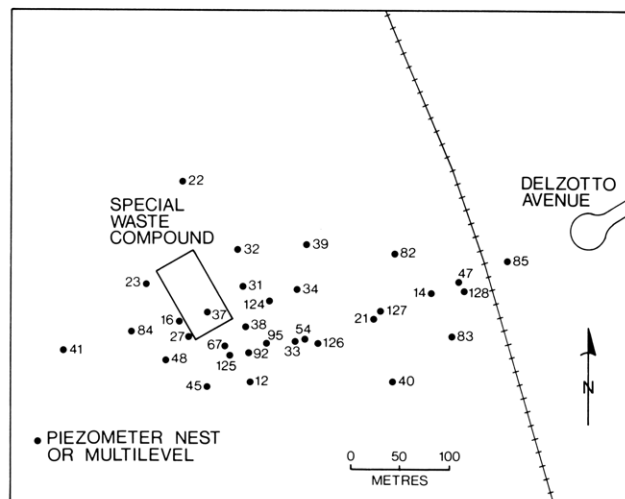
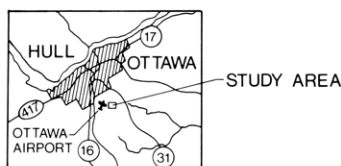
The objectives of the study were (1) the identification and quantitation of toxic organic chemical residues in groundwaters beneath one part of the landfill and (2) the examination of the processes affecting the migration and fate of the identified contaminants. It is shown that the disposal and incineration of the wastes resulted in the probable formation of a series of polychlorinated dioxins and furans and the contamination of the underlying outwash aquifer by organic solvent residues and their transformation products. Furthermore, while it appears that the migration of most of these organic chemicals is governed by aqueous-phase solute transport and sorption, small quantities of nonaqueous-phase liquids may be present beneath the trenches and in the aquifer.

### Site Description

Between 1969 and 1980, the Government of Canada disposed of hazardous wastes, principally organic chemicals from its laboratories in Ottawa, at the nearby Gloucester landfill (Figure 1). The disposal operations took place within a "Special Waste Compound", hereafter referred to as the SWC, located at the southwest corner of the landfill. These operations involved the excavation of trenches (12 m long  $\times$  3 m  $\times$  3 m) into which bottles of liquid chemical wastes were placed and subsequently combusted by detonation of explosive charges set within them. The wastes consisted of nonchlorinated solvents (56.4 m<sup>3</sup>), unspecified wood preservatives (30 m<sup>3</sup>), chlorinated solvents (8.6 m<sup>3</sup>), and smaller amounts of acidic and ferric chloride and other wastes (12).

Detailed soil coring and hydrogeological testing have resulted in the identification of the five hydrostratigraphic units shown in Figure 2. Unit A, the fractured limestone bedrock, is encountered at depths between 25 and 30 m and is partly covered by a till (unit B) of relatively low hydraulic conductivity. Unit C, overlying the till and/or bedrock, is a thick (up to 25 m) sequence of silts, sands, gravel, and boulders known as glacial outwash and forms a semiconfined aquifer beneath the landfill. This outwash is overlain by a discontinuous layer of silt, unit D. The surficial aquifer, unit E, may be up to 10 m thick and its composed of sands and gravels.

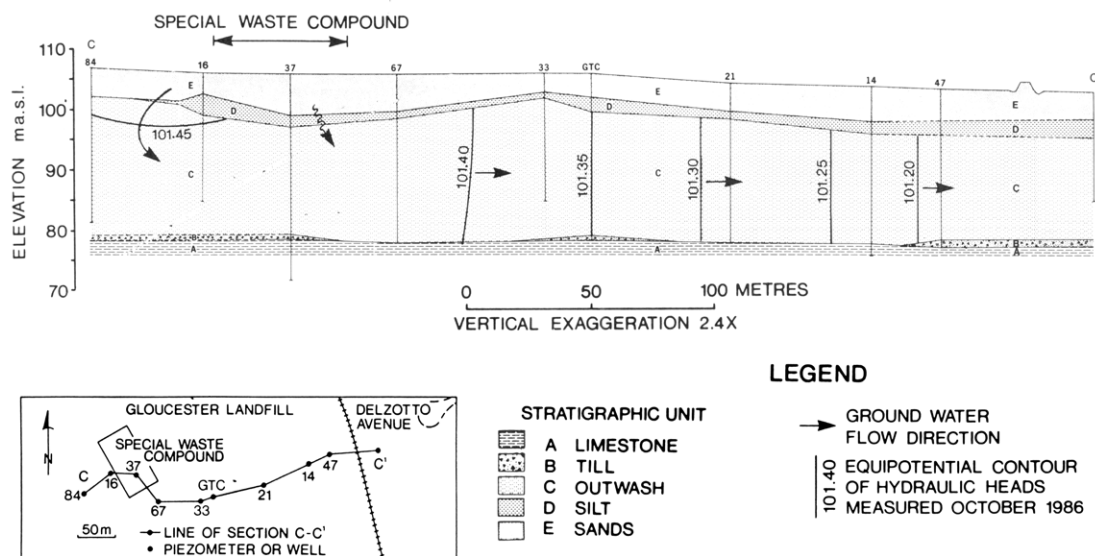
The outwash aquifer, unit C, is composed mineralogically of feldspar (50+%), quartz (20%), and minor



**Figure 1.** Location of study area (upper inset) near Ottawa and the locations of piezometers and multilevels in the monitoring well network. The property boundary of the site is identified by the railroad tracks running northwestward across the figure.

amounts of mica, calcite, dolomite, and hornblende. The organic carbon content of the aquifer sediments averages 0.06%. The aquifer has a mean hydraulic conductivity of  $10^{-4}$  m/s, a porosity of 0.30–0.35, and an average linear groundwater flow velocity of 0.05 m/day (3, 13). The groundwater temperature is in the range 9–10 °C.

The groundwater flow pattern beneath the SWC is shown in Figure 2. Downward groundwater flow occurs from the surficial aquifer, unit E, to the confined outwash aquifer. Some seepage appears to occur through permeable windows in the silty confining layer, unit D. Once solutes enter the outwash aquifer, the vertical equipotential lines dictate that they are transported horizontally to the east. Monitoring of the observation well network shown in Figure 1 has verified that contaminant transport is indeed in this direction (3, 5).



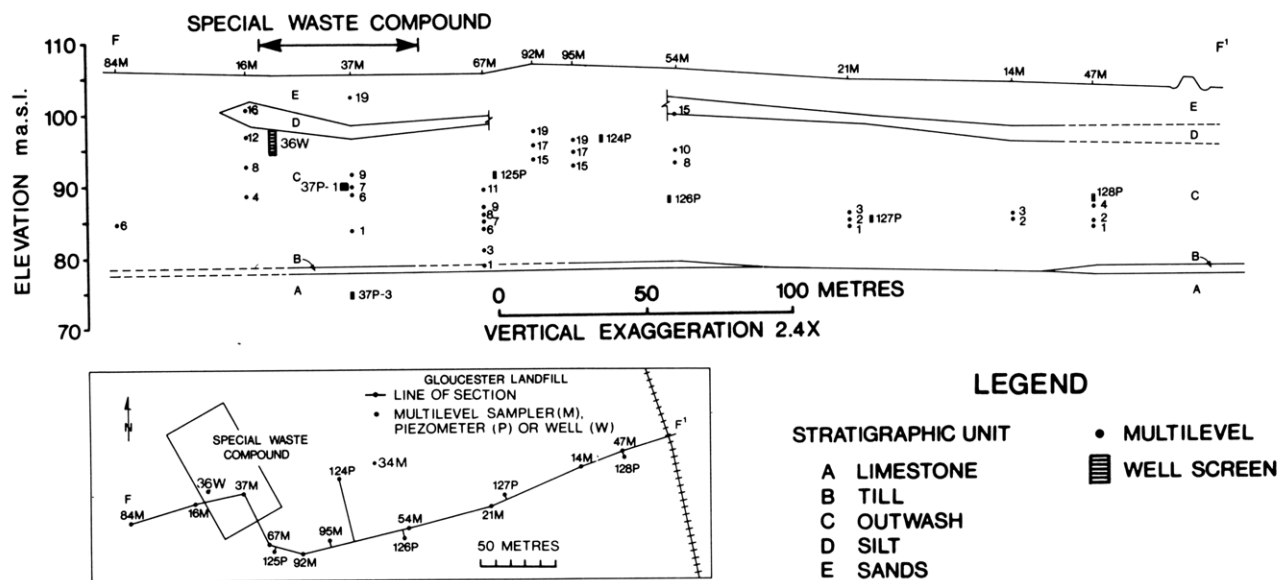
**Figure 2.** Hydraulic head contours in meters above mean sea level (m a.s.l.) along the cross section identified in the inset as measured during October 1986. Squiggly arrow beneath the SWC indicates the potential for leakage through confining unit D. Note vertical exaggeration. Refer to text for description of hydrostratigraphy.

## Sampling and Analysis

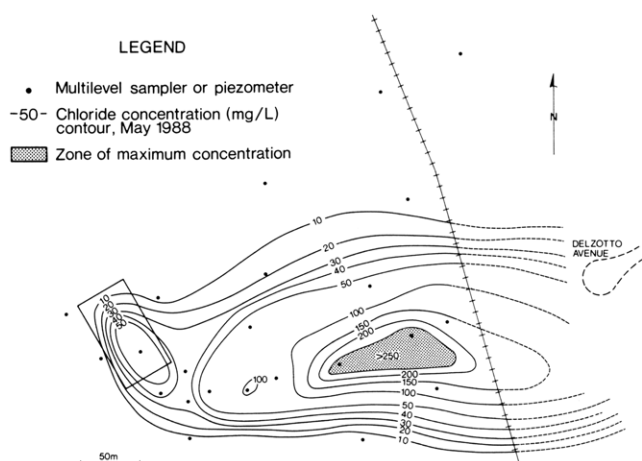
**Sampling.** Groundwater samples were collected during May 1988 from selected monitoring points within the monitoring well network. These points are shown in cross section in Figure 3. A set of five samples was collected from 5-cm-i.d. piezometers (denoted by 124P–128P) each completed with stainless steel screens and dedicated Teflon bladder pumps and inflatable packers (QED Environmental Systems Inc., Ann Arbor, MI), which were inflated above the well screens to contact a stainless steel pipe extension of the screen. Prior to sampling, at least three well-screen volumes were discharged to waste. The remainder of the samples were obtained from bundle-type multilevel samplers (denoted by 16M, 37M etc., ref 14) by using peristaltic pumps. Samples were collected in 25- or 40-mL amber glass vials and kept on ice until reaching the laboratory.

Measurements of pH and  $E_H$  were conducted in the field using combination glass and Pt electrodes fitted into airtight flow cells (3). Dissolved oxygen was determined with an Orbisphere Laboratories (York, ME) 2606 oxygen meter. Sulfide measurements were performed by using a glass/sulfide electrode couple in acidic solution (pH < 5) under closed, continuous-flow conditions (15).

**Analytical Methods.** Volatile organic compound analysis was carried out by following EPA method 624 (16). A Model 810 Unacon (Envirochem Inc., Kemblesville, PA) purge and trap was used to concentrate the analytes. This unit was interfaced to a Hewlett-Packard Model 5970 GC-MSD. The analytical column was a 30-m DB-624 (J&W Scientific), 0.32-mm i.d., 1- $\mu$ m film thickness, directly interfaced into the source of the MSD. The gas chromatograph was cooled to –5 °C with liquid  $CO_2$  to allow the analyses of the purgeable gases and programmed in two ramps to 140 °C (–5 to +35 °C at 10 °C/min and then at 4 °C/min). Difluorobenzene and chlorobenzene- $d_5$  internal standards were added to 10-mL samples immediately prior to purging. Mass acquisition was from 40 to 250 amu at 2 scans/s, but quantitation was done on extracted ions specific for each analyte, using one qualifier ion for confirmation. Analytical standards were prepared from the purest available chemicals purchased from a variety of sources. Unknowns for which no standards were available were tentatively identified by comparison of their spectra to an NBS library containing 42 000 compounds.



**Figure 3.** Vertical location of multilevel inlet tubes and monitoring wells screens along the cross section identified in the inset. As shown in the inset, some wells off the cross section are projected onto the line of section so as to indicate their well depth.



**Figure 4.** Concentration contours (in mg/L) of the maximum values of chloride from multilevel samplers within the outwash aquifer, May 1988. The SWC is outlined at left.

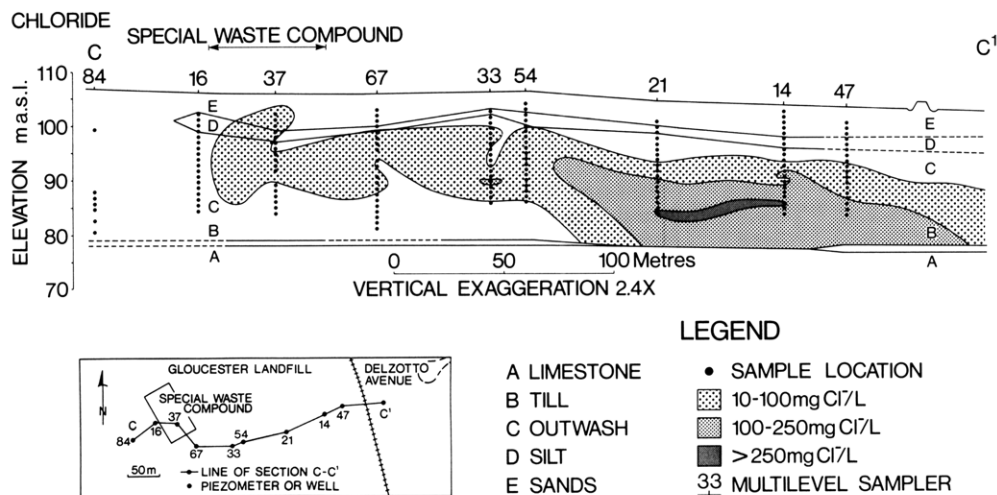
Prior to 1983, the majority of the data was obtained by using an HP7675 purge and trap interfaced to a GC-FID, with some of the analyses being confirmed on a Finnigan 4000 mass spectrometer. From 1984, a combination of FID and Hall detectors was used, until 1987, when the GC-

MSD system described above was acquired.

Semivolatiles and dioxins were analysed by following the EPA 625 and 613 protocols (16), except that a 10-L sample was extracted for dioxins. The analysis was done on a Finnigan 4000 GC-MS (17).

#### Results and Discussion

**Inorganic Parameters.** The distribution of chloride in plan and cross section in the outwash aquifer is shown in Figures 4 and 5, respectively. The first samples collected at the Gloucester landfill in November 1977 showed values less than 5 mg of  $\text{Cl}^-/\text{L}$  in that area (see Figure 4) where concentrations are now in excess of 250 mg of  $\text{Cl}^-/\text{L}$ . Background chloride concentrations in groundwaters from upgradient areas west of the SWC (e.g., 41P; see Figure 1) are less than 10 mg/L. Much higher levels occur beneath and downgradient from the SWC. The vertical configuration of the chloride plume (Figure 5) along a section extending downgradient from the SWC indicates that chloride is transported downward from the trenches within the SWC into the outwash aquifer and then downgradient to the east. The leading edge of this plume has crossed beneath the railroad tracks near Delzotto Ave. (Figure 4). This pattern of migration is consistent with the groundwater flow directions shown in Figure 2. On the basis of groundwater velocity measurements in the



**Figure 5.** Concentration contours (in mg/L) of the chloride plume along the indicated cross section (see inset), May 1988.

**Table I. Volatile Organic Compounds Present in the Outwash Aquifer, May 1988**

compound	concn, $\mu\text{g/L}$	freqcy, <sup>a</sup> %	aq solub, <sup>b</sup> mg/L	% of aq solub <sup>f</sup>
dioxane	~300-2000	13	$\infty^e$	
diethyl ether	<2-658	68	84300 (15) <sup>c</sup>	0.0008
tetrahydrofuran	20-230	32	$\infty^e$	
benzene	0.9-646	65	1780 (20) <sup>c</sup>	0.04
toluene	<0.5-2.5	30	470 (16) <sup>c</sup>	0.0005
ethylbenzene	2	3	140 (15) <sup>c</sup>	0.001
<i>o</i> -xylene	10	3	175 (20) <sup>c</sup>	0.006
2-ethyltoluene	2.1	3	<sup>d</sup>	
dichloromethane	4-60	16	15938	0.0004
trichloromethane	<2-164	51	8983	0.002
tetrachloromethane	<2-7.5	11	683	0.001
chloroethane	<6	3	5742	0.0001
chloroethene	<1-40	13	2763 (25)	0.0015
1,1-dichloroethane	<1-614	54	5193	0.012
1,1-dichloroethene	0.9-60	43	6650	0.0009
1,2-dichloroethane	3.9-58	30	8579	0.0007
<i>trans</i> -1,2-dichloroethene	<1-2.8	16	6260 (25)	0.00004
<i>cis</i> -1,2-dichloroethene	<1-7.5	19	4000	0.0002
1,1,1-trichloroethane	<3-520	43	1707	0.03
1,1,2-trichloroethane	<2	3	4564	0.00004
trichloroethene	7.4-583	41	1061	0.055
tetrachloroethane	5-15	8	763	0.002
tetrachloroethene	2-105	27	149	0.07
1,2-dichloropropane	3.2-11	5	2300	0.0005
chlorobenzene	1.1-134	11	193	0.069
1,1,2-trichloro-1,2,2-trifluoroethane	<5-2725	35	136	2

<sup>a</sup> Frequency of identification of compounds in 37 samples collected from the network shown in Figure 3. <sup>b</sup> Solubilities from ref 22 at 10 °C unless otherwise indicated in parentheses. <sup>c</sup> Solubility from ref 23, temperature in parentheses. <sup>d</sup> No data available. <sup>e</sup> Miscible. <sup>f</sup> Value indicates the percentage of aqueous solubility represented by the maximum measured concentration.

outwash aquifer and assuming no retardation, the plume is advancing at a rate of approximately 5 cm/day.

The pH of shallow groundwaters upgradient of the waste site is on the order of 8.0. Since rainfall and snowmelt are generally acidic (pH <5), there is considerable neutralization occurring during infiltration and percolation as a result of the dissolution of carbonate minerals, which are a significant component of the aquifer materials. Saturation index data (3) indicate that all groundwaters are near or above saturation with respect to calcite and dolomite. Within the chloride plume the pH is generally less than 8.0 and occasionally less than 7.0. This is probably due to the hydrolysis of CO<sub>2</sub> evolved during the oxidation of the organic residues from the SWC, which produces titration alkalinities in excess of 10 mequiv/L as compared with 3-4 mequiv/L in uncontaminated groundwaters (3).

Because of its importance in the transformation of organic compounds, the redox state of the groundwater flow system was determined in detail and has been monitored over an 8-year period. Uncontaminated groundwaters upgradient of the SWC (e.g., 41P) contain measurable quantities of dissolved oxygen (2-6 mg/L) and exhibit  $E_H$  values greater than 0.5 V. Within the chloride plume, groundwaters have nondetectable quantities of dissolved oxygen (i.e., <0.3 mg/L) and  $E_H$  values ranging from -0.04 to +0.2 V; such values have been previously associated with sulfate reducing environments in groundwater flow systems (18, 19). Groundwater sulfide data for the outwash aquifer measured in 1983 from two multilevel monitors (37M and 67M) ranged from 0.005 to 1.1 mg/L. Because the highest levels of organic contamination of the outwash aquifer occurred in the period 1982-1984, prior to some pumping at well 36W, it is important to note that no significant change in the pH or redox environment has occurred over the past 6 years.

**Semivolatile Organic Compounds.** Because most disposals of liquid organic chemicals at the site involved

their incineration, and because pentachlorophenol wastes were thought to be included (i.e., as wood preservatives), the presence of chlorinated dibenzodioxins (CDDs) and dibenzofurans (CDFs) in groundwater was suspected (20). The most prominent species detected in multilevel 37M-19 were octachlorodibenzodioxin and heptachlorodibenzofuran (3). No tetrachlorodibenzodioxins were detected. The total concentrations for CDFs and CDDs were 43 and 59 pg/L, respectively. The distribution pattern was similar to that observed for combustion of chlorinated organic products (21).

Several GC-MS analyses were made in 1983 to detect semivolatile contaminants directly beneath the SWC. Very few compounds were identified, most of which were naturally occurring fatty acids. The only priority pollutant identified was phenol at approximately 90  $\mu\text{g/L}$  in 37P-1. An independent laboratory reported silvex and 2,4-D at approximately 20  $\mu\text{g/L}$  in 36W. More recently, analysis of multilevel sample 92M-15 using a dynamic thermal stripper (purge and trap at 95 °C) did not reveal any anthropogenic semivolatile compounds. This is not entirely surprising given the nature of the waste and also given the fact that most of these compounds have relatively high octanol-water partition coefficients and would not be expected to migrate very far (3, 5).

**Volatile Organic Compounds.** Volatile organic compounds, most of them clearly identifiable laboratory solvents that survived incineration, constitute the bulk of the contaminants at Gloucester and are listed in Tables I and II. Their behavior will be discussed by groups, according to their mobility, with special attention paid to potential biotransformation products and their distribution. Absolute concentrations (see Table III) were generally much lower in May 1988 than during previous sampling periods (3, 5), because of the large volume of contaminated groundwater pumped from well 36W, used for the assessment of alternative treatment technologies, and re-

**Table II. Volatile Organic Compounds Tentatively Identified by Computerized Library Searches<sup>a</sup>**

1,2-dichloro-1,2,2-trifluoroethane	diethyl sulfide
1,1,2-trichloro-1,2-difluoroethane	dimethyl sulfide
dichlorodifluoromethane	methylethyl sulfide
chlorotrifluoroethene	tetrahydrothiophene
diisopropyl ether	chloropropene
pentane	1,2-dibromoethene
methoxybenzene	

<sup>a</sup> All concentrations estimated to be <50 µg/L.

**Table III. Volatile Organic Compounds (in µg/L) Identified in Monitoring Well Network, May 1988<sup>a</sup>**

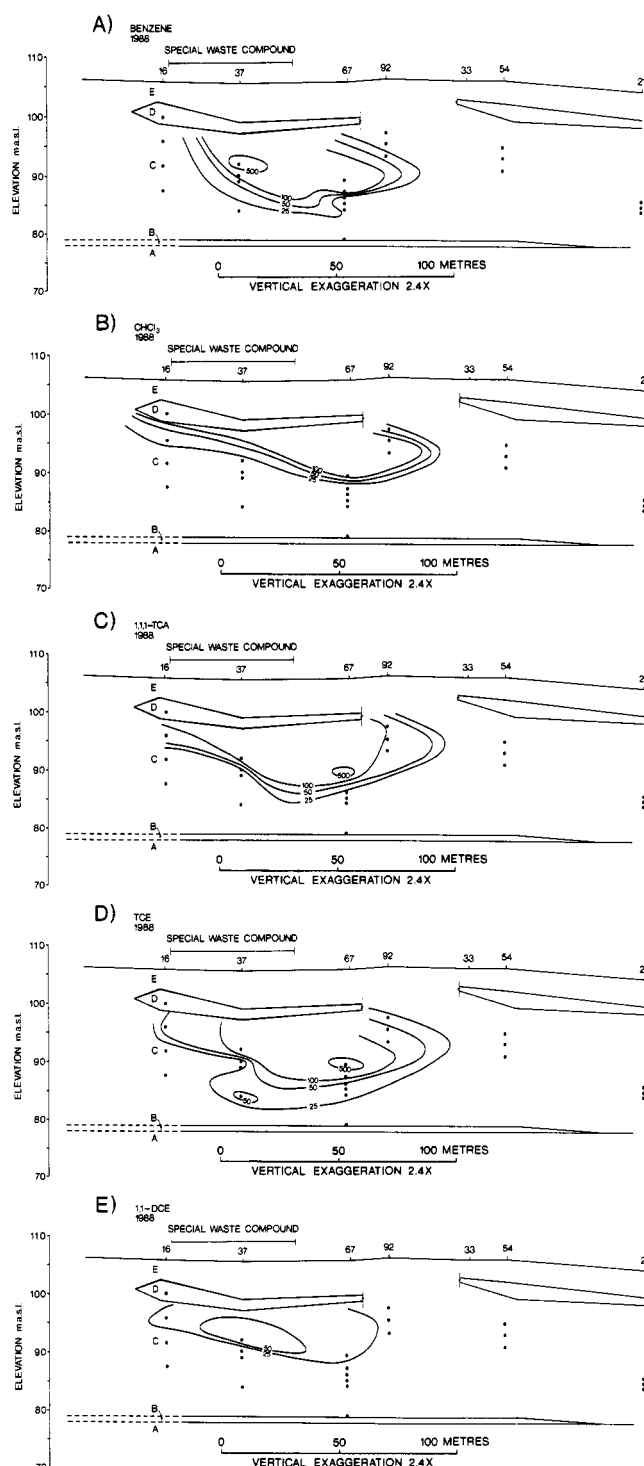
sample	124P	125P	126P	127P	128P
dioxane				~330	
diethyl ether	643	72	331	122	
tetrahydrofuran	70		230	180	
benzene	2.8	120			
toluene		3			
ethylbenzene		3			
<i>m</i> - + <i>p</i> -xylene		2.6			
<i>o</i> -xylene		10			
trichloromethane		52			<2
tetrachloromethane					<4
chloroethane	<1				
1,1-dichloroethane	2.6	24			0.9
1,2-dichloroethane	10.3	14			
1,1-dichloroethene		155			<2
<i>trans</i> -1,2-dichloroethene					<1
<i>cis</i> -1,2-dichloroethene					<1
1,1,1-trichloroethane		193			<3
trichloroethene		505			
tetrachloroethene		60			
1,2-dichloropropane		12			
chlorobenzene		68			
1,1,2-trichloro-1,2,2-trifluoroethane		200			

<sup>a</sup> Blank spaces indicate compound not detected.

turned to the aquifer through 36W (Figure 3). These operations only affected groundwater quality directly beneath the SWC, where they caused a dilution of concentrations.

**(a) Aliphatic Ethers.** These compounds are of particular concern because of their rapid migration in the aquifer (3, 5) as demonstrated by their presence in 126P and 127P, 100 and 200 m away, respectively, from the source (Table III). The apparent center of mass of the diethyl ether and tetrahydrofuran plume moved from 34M to 21M (80 m) from 1982 to 1988. The area of highest concentration of dioxane moved from 21M in 1982 to 47M (100 m) in 1988. The movement of dioxane is of special concern because it has been recognized as a carcinogen. Although the U.S. EPA has not officially classified this chemical, a 7 µg/L drinking water concentration was estimated to increase cancer risk by 1 in a population of 10<sup>6</sup> (24). The current analytical methodology (25) only achieves a practical detection limit of 150 µg/L, making the monitoring of the dioxane plume difficult. Also, this compound appears to have been refractory to degradation in the anoxic environment because its concentration has not changed significantly over time (3).

**(b) Aromatic Hydrocarbons.** The concentration of these contaminants was very low, except for benzene. Therefore, it is most likely that there were no petroleum products other than laboratory solvents disposed of at the site, since one would then expect to find a larger number of alkylbenzenes. Benzene concentrations were reduced

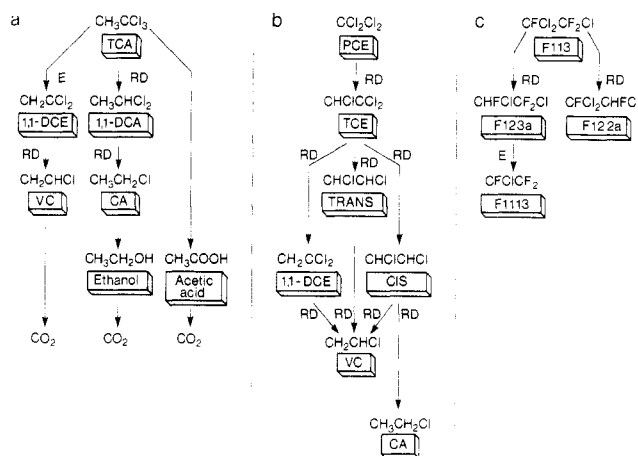


**Figure 6.** Concentration contours (in µg/L) of (A) benzene, (B) trichloromethane, (C) 1,1,1-trichloroethane, (D) trichloroethene, and (E) 1,1-dichloroethene along the cross section shown in Figure 3, May 1988.

between 1982 and 1988 from 17 to 0.6 mg/L, the highest concentration still residing at the point of origin and low level residues (10 µg/L) having migrated 100 m (54M; see Figure 6A).

This reduction is largely attributable to the experimental remedial operations and dispersion. From evidence gathered in microcosm studies (26, 27) and in an anoxic aquifer elsewhere (28), biodegradation of benzene in the Gloucester aquifer was expected to be negligible because of the lack of oxygen.

**(c) Chlorinated Aliphatics.** Plumes for these compounds as found in May 1988 are depicted in Figure 6B-E. The areas of highest concentration for trichloro-



**Figure 7.** Proposed anoxic biotransformation pathways for (a) 1,1,1-trichloroethane (TCA) under methanogenic conditions (ref 29), (b) tetrachloroethene (PCE) (ref 30), and (c) 1,1,2,2-trichloro-1,2,2-trifluoroethane (F113) (this paper). See text for other abbreviations. RD, reductive dehalogenation reaction. E, elimination or dehydrodehalogenation reaction.

**Table IV. Product Distribution Expressed as Percentage of Total Chlorinated Ethanes/Ethenes Found in 37M, 67M, and 92M**

compound	1983	1988
TCA	27.3	27.6
1,1-DCA	39.5	25.4
1,1-DCE	1.4	5.1
PCE	9.7	3.3
TCE	22.0	36.8
CIS	na <sup>a</sup>	0.5
TRANS	0.1	0.2
VC	na <sup>a</sup>	1.0

<sup>a</sup> na, not available.

methane ( $\text{CHCl}_3$ ), 1,1,1-trichloroethane (TCA), and trichloroethene (TCE) occur at multilevel 67M, 40 m down-gradient from the disposal zone, whereas that of the 1,1-dichloroethene (1,1-DCE) degradation product still resides in the disposal zone.

Degradation of tetrachloroethene (PCE) and TCA appears to have occurred based on the presence in the same or adjacent wells of several compounds such as 1,1-dichloroethane (1,1-DCA), chloroethene (VC), *cis*- and *trans*-1,2-dichloroethene (CIS and TRANS), and 1,1-DCE (Tables III and IV, Figure 7), which are known transformation products (29) and are not common laboratory solvents. Most samples contained both TCA and TCE and mixtures of their respective metabolites such that it is difficult to ascertain which pathway predominates, since some metabolites such as 1,1-DCE and VC are common to both. Possible inferences from spatial distribution are obscured because of the physical disturbances of the groundwater. By integrating the concentration over the wells that have shown greatest contamination over the time period and considering the total product distribution, it is possible to evaluate the results of biotransformation without having to consider differences in analytical methodologies, absolute concentrations, or the transport component. The relative product distributions for 1983 and 1988 are listed in Table IV. From this data, it is possible to infer that degradation was indeed occurring since lesser chlorinated compounds increased relative to the more highly chlorinated compounds.

(d) **Freons.** The presence of 1,1,2-trichloro-1,2,2-trifluoroethane (F113) had not been reported initially.

probably because the analytical methodology was not adequate. Its presence in a laboratory waste disposal site such as Gloucester is not surprising because this solvent is used in oil and grease determinations. Its mobility would be expected to be similar to that of PCE because their octanol-water partition coefficients are similar ( $\log K_{ow}$  2.57 for F113 vs 2.60 for PCE; ref 32), and indeed it had migrated to the same area. It is much more refractory to biological transformation and is now the compound found in largest concentration at the site (2.7 mg/L in 67M-11), more than 5 times the current maximum TCE and PCE concentrations. Unfortunately, no historical disposal data are available for F113, which means that its attenuation over time cannot be assessed.

1,2-Dichloro-1,2,2-trifluoroethane (F123a) was also found in the same samples, but at much lower concentrations (10–50  $\mu\text{g/L}$ ) than F113. F123a could conceivably have been present as an impurity in F113. According to the manufacturer (33), it can comprise up to 0.07% of the product in the synthesis reactor, prior to initial purification. The concentration of F123a found in the samples comprised from 0.5 to 50% of the F113 concentration, far in excess of the possible impurity level. Furthermore, a sample of the technical product as sold to redistillers was analyzed and found not to contain any detectable F123a.

The possibility of the formation of F123a by pyrolysis was also considered. Indeed, F123a has been identified in the combustion products of F113 in the presence of steel, copper, and lubricating oil (34). However, the major product of combustion they observed was chlorotrifluoroethene (F1113), which was also identified in multi-level 67M-11 at an estimated concentration of  $<10 \mu\text{g/L}$ . Therefore, the observed degradation product ratio (F123a/F1113) was the reverse of what would be expected from combustion of F113 alone.

F123a could also have been the product of in situ microbial degradation. In support of this hypothesis was the fact that in spite of their predicted higher mobility, F123a and F1113 were found in the same multilevels as F113, and their ratio was not consistent with the known pyrolysis products. Furthermore, these compounds were found in the midst of an anoxic zone where there was evidence of sulfate reduction. A possible pathway for the formation of F1113 from F113 is shown in Figure 7c. The first reaction is one of reductive dehalogenation, followed by the elimination of HCl to form the olefin. These two reactions have been proposed in the degradation of TCA to VC (Figure 7a). The mechanism of the reaction has been postulated as involving free-radical formation involving cytochrome P-450 in the case of the metabolism of haloethane (2-bromo-2-chloro-1,1,1-trifluoroethane) (35). The defluorination product 1,1,2-trichloro-1,2-difluoroethane (F122a) was also identified in low concentration ( $<5 \mu\text{g/L}$ ). It most likely arises via the same free-radical mechanism.

Additional experiments were conducted in collaboration with several groups of researchers to verify the biodegradability of F113. The formation of free radicals in the liver of rats exposed to F113 was proven by using electron-spin resonance with a spin-trapping agent (36). The reaction was blocked by metyrapone, a cytochrome P-450 inhibitor, proving that the enzyme system that has been associated with the reductive dehalogenation of chlorinated ethanes is also responsible for the metabolism of F113. This is the first evidence of F113 metabolism in mammalian systems. To verify its biodegradability in anaerobic groundwater, F113 was introduced into fixed biofilm reactors (37). The metabolite F123a was observed in the effluent of reactors containing either sulfate-reducing or



methanogenic bacteria. In a third experiment where F113 was incubated with anaerobic landfill leachate, both F123a and F1113 were formed (38). The product F122a was not found in these experiments, but it is possible either that its concentration was too low or that the incubation period or media were inadequate. Loss of fluorine has been shown in the metabolism of halothane (37).

F113 is gradually replacing PCE as a dry-cleaning solvent and is widely used in the electronic industry, where it caused substantial groundwater contamination (39). This work shows that it may be even more of a threat to groundwater, because it appears more persistent than PCE. It was found to act as a cocarcinogen with polyaromatic hydrocarbons without any inference to the possible pathway (40). Both F113 and F123a were found to be non-mutagenic in Ames tests; however, the authors cautioned this may not be a valid indicator of mammalian toxicity (41). F1113 is used in its gaseous form in the polymer industry and is classified as highly toxic (268 mg/kg oral, ref 42); its presence in groundwater is, therefore, of concern.

**(e) Sulfur-Containing Compounds.** As noted above, that part of the outwash aquifer associated with the chloroalkane/chloroalkene plume is a sulfide redox zone, and the presence of organosulfur compounds was suspected from their characteristic odor. The organosulfur compounds identified (Table II) were dimethyl sulfide, diethyl sulfide, methyl ethyl sulfide, and tetrahydrothiophene in monitors 37M, 67M, and 125P.

Because these were found in areas where chlorinated organic solvents were present in high concentrations, the possibility of reaction between the two species was considered, but no chlorinated organosulfur products were identified. Indeed, although sulfides may react with halogenated aliphatics to form mercaptans (43), and although sulfur nucleophiles are more reactive than their oxygen analogues, their relative concentrations in aqueous systems are so much smaller that these reactions are seldom observed (44). The formation of chloroalkyl sulfones, which are resistant to biodegradation, has been reported (45), but their presence has been attributed to discharge from biologically treated kraft mill effluents, which means that their occurrence would constitute an exception rather than the norm in groundwater systems.

### Summary of Conclusions

A wide variety of toxic organic chemical residues were identified and quantitated in anoxic (sulfate-reducing) groundwaters beneath the SWC at the Gloucester Landfill. These include polychlorinated dibenzodioxins and dibenzofurans, aliphatic ethers, aromatic and halogenated aliphatic hydrocarbons and volatile sulfur compounds. The aliphatic ethers are very mobile, as is chloride; however, because it is also toxic and persistent, 1,4-dioxane is the contaminant of greatest concern in groundwater. The chlorinated aliphatics showed evidence of in situ transformation with the detection of several lesser chlorinated aliphatics such as chloroethene and 1,1-dichloroethene. The organic chemical found in greatest concentration was the Freon F113. Although obviously very persistent in the subsurface, it, too, appeared to have undergone transformation as one defluorinated and two dechlorinated products, one of which is known to be toxic (F-1113), were identified.

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**Registry No.** TCA, 71-55-6; TCE, 79-01-6; 1,1-DCA, 75-34-3; *cis*-1,2-DCE, 156-59-2; *trans*-1,2-DCE, 156-60-5; PCE, 127-18-4; VC, 75-01-4; CA, 75-00-3; F113a, 76-13-1; 1,4-dioxane, 123-91-1; diethyl ether, 60-29-7; tetrahydrofuran, 109-99-9; benzene, 71-43-2; toluene, 108-88-3; ethylbenzene, 100-41-4; *o*-xylene, 95-47-6; 2-ethyltoluene, 611-14-3; dichloromethane, 75-09-2; trichloromethane, 67-66-3; tetrachloromethane, 56-23-5; 1,1-dichloroethane, 75-35-4; 1,2-dichloroethane, 107-06-2; 1,1,2-trichloroethane, 79-00-5; tetrachloroethane, 25322-20-7; 1,2-dichloropropane, 78-87-5; chlorobenzene, 108-90-7.

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## Acid-Catalyzed Oxidation of 2,4-Dichlorophenoxyacetic Acid by Ammonium Nitrate in Aqueous Solution

David D. Leavitt<sup>†</sup> and Martin A. Abraham\*

Department of Chemical Engineering, University of Tulsa, Tulsa, Oklahoma 74104

■ 2,4-Dichlorophenoxyacetic acid (2,4-D) was oxidized to CO<sub>2</sub> and water by homogeneous, liquid-phase reaction with ammonium nitrate at temperatures between 250 and 450 °F and pressures below 100 psi. N<sub>2</sub> and N<sub>2</sub>O were produced from the thermal decomposition of the ammonium nitrate oxidant. An unexpected maximum in conversion was observed at an intermediate reaction temperature, which was consistent with rapid thermal decomposition of the NH<sub>4</sub>NO<sub>3</sub> oxidant. Postulated reaction pathways consisting of simultaneous oxidation of 2,4-D and decomposition of the oxidant allowed estimation of kinetic constants from best-fit analysis of the data. The proposed reaction model provided a mathematical description of 2,4-D conversion, which allowed extrapolation of the results to reaction conditions and reactor configurations that were not experimentally investigated.

### Introduction

Oxidation of organic materials to CO<sub>2</sub> and H<sub>2</sub>O provides a suitable (although certainly not the only) means of reducing the toxicity of many waste products. These wastes may be present in water, in solids, or in air, typically as complicated mixtures of many components within a solvent stream. Depending on the concentration and the phase of the undesired organic components, a variety of destruction processes may be used, including thermal treatment techniques such as incineration or wet air oxidation (1), pure chemical processes such as ozonation and chlorination (2), and biological oxidation processes (3). Physical treatment may also be accomplished to adjust the concentration of the pollutant prior to further processing. Particularly, in cases involving cleanup of contaminated

solids, physical removal of the organic contaminant from the solid is often accomplished through solvent extraction prior to destructive oxidation of the waste (4, 5) through one of the treatment methods mentioned above.

Regardless of the specific wastes within a particular waste stream or the specific oxidation technique that is being considered, an understanding of the oxidation reaction chemistry is beneficial for process development. In addition, knowledge of the reaction pathways and kinetics permits one to predict, a priori, the conversion of specific wastes within a waste stream. Through kinetic measurements, it is possible to extend experimental results beyond the specific conditions that have been investigated and optimize specific destruction processes. Since organic compounds may be grouped into broad classes of materials that undergo similar reactions, this fundamental kinetic information may be generally applied within these chemical classes.

Unfortunately, the interaction between the many and varied materials present within an industrial waste stream hinders interpretation of results from experiments with actual wastes. For this reason, we chose to accomplish experiments with well-defined systems, wherein known concentrations of selected organic compounds were oxidized. In the current study, pure compounds were used (in place of actual industrial waste) to provide preliminary information on the feasibility of oxidizing chlorinated organic wastes within an aqueous acid. Although the current experiments with single compounds did not approach the complexity of an actual waste stream, fundamental reaction information necessary for the interpretation of future experiments involving multiple components was obtained.

The current study is based on technology developed for the purification of crude phosphoric acid. In that operation, high molecular weight organic components are con-

<sup>†</sup>Current address: Allied-Signal, P.O. Box 580970, Tulsa, OK 74158.