

Abstract

Wagner, Travis B. Factors Controlling Hydrophobic Organic Contaminant Sorption to and Desorption from Municipal Solid Waste (Under the direction of Dr. Detlef R. U. Knappe and Dr. Morton A. Barlaz).

The objectives of this research were to (1) determine the sorption capacity of individual municipal solid waste (MSW) components for tetrachloroethylene (PCE) and *cis*-1,2-dichloroethylene (DCE), (2) evaluate the importance of the amorphous fraction of sorbent organic matter on HOC sorption to polyethylenes, (3) measure the toluene sorption capacity of newsprint samples collected at the Norman, OK, landfill (NLF), (4) determine sorbate and sorbent characteristics that affect HOC sorption, and (5) determine PCE desorption kinetics from individual MSW components. PCE and toluene were selected as model HOCs because they frequently occur in landfill leachates. DCE was of interest because it is a product that forms during the reductive dehalogenation of PCE. The MSW components that were tested included high-density polyethylene (HDPE), medium-density polyethylene (MDPE), low-density polyethylene (LDPE), poly(vinyl chloride) (PVC), a model food and yard waste (rabbit food), office paper, and newsprint. Biodegradable sorbents were evaluated in both fresh and anaerobically degraded form. In addition, the toluene sorption capacity was measured for newsprint samples that were collected from three depths at the NLF. Isotherm experiments were conducted to determine the HOC sorption capacity of individual MSW components in ultrapure water, acidogenic leachate, and methanogenic leachate. Batch desorption tests were conducted in the same liquid phases. The sorbents had been characterized in previous research [i.e., cellulose, hemicellulose, and lignin contents,

elemental analysis, solid-state ^{13}C -nuclear magnetic resonance (NMR) spectra, and BET surface areas].

Single-solute isotherm results showed that PVC had the largest HOC sorption capacity of the MSW components while fresh office paper had the lowest. In general, changes in sorption capacity were negligible when HOC isotherm experiments were conducted in acidogenic and methanogenic leachates. However, organic constituents in acidogenic leachate appeared to have a plasticizing effect on PVC such that HOC sorption capacity decreased and isotherm linearity increased. The importance of the amorphous fraction of sorbent organic matter on HOC sorption capacity was tested by conducting toluene isotherm experiments with three polyethylenes (HDPE, MDPE, and LDPE). Among the polyethylenes, LDPE, the sorbent with the highest amorphous fraction, exhibited the highest sorption capacity while HDPE, the sorbent with the lowest amorphous fraction, exhibited the lowest. For NLF newsprint, the most degraded sample, which was collected near the landfill bottom, exhibited the largest toluene sorption capacity. With respect to sorbent characteristics that control HOC sorption, the increases in the O-alkyl/alkyl ratio of biopolymer composites effectively predicted decreases in HOC sorption capacity. The usefulness of the O-alkyl/alkyl ratio for the prediction of HOC sorption capacities was further demonstrated using literature data for phenanthrene and pyrene sorption to sorbents that were less polar than those evaluated in this study. A comparison of fresh and anaerobically degraded MSW components showed that the O-alkyl/alkyl ratio decreased during degradation. Thus, the overall results of the isotherm study show that the affinity of sorbent organic matter for HOCs increases with increasing

extent of MSW decomposition because of the preferential degradation of polar biopolymers and the recalcitrance of plastics.

Batch desorption tests after an aging time of 30 days showed that PCE desorption from PVC was slowest while that from newsprint and degraded office paper was fastest. Toluene desorption rate predictions for simulated mixed MSW were made for two landfill scenarios: (1) a 1960 MSW composition with a low plastics content and (2) a 1997 MSW composition containing a larger proportion of plastics. Experimental results for the 1960 scenario showed that the model prediction closely matched the experimental data. Additional experiments are required to verify the model prediction for simulated mixed refuse with a 1997 composition. Overall, the results of the desorption tests illustrated that the presence of plastics decreases HOC release rates. Therefore, HOC release rates should be smaller in landfills containing sizable quantities of synthetic polymers.

**Factors Controlling Hydrophobic Organic Contaminant Sorption to and
Desorption from Municipal Solid Waste**

By

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1 Introduction

Before 1980, few restrictions were placed on the codisposal of municipal solid waste (MSW) and industrial waste in landfills. A survey in 1986 indicated that as many as 6,000 operating landfills had once accepted some hazardous waste (US EPA 1988). Many of these sites did not have an engineered liner or leachate collection system. Consequently, groundwater contamination with priority pollutants such as alkylbenzenes and chlorinated aliphatic hydrocarbons is a frequent occurrence (Christensen et al. 1994). Currently, over 15% of the sites on the National Priority List (NPL) of Superfund are municipal landfills that previously accepted hazardous waste (US EPA 2003). It is important to understand the factors that control the fate of contaminants in these landfills to determine management strategies that are both cost-effective and protective of the environment.

Sorption/desorption processes limit both biodegradation (Sanin et al. 2000) and transport (Reinhart et al. 1991a, 1991b, Oman and Rosqvist 1999, Oman 2001) of HOCs in landfills. The bioavailability of sorbed contaminants is reduced due to partitioning into glassy/hard organic matter (Pignatello and Xing 1996, Weber et al. 1995), strong hydrophobic interactions such as encapsulation in paraffinic organic matter (Lerch et al. 1997, Guthrie et al. 1999), and adsorption on hydrophobic micropore surfaces (Nam and Alexander 1998). Bioavailability of HOCs is reduced because these mechanisms greatly decrease contaminant desorption rates into the bulk liquid, where contaminants are readily available to microorganisms (Ogram et al. 1985).

Factors such as sorbent and sorbate properties, dissolved organic compounds in the aqueous phase, pH, and temperature can influence sorption capacities and desorption rates of contaminants. The biodegradation of sorbents also affects HOC sorption in landfills because the organic carbon content of MSW decreases (Reinhart et al. 1990, Pichler and Kögel-Knabner 2000) and the polarity of the remaining organic carbon decreases due to the preferential degradation of polar constituents such as cellulose and hemicellulose over less polar components such as lignin and lipids (Pichler and Kogel-Knabner 2000, Eleazer et al. 1997, Wu et al. 2001). For HOCs sorbed to sediments, contaminant sequestration increased when sorbent hydrophobicity increased as a result of biological activity (Guthrie et al. 1999). Similar effects are expected in landfills, where sorbent organic matter is slowly degraded under methanogenic conditions. When contaminants are exposed to sorbents for long periods of time, as would be expected in landfills, bioavailability of HOCs may also decrease. Slow partitioning of HOCs into glassy organic matter or slow diffusion into micropores could take place, thus reducing the HOC desorption rate and therefore its bioavailability (Hatzinger and Alexander 1995, Pignatello et al. 1993). Landfill leachate contains high concentrations of dissolved organic matter that can affect HOC sorption (Chian 1977, Harmsen 1983, Schultz and Kjeldsen 1986), and some dissolved organic compounds in landfill leachate can bind HOCs (Larsen et al. 1992, Bauer and Herrman 1998). Wu et al. (2001) showed that constituents of acidogenic leachate can act as plasticizers and change a glassy polymer (PVC) to a rubbery state. As a result, toluene isotherms on PVC were linear in acidogenic leachate while they were non-linear in ultrapure water and methanogenic leachate.

A large body literature covers HOC sorption to geosorbents such as soils and sediments but there is a limited understanding of the factors that control sorptive processes in landfills. Landfills differ from soils and sediments because MSW has a large organic carbon content (Barlaz 1998), a large fraction of MSW consists of readily degradable young organic matter (Pichler and Kögel-Knabner 2000, Eleazer et al. 1997), and landfill leachates have a high concentration of dissolved organic carbon (Chian 1977, Harmsen 1983, Schultz and Kjeldsen 1986).

1.1 Factors Controlling HOC Sorption

HOC sorption is strongly influenced by the properties of the sorbate (nature, size, and reactivity of functional groups) (Brusseu and Rao 1989, Brusseu 1991). Studies conducted over the past twenty years with soil and sediment samples showed that sorption capacity is affected by sorbate hydrophobicity. Specifically, a linear correlation exists between the partition coefficient describing HOC sorption to the sorbent organic matter ($\log K_{oc}$) and $\log K_{ow}$, the sorbate octanol/water partition coefficient (Karickhoff et al. 1979, Schwarzenbach and Westall 1981). These studies showed that sorption capacity increases with increasing K_{ow} , or hydrophobicity, of the sorbate. Similar correlations have been developed for HOC sorption to mixed MSW and to individual MSW components (Reinhart et al. 1990, Wu et al. 2001). Wu et al. (2001) found that the relationship between $\log K_{oc}$ and $\log K_{ow}$ was not unique for individual MSW components. Therefore, the importance of sorbent organic matter characteristics on HOC uptake must also be considered before the HOC sorption capacity for a given sorbent/sorbate pair can be predicted. Instead of K_{ow} , the aqueous solubility (S_w) of sorbates has also been used to evaluate sorbate effects on sorption

capacity. Grathwohl and Rahman (2002) successfully normalized HOC isotherm data by dividing equilibrium liquid phase concentrations by the aqueous solubility of the HOC. For HOCs that are a solid at the temperature of the isotherm experiment, the supercooled liquid solubility (S_{scl}) is used to normalize the data instead of the aqueous solubility. From the isotherm data, the organic carbon fraction of the sorbent, and the solubility of a compound, a unit equivalent partition coefficient ($K_{oc}^* = K_{oc}S$) can be calculated. Using solubility normalized isotherms, the prediction of HOC sorption capacities for different contaminants on a particular sorbent is possible from isotherm data of just one sample compound.

Sorbent effects also play an important role in HOC sorption. The polarity of sorbent organic matter is controlled by its oxygen and nitrogen contents (Garbarini and Lion 1986, Kile et al. 1995, Grathwohl 1990). The polarity index of a sorbent $[(O+N)/C]$, which is calculated from elemental analysis data of the sorbent organic matter, describes the ratio of polar to non-polar groups. As the polarity index of a sorbent increases, the HOC sorption capacity, as measured by K_{oc} , decreases (Rutherford et al. 1992, Xing et al. 1994a, b). Wu et al. (2001) also found that the sorption capacity of MSW components decreased with increasing polarity index of a sorbent. Despite a good correlation between sorption capacity and sorbent polarity index, differences in sorption capacity were caused by small amounts of lipophilic extractives and these differences were not captured well by the polarity index (Wu et al. 2001). ^{13}C -NMR spectra data were used to define a new sorbent organic matter descriptor, the O-alkyl to alkyl ratio, to recognize the importance of both sorbent polarity and lipophilic extractives content on HOC sorption. O-alkyl regions are attributed to polar groups such as carbohydrates, alcohols, esters, and amines while alkyl regions represent non-polar paraffinic carbon

(Chefetz et al. 2000). Aliphatic poly(methylene) groups in the alkyl region have a high affinity for pyrene and phenanthrene and are expected to control the sorption of other HOCs as well (Chefetz et al. 2000, Salloum et al. 2002). Mao et al. (2002) also found a significant positive correlation between non-polar, aliphatic, poly(methylene)-rich domains in natural organic matter and phenanthrene sorption capacity. In contrast, they found little dependence of phenanthrene sorption on other structural components of organic matter, such as aromatic or polar groups. The O-alkyl to alkyl ratio is also a good indicator of the degradation state of organic matter since cellulose and hemicellulose attributed to the O-alkyl region are readily degradable compared to the paraffinic materials represented by the alkyl region (Baldock et al. 1997).

1.2 Desorption

To describe HOC desorption rates from soils and sediments, a one-compartment diffusion model was initially evaluated by Harmon and Roberts. (1994a). This model underestimated the experimentally observed desorption rate at early times and overestimated it at later times (Harmon and Roberts 1994a). Thus, a single-parameter model does not take into account the heterogeneity of the sorbent and therefore does not accurately estimate desorption kinetics. Since sorbent organic matter contains a glassy fraction, from which HOCs desorb slowly, and a rubbery fraction, from which HOCs desorb more rapidly, a two-compartment model was proposed to describe HOC desorption rates from geosorbents (Carroll et al. 1994). Karickhoff and Morris (1985) found that a two-compartment model described desorption kinetics of a heterogeneous soil quite well. Because MSW primarily consist of heterogeneous biopolymer composites, a two-compartment model was used by Wu (2002) to

determine desorption rate parameters for fresh and degraded forms of office paper, newsprint, and rabbit food. In contrast, a one-compartment diffusion model was used by Wu (2002) to describe alkybenzene desorption rates from homogeneous plastics (HDPE and PVC).

1.3 Research Objectives

The principal objectives of this research were to:

1. Measure the sorption capacity of individual MSW components for PCE and DCE
2. Evaluate the importance of the amorphous fraction of sorbent organic matter on toluene sorption capacity using low-, medium-, and high-density polyethylenes.
3. Measure toluene sorption capacities of newsprint samples collected at three depths from the Norman, OK, landfill, and compare the results with toluene sorption capacities of fresh and laboratory-degraded newsprint samples.
4. Determine sorbate and sorbent characteristics that control HOC sorption to MSW components using PCE and DCE isotherm data obtained in this study as well as toluene and *o*-xylene isotherm data of Wu et al. (2001).
5. Determine PCE desorption kinetics from MSW components.

2 Experimental Design and Methods

2.1 MSW Components

The primary components of MSW are paper (38.6%), yard waste (12.8%), food waste (12.1%), plastics (9.9% with high and low density polyethylene as the major contributors), metals (7.7%), rubber/leather/textiles (6.8%), glass (5.5%), and wood (5.3%, US EPA 1999).

Major components expected to sorb HOCs include paper, food and yard waste, and plastics. Office paper and newsprint were chosen to represent the range of paper types in landfills. Newsprint is a mechanical pulp that contains nearly all of the lignin present in wood while office paper is a chemical pulp from which most of the lignin has been removed. Newsprint represents about 5.1% of MSW and office paper 3.2% (US EPA 1999). Newsprint was collected from The News & Observer Recycling Division (News & Observer Publishing Co., Garner, NC). Office paper was collected from the NC State University recycling center. Upon receipt, both office paper and newsprint were shredded into 2-cm squares. Rabbit food (Manna Pro® Corporation, St. Louis, MO) was used to represent a combination of food and yard waste. Rabbit food contains both simple and complex carbohydrates as well as proteins in the form of alfalfa, wheat, soy, and oat products, and it has been used to represent food and yard waste previously (Schwab 1994). High-density polyethylene [HDPE] and poly(vinyl chloride) [PVC] (Catalog numbers 42,799-3 and 18,958-8, Sigma-Aldrich Milwaukee, WI) were tested to represent rubbery and glassy plastic components of MSW, respectively. Medium-density polyethylene [MDPE] and low-density polyethylene [LDPE] were used along with HDPE to determine the importance of the amorphous polymer fraction on toluene sorption capacity. Pure cellulose (filter paper) was also tested as a sorbent to determine the importance of sizing agents used in office paper on HOC sorption capacity.

Office paper, newsprint, and rabbit food were prepared anaerobically in laboratory reactors using leachate recycle and neutralization as described (Eleazer et al. 1997), with the exception that substrates were seeded with anaerobic sewage sludge rather than well-decomposed refuse. Reactors containing shredded office paper and newsprint were operated

for about 9 months to obtain materials that, based on their methane yield, were significantly decomposed relative to the starting materials. Reactors containing rabbit food were operated in semi-batch mode to control excessive volatile fatty acid (VFA) production that otherwise resulted from its rapid biodegradation. Over a 9-month period, rabbit food was added to reactors on a daily to weekly basis, depending on the stability of methane production in the system.

Newsprint samples were also collected from three cores at the Norman, Oklahoma landfill, in April and May of 2001. These samples were obtained from the research group of Dr. Mark Nanny in the School of Civil Engineering and Environmental Science at the University of Oklahoma in Norman, OK. A Macro-Core Piston Rod Sampler (geoprobe®system) was used by a geoprobe direct push machine to obtain newsprint samples from various depths within the landfill. Aerial photographs of the landfill site indicate that the area where samples were taken accepted municipal solid waste from 1970 to 1985. A 1.5 inch diameter probe rod was used to collect samples in four foot intervals until the bottom of the landfill was reached (approximately 40 feet from the cover). Core samples from 12-16 feet, 20-24 feet, and 32-36 feet from the top of the landfill were selected for analysis to represent different degradation stages of the waste, i.e., top layer, middle layer, and bottom layer, respectively. The samples were stored on ice until they reached the University of Oklahoma, where they were then stored at 4°C. Newsprint samples were removed by visual inspection from the core samples and soaked in nanopure water for 24 hours, then freeze-dried and ground with a mortar and pestle prior to analysis.

2.2 MSW Component Characterization

MSW component characterization was conducted by Wu et al (2001). Sorbents were analyzed for cellulose, hemicellulose, lignin, lipophilic extractives, crude protein, ash content, and BET surface area. These values are listed in Table 2.1. Elemental analysis of acid washed sorbents was conducted to determine carbon, hydrogen, nitrogen, oxygen, and ash contents (Table 2.2). ^{13}C nuclear magnetic resonance (NMR) spectra were obtained from the research group of Dr. Mark Nanny for biopolymer-containing sorbents to determine the distribution of carbonyl, aromatic, O-alkyl, and alkyl functional groups (Table 2.3). The NMR data were used to calculate the O-alkyl/alkyl ratio (Table 2.3).

2.3 Sorbates

Toluene (an alkylbenzene), PCE, and DCE (chlorinated aliphatics) were selected because they are frequently detected in landfill leachates (Christensen et al. 1994), sorb to refuse (Sanin et al. 2000); and biodegrade [toluene (Sanin et al. 2000), PCE and DCE (Reinhart et al. 1991)] in the refuse ecosystem. Experiments were conducted with ^{14}C -labeled compounds (Sigma-Aldrich). Stock solutions were prepared by dissolving neat ^{14}C -labeled compounds in 6 mL methanol (HPLC-grade, Fisher Scientific, Pittsburgh, PA) and stored at -10°C .

Toluene, PCE, and DCE concentrations were assayed by liquid scintillation counting. Purity of ^{14}C -labeled compounds was assessed by gas chromatographic analysis that showed peaks corresponding to toluene, PCE, and DCE only. Sparging tests showed that 99.85% and 99.9% of the ^{14}C was volatile in aqueous toluene and DCE solutions, respectively.

Table 2.1. Sorbent characteristics (from Wu et al. 2001) ^a

Sorbent	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Lipophilic extractives (%)	Crude protein (%)	Ash (Wt %)	f _{oc}	BET surface area (m ² /g)
Poly(vinyl chloride)	N/A ^b	N/A	N/A	N/A	N/A	0.00	0.389	0.8
High density polyethylene	N/A	N/A	N/A	N/A	N/A	0.01	0.876	0.6
Fresh office paper	64.7	13.0	0.93	0.7	0.31	11.6	0.373	2.8
Degraded office paper	36.2	6.9	4.8	3.3	4.99	38.4	0.278	6.0
Fresh newsprint	48.3	18.1	22.1	1.6	0.44	2.0	0.451	2.6
Degraded newsprint	35.1	16.0	32.3	1.4	3.74	6.4	0.455	3.4
Fresh rabbit food	30.6	15.4	9.5	4.9	18.1	7.7	0.423	0.6
Degraded rabbit food	7.1	5.7	25.2	4.5	20.6	34.5	0.329	0.5

^a values are averages of replicate analyses

^b N/A: not analyzed

Table 2.2. Elemental composition of acid-washed sorbents (from Wu et al. 2001) ^{a, b}

Sorbent	C (Wt.%)	H (Wt.%)	N (Wt.%)	O (Wt.%)	Ash (Wt.%)	Total (Wt.%)	(O+N)/ C ^c
Poly(vinyl chloride) ^d	38.9	4.7	0.1	1.7	0.0	102.1 ^e	- ^f
High density polyethylene ^d	87.6	14.5	0.08	0.1	0.01	102.3	- ^f
Fresh office paper	41.7	5.2	0.04	49.6	1.1	97.6	0.89
Degraded office paper	41.7	5.0	0.8	43.4	7.6	98.5	0.80
Fresh newsprint	45.0	4.9	0.07	47.5	2.3	99.8	0.79
Degraded newsprint	47.6	5.0	0.4	43.7	2.0	98.7	0.70
Fresh rabbit food	45.3	5.4	2.4	45.4	1.1	99.6	0.80
Degraded rabbit food	48.8	5.3	3.2	39.0	2.9	99.2	0.66

^a Values are averages of replicate analyses

^b Sulfur content was not measured but should be 0.4 % (wt/wt) or less for the tested materials (Tchobanoglous et al. 1993)

^c Atomic ratio on a dry, ash-free basis

^d HDPE and PVC were not acid-washed

^e Includes theoretical chlorine content of 56.7%

^f Ratios for PVC and HDPE are not meaningful because of very low oxygen and nitrogen contents

Table 2.3. Distribution of functional groups in biopolymer composites based on ^{13}C CP-MAS NMR spectra

Sorbent	Carbonyl ^a (%)	Aromatic ^b (%)	O-alkyl ^c (%)	Alkyl ^d (%)	O-alkyl/alkyl
Fresh office paper ^e	0.9	3.4	94.0	1.7	55.3
Degraded office paper ^e	2.7	8.0	82.8	6.5	12.7
Fresh newsprint ^e	2.1	12.2	82.4	3.3	25.0
Degraded newsprint ^e	2.8	17.1	74.8	5.4	13.9
Fresh rabbit food ^e	7.8	3.4	79.6	9.3	8.6
Degraded rabbit food ^e	8.3	10.9	63.4	17.4	3.6
Newsprint Top Layer (12'-16')	0.6	18.9	70.1	10.5	6.7
Newsprint Middle Layer (20'-24')	1.7	17.8	72.6	7.9	9.2
Newsprint Bottom Layer (32'-36')	1.3	23.4	61.3	14	4.4

Chemical shifts: ^a 200-160 ppm; ^b 160-110 ppm; ^c 110-50 ppm; ^d 50-0 ppm

^efrom Wu et al. 2001

Two PCE stock solutions were used in isotherm and desorption test with purities of 94.0% and 97.0%. The remaining non-volatile ^{14}C counts were non-sorbable, and all data were corrected for this non-sorbing impurity.

Following receipt of ^{14}C -PCE from the manufacturer, it was purified through a nitrogen gas sparging procedure. Six milliliters of PCE-methanol stock were injected into 100 mL DI water in a serum bottle with a Teflon-lined stopper. Nitrogen gas was introduced into the bottom of the 106-mL solution at a flow rate of about 10 mL/min. The off-gas was trapped in two glass ampules placed in series with each containing 10 mL HPLC-grade methanol. A third vial containing scintillation liquid was placed after the two methanol traps. Both glass ampules were sealed using Swagelok fittings and connected by stainless steel tubing. After two hours of sparging, purified PCE solutions were transferred separately into two amber bottles (10 mL) and stored at 5°C. PCE purities and specific activities in both ampules were determined using gas chromatography (GC) and scintillation counting.

^{14}C -DCE was prepared by growing *Dehalospirillum multivorans* on ^{14}C -PCE in 500 mL anaerobic growth medium in a serum bottle capped with a Teflon-lined stopper. The biological degradation products were *cis*-1,2-DCE and trace amount of *trans*-1,2-DCE. ^{14}C -DCE was purified using the same sparging procedure as above for ^{14}C -PCE except that the serum bottles were placed in a 60°C water bath.

2.4 Leachates

Acidogenic leachate was produced by recirculating water through fresh residential refuse (Barlaz et al. 1989). The leachate was not neutralized to maintain the refuse in the acid-phase of decomposition, which was confirmed by a low leachate pH and the absence of gas production. Methanogenic leachate was generated by recirculating water through refuse in the methane-phase of decomposition (Barlaz et al. 1989), which was confirmed by a leachate pH near neutral and methane production. Both acidogenic and methanogenic leachates were vacuum-filtered through the following series of filters before finally passing the liquid through a 0.45- μm cellulose-acetate membrane filter: Whatman GF-D, Whatman GF-A, Pall A/E, and Millipore prefilters. Anaerobic conditions were maintained at all times for the methanogenic leachate by vacuum filtering in the anaerobic hood. Following filtration through the 0.45- μm cellulose-acetate membrane filter, acidogenic leachate was stored in brown glass containers at 4°C. Methanogenic leachate was filtered under anaerobic conditions, then stored in a 25-gallon stainless steel drum at 4°C with minimum headspace that was filled with argon gas to minimize contact with oxygen. Leachate characterization included measurement of pH, dissolved organic carbon (DOC), and chemical oxygen demand (COD) according to standard methods (APHA, AWWA, WEF 1998). Leachate characteristics are listed in Table 2.4.

2.5 Isotherms

Isotherm experiments were conducted with individual MSW components after they had been ground in a Wiley mill to pass a 1-mm screen. PVC was obtained in powdered form (diameter = 140 μm) and used directly.

Table 2.4. Leachate characteristics

Leachate	COD (mg/L)	DOC (mg/L)	pH
Acidogenic	17907	5629	5.55
Methanogenic	1072	120	7.55

All materials were oven-dried at 100-105°C for 24 h and stored in a desiccator until use. Flame-sealed glass ampules (20 mL) were used to collect batch isotherm data in phosphate-buffered (1 mM) organic-free water and in acidogenic and methanogenic leachates (Ball and Roberts 1991). Ampules were washed and baked in a muffle furnace at 550°C overnight prior to use. Sodium azide (200 mg/L) was added as a microbial growth inhibitor to prevent aerobic sorbent and sorbate degradation. Isotherm experiments were conducted at initial sorbate concentrations of 1-1000 µg/L. Liquid:solid mass ratios ranged from 10:1 to 50:1 for fresh and degraded rabbit food, newsprint and office paper, 8:1 to 500:1 for the three polyethylenes, and 10:1 to 1000:1 for PVC at each initial sorbate concentration. Using a gas-tight syringe, toluene, PCE, or DCE were spiked into the suspension at the ampule bottom immediately prior to ampule sealing. Methanol contributions from toluene, PCE, and DCE stock solutions were kept below 0.1% v/v in isotherm tests to avoid cosolvent effects (Brusseau et al. 1991). To reach sorption equilibria, ampules were tumbled end-over-end to assure effective mixing. Once equilibrated, ampules were centrifuged at 2000 rpm for 15 min after which a 1-mL sample was removed for scintillation counting.

Toluene sorption to NLF newsprint samples was measured in flame-sealed glass ampules (1.5 mL). Ampules were baked in a muffle furnace at 550°C for 4 hours prior to use.

Ultrapure water amended with a phosphate buffer (1mM) and sodium azide (200 mg/L) to prevent aerobic sorbent and sorbate degradation served as the liquid phase. Initial sorbate concentrations ranged from 10-100 µg/L, and liquid:solid mass ratios ranged from 10:1 to 17:1. Using a gas-tight syringe, ¹⁴C-toluene was spiked into the suspension at the ampule bottom immediately prior to ampule sealing. Methanol contributions from the toluene stock solution were kept below 0.1% v/v in isotherm tests to avoid cosolvent effects. During the 5-

day equilibration period, ampules were tumbled end-over-end to assure effective mixing. Once equilibrated, ampules were centrifuged at 2000 rpm for 20 minutes, after which a 1-mL sample was removed for scintillation counting.

With each isotherm experiment, triplicate blanks containing HOC but no solids were included. Results from these blanks showed that no HOC losses occurred during the equilibration period. Solid-phase HOC concentrations were calculated using a mass balance approach.

For isotherm experiments conducted in leachates, all glassware was autoclaved prior to use. For isotherms experiments in methanogenic leachate, ampules were filled with methanogenic leachate in an anaerobic hood to minimize oxygen dissolution. Before removal from the anaerobic hood, ampules were covered with Parafilm to avoid contact with oxygen. Upon removal from the anaerobic hood, ampules were spiked immediately with toluene, PCE, or DCE and flame-sealed.

To determine the time required to reach PCE sorption equilibria with PVC, multiple replicate glass ampules were set up using one water:solid ratio and one initial sorbate concentration. Replicate ampules were sampled once per week after 8 months of equilibration until no measurable changes in liquid-phase concentrations were detected.

2.6 Desorption Tests

Desorption experiments were conducted with individual MSW components. All materials were oven-dried at 100-105°C for 24 h and stored in a desiccator until use. Twenty-mL gold band, flame-sealed ampules were baked at 550°C for 4 hours prior to use and then filled with known sorbent masses. All glassware used in filling ampules was autoclaved prior to use. The openings of the ampules were then covered with Parafilm and the solids were sterilized by 2.2 Mrad of γ -irradiation from a ^{60}Co source. Upon γ -irradiation, ampules were filled with autoclaved, phosphate-buffered, ultrapure water or with filter-sterilized acidogenic or methanogenic leachate. To further prevent aerobic microbial growth, each sample was amended with sodium azide (200 mg/L). After ampules were filled, openings were covered with Parafilm to reduce the risk of microorganism introduction to the system. For tests in methanogenic leachate, ampules were filled with methanogenic leachate in an anaerobic hood to minimize oxygen effects. Before removal from the anaerobic hood, ampules were covered with Parafilm to avoid contact with oxygen. Immediately after filling ampules with the desired liquid phase, they were spiked with PCE and flame-sealed.

To determine desorption rates, an intermittent purging system was used (Harmon and Roberts 1992, 1994a, b). The desorption test procedure included the following steps: (1) centrifuge the ampule at 2000 RPMs for 15 minutes, (2) add additional scoring to the ampule where the break is going to occur to insure a clean break, (3) break the ampule and remove 6 mL of the liquid to measure the liquid phase concentration of the contaminant, (4) add a stir bar to the ampule and then attach the swagelok cap with the exhaust tubing emptying into a scintillation vial containing 10 mL of scintillation cocktail, (5) attach the inflow tubing of the

swagelok cap to a water-saturated nitrogen stream and purge the sample at a flowrate of 40 mL/min while mixing the samples with the stir bar several times during purging, and (6) check for leaks around the swagelok cap to insure no leakage. Purging was continuous for the first hour and the scintillation vial was changed every 5 minutes for the first 30 minutes. Subsequently, the scintillation vial was changed every 15 minutes and the ampule contents stirred every 5 minutes until the purging time reached 1 hour. After the first hour of purging, the sample was purged every 12 to 24 hours for 15 minutes and stirred every 5 minutes during purging. The radioactivity trapped in each scintillation vial was counted, and a scintillation vial containing fresh cocktail replaced the vial removed for analysis after each purging step

All desorption tests were conducted in duplicate. Blank samples containing liquid and sorbate only were used to determine the initial contaminant mass spiked into samples containing solids (M_0). The normalized contaminant mass remaining in the solid-phase during desorption tests was calculated from:

$$\frac{q_t}{q_0} = \frac{q_0 m_s - (M(t) - C_{eq} V_1)}{q_0 m_s}$$

where $q_0 = \frac{M_0 - C_{eq} V}{m_s}$ is the initial solid-phase concentration, m_s is the solid mass in the ampule, $M(t)$ is the cumulative contaminant mass recovered by the purges, C_{eq} is the liquid phase concentration at the end of the aging period, V is the total liquid volume, and V_1 is the liquid volume remaining after 6 mL of supernatant was removed prior to purging. Both M_0 and C_{eq} were corrected for non-sorbing, non-spargable impurities.

2.7 Mass balances

To quantify the amount of contaminant remaining on the solids at the end of desorption tests, benzyl alcohol extractions were conducted. Solid samples were transferred from glass ampules to 30-ml Teflon bottles, to which 15-mL benzyl alcohol was added. After a contact time of 5 days on a shake table, the Teflon bottles were centrifuged at 4000 rpm for 15 minutes. A 0.5-mL benzyl alcohol sample was added into 6-mL scintillation cocktail to quantify desorbed ^{14}C and the remaining supernatant volume that could be removed was measured and discarded. Benzyl alcohol extractions were repeated until no additional desorption of ^{14}C was detected in the liquid phase.

3 Results and Discussion – Sorption

Single-solute isotherms were obtained for PCE and DCE with each model MSW component. In conjunction with toluene and *o*-xylene data previously collected by Wu et al. (2001), the factors that control HOC sorption to MSW were determined. PCE and DCE were chosen as sorbates to determine whether trends obtained by Wu et al. (2001) for aromatic compounds would also be valid for aliphatic compounds. Furthermore, the sorptive behavior of DCE was of interest because it is a daughter product that forms during the deductive dehalogenation of PCE. Toluene isotherm tests were also conducted with low-, medium, and high-density polyethylene to determine the importance of amorphous regions in sorbent organic matter on sorption capacity. Toluene isotherm experiments were also conducted with three newsprint samples collected from different depths at the Norman, OK, landfill. These isotherm experiments were conducted to compare the toluene sorption capacity of newsprint samples in different stages of degradation and to test whether the O-alkyl/alkyl

ratio of sorbent organic matter is an effective predictor of HOC sorption capacity for field samples.

3.1 PCE Sorption Capacity of MSW Components

3.1.1 Single-Solute Isotherms

Single-solute PCE isotherms were obtained for each model MSW component (Table 3.1, Figure 3-1). To mathematically describe the isotherm data, the nonlinear Freundlich model ($\log q = \log K_F + n \log C_e$) and the linear partition model ($q = K_p C_e$) were compared, and resulting single-solute isotherm parameters are summarized in Table 3.1. In these models, q ($\mu\text{g}/\text{kg}$) and C_e ($\mu\text{g}/\text{L}$) represent the equilibrium solid- and liquid-phase concentrations, respectively. In the two-parameter Freundlich isotherm model, K_F is indicative of sorption capacity at $C_e = 1 \mu\text{g}/\text{L}$ (for the units chosen in this study), and n indicates the site energy distribution of a sorbent, where sorbent heterogeneity increases as n decreases from 1 (Carter et al. 1995). The relatively high PCE sorption capacity of PVC (K_F -values in Table 3.1, Figure 3-1) can be explained on the basis of solubility parameters (δ), where sorbate/sorbent systems with matching solubility parameters represent a compatible solute/solvent system (Barton 1975). Thus, PVC [$\delta = 7.8\text{-}11 \text{ (cal/cm}^3)^{1/2}$ (Barton 1975)] represented a suitable sorbent for PCE [$\delta = 9.09 \text{ (cal/cm}^3)^{1/2}$ (Barton 1991)] because its solubility parameter range includes that of PCE. PVC also contains a nonlinear adsorptive component in which PCE adsorbs on the internal surfaces of nanovoids in the glassy polymer (Xing and Pignatello 1997). HDPE exhibited a smaller PCE sorption capacity than PVC since the solubility parameter for PCE fell outside the range for HDPE [$\delta = 7.7\text{-}8.2 \text{ (cal/cm}^3)^{1/2}$ (Barton 1975)] and because there was no adsorption component present for this rubbery polymer.

Table 3.1. Single-solute isotherm parameters describing PCE sorption to MSW components

Sorbent	N ^a	log K _F ^b	n ^c	R ²	K _p ^d	R ²	K _{oc} ^e
Poly(vinyl chloride)	38	3.47 (±0.17)	0.918 (±0.112)	0.985	1648 (±210)	0.972	4240 ^f
High density polyethylene	50	2.57 (±0.08)	1.01 (±0.046)	0.997	385 (±9)	0.999	440
Fresh office paper	28	1.24 (±0.21)	0.932 (±0.094)	0.994	11.5 (±1.6)	0.967	30.8
Degraded office paper	39	2.05 (±0.05)	0.940 (±0.027)	0.999	78.3 (±4.1)	0.995	281
Fresh newsprint	23	1.59 (±0.14)	0.986 (±0.071)	0.951	35.6 (±3.2)	0.989	78.9
Degraded newsprint	30	1.86 (±0.07)	0.968 (±0.037)	0.999	59.3 (±2.6)	0.997	130
Fresh rabbit food	40	1.94 (±0.11)	0.979 (±0.069)	0.993	76.5 (±3.5)	0.995	180
Degraded rabbit food	40	1.98 (±0.07)	0.984 (±0.038)	0.998	90.9 (±3.3)	0.997	276
Fresh filter paper	15	0.25 (±3.79)	1.16 (±1.54)	0.695	1.05 (±1.2)	0.563	2.63 ^g

^a Number of observations.

^b K_F units are (μg/kg)(L/μg)ⁿ, 95% confidence interval of log K_F in parentheses.

^c Dimensionless Freundlich exponent, 95% confidence interval in parentheses.

^d Partition coefficient units are (μg/kg)(L/μg), 95% confidence interval in parentheses.

^e K_{oc} units are (μg/kg organic carbon)(L/μg).

^f Based on K_F, units are (μg/kg organic carbon)(L/μg)ⁿ.

^g Based on theoretical f_{oc} of cellulose (f_{oc}=0.4)

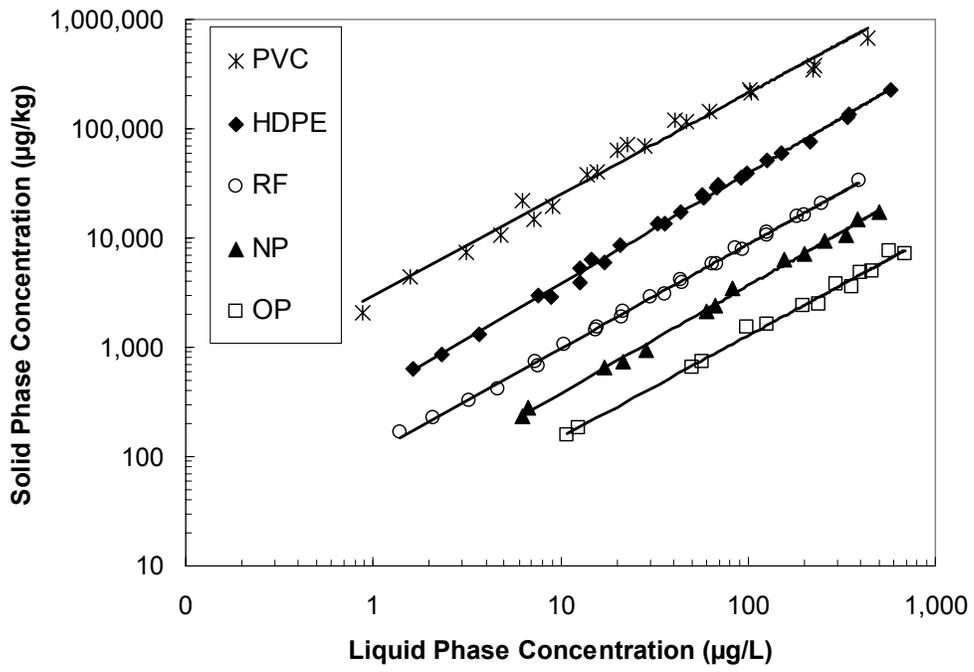


Figure 3-1. Single-solute PCE isotherms for fresh MSW components.

Rabbit food had the highest sorption capacity of all the biopolymer-containing sorbents, most likely due to its relatively high lipophilic extractives content (Table 2.1). The solubility parameter for soybean oil [$\delta = 8.4\text{-}8.9 \text{ (cal/cm}^3)^{1/2}$] (Hancock et al. 1997), which should be present in rabbit food based on its ingredients, is very close to that of PCE. Also, the presence of lignin [$\delta = 9.8\text{-}14.3 \text{ (cal/cm}^3)^{1/2}$] (Barton 1991) and protein, which exhibits HOC sorption capacities similar to lignin (Garbarini and Lion 1986), contributed to PCE sorption to rabbit food. Consistent with solubility parameters, newsprint with a 22% lignin content exhibited a larger sorption capacity than office paper that contained primarily cellulose [$\delta = 14.5\text{-}16.5 \text{ (cal/cm}^3)^{1/2}$] (Barton 1975) and hemicellulose. Other than cellulose and hemicellulose, office paper contains hydrophobic sizing agents that may alter its capacity to sorb PCE. The importance of the hydrophobic sizing agents on PCE sorption was demonstrated by the low PCE sorption capacity of pure cellulose, for which the K_p value was approximately 11 times lower than for office paper (Table 3.1). Anaerobically degraded forms of biopolymer composites had higher K_p and K_{oc} values than fresh materials but the order of the sorption capacities differed from that for fresh materials, (Table 3.1). The higher sorption capacity of degraded office paper compared to degraded newsprint is likely due to the higher percentage of lipophilic extractives in degraded office paper (Table 2.1). Overall, both fresh and degraded biopolymer composites exhibited lower sorption capacities than plastics because (1) the differences in solubility parameters between PCE and lignin or cellulose were greater than those between PCE and PVC or HDPE, and (2) the content of highly compatible sorbent fractions, such as lipophilic extractives, was small in the biopolymer composites.

Apart from degraded office paper, 95% confidence intervals for the Freundlich exponents suggest that all isotherms were linear. Isotherm linearity for PCE with PVC contradicts results obtained for toluene and *o*-xylene on PVC by Wu et al. (2001). Non-linear isotherms are expected for PVC due to adsorption to internal surfaces of nanovoids in the glassy polymer. Suggesting that the PCE isotherm on degraded office paper in DI water is non-linear ($n=0.940\pm 0.027$) is questionable since it is linear in acidogenic and methanogenic leachate. Linear PCE sorption to degraded office paper would be expected for two additional reasons. First, degraded office paper consists primarily of cellulose, and amorphous regions in cellulose are plasticized by water at room temperature (Akim 1978). Consequently, wet cellulose is a partitioning medium and should exhibit linear isotherms (LeBouef and Weber 2000). Second, the presence of small quantities of hydrophobic sizing agents on degraded office paper, such as alkyl ketene dimers of C₁₄-C₁₈ unsaturated fatty acids (Roberts 1996), should lead to linear partitioning.

Because lignin constituted a large percentage of fresh and degraded newsprint and because their lipophilic extractive contents were low, it can be assumed that lignin controlled sorption to both fresh and degraded newsprint. HOC sorption to lignin, a glassy polymer, should be nonlinear, and a Freundlich *n*-value of about 0.80 was recently obtained for phenanthrene sorption to extracted lignin (LeBouef and Weber 2000). The greater isotherm linearity observed in this study with newsprint may have resulted from (1) the topological or covalent bonding between hemicellulose and lignin in wood and wood pulp (Gerasimowicz et al. 1984, Shevchenko and Bailey 1996, Salmen and Olsson 1998, Helm 2000) that led to a new glass transition temperature for the intimately mixed lignin-carbohydrate complex (Kaplan

1976), and/or (2) the introduction of hydrophilic sulfone groups into the lignin structure during the preparation of newsprint (e.g. bisulfite addition during pulping) that enhanced the ability of water to plasticize lignin (Roberts 1996).

Lipophilic extractives likely dominated the linear partitioning of PCE into fresh and degraded rabbit food, which led to overall linear isotherms. Protein also represented a partitioning medium since amorphous protein regions are plasticized by water at room temperature (Green et al. 1994, Sochava 1997). Finally, the behavior of lignin-carbohydrate complexes in rabbit food may have deviated from that of glassy lignin extracts (LeBoeuf and Weber 2000) as explained above. PCE sorption to PVC was nonlinear, which is consistent with the dual-mode partitioning and adsorption mechanism (Weber et al. 1992) that is typically observed for glassy polymers (Xing and Pignatello 2001, Xing and Pignatello 1997). A linear isotherm for PCE and HDPE was consistent with previously observed linear partitioning into rubbery polymers (Xing et al. 1996, Wu et al. 2001).

3.1.2 Leachate Effects on Sorption Isotherms

To evaluate the effects of leachate composition on PCE sorption to MSW components, isotherm data were collected for sorbents in acidogenic and methanogenic leachates. Freundlich isotherm parameters and partition coefficients are summarized in Tables 3.2 and 3.3 for PCE isotherm experiments completed in acidogenic and methanogenic leachates, respectively. Apart from PVC, PCE isotherms in organic-free water and the two leachates were similar with respect to sorption capacity and isotherm nonlinearity (Tables 3.1 to 3.3).

Table 3.2. Isotherm parameters describing PCE sorption to MSW components in acidogenic leachate

Sorbent	N ^a	log K _F ^b	n ^c	R ²	K _p ^d	R ²	K _{oc} ^e
Poly(vinyl chloride)	40	3.22 (±0.10)	0.957 (±0.063)	0.996	1181 (±117)	0.983	3040 ^f
High density polyethylene	50	2.56 (±0.09)	1.01 (±0.051)	0.997	417 (±13)	0.998	476
Fresh office paper	28	0.93 (±0.16)	1.03 (±0.069)	0.991	10.4 (±1.0)	0.986	27.9
Degraded office paper	32	1.77 (±0.07)	1.04 (±0.032)	0.999	75.1 (±4.2)	0.994	270
Fresh newsprint	30	1.44 (±0.17)	1.00 (±0.086)	0.955	28.2 (±1.2)	0.997	62.5
Degraded newsprint	30	1.79 (±0.08)	0.980 (±0.042)	0.999	53.8 (±3.4)	0.994	118
Fresh rabbit food	50	2.08 (±0.07)	0.942 (±0.042)	0.997	91.9 (±2.3)	0.999	217
Degraded rabbit food	40	1.94 (±0.09)	1.03 (±0.054)	0.997	107 (±6.1)	0.994	325

^a Number of observations.

^b K_F units are (μg/kg)(L/μg)ⁿ, 95% confidence interval of log K_F in parentheses.

^c Dimensionless Freundlich exponent, 95% confidence interval in parentheses.

^d Partition coefficient units are (μg/kg)(L/μg), 95% confidence interval in parentheses.

^e K_{oc} units are (μg/kg organic carbon)(L/μg).

^f Based on K_F, units are (μg/kg organic carbon)(L/μg)ⁿ.

Table 3.3. Isotherm parameters describing PCE sorption to MSW components in methanogenic leachate

Sorbent	N ^a	log K _F ^b	n ^c	R ²	K _p ^d	R ²	K _{oc} ^e
Poly(vinyl chloride)	40	3.52 (±0.08)	0.866 (±0.053)	0.996	1461 (±180)	0.974	3757 ^f
High density polyethylene	49	2.60 (±0.08)	0.994 (±0.047)	0.997	355 (±23)	0.991	406
Fresh office paper	28	1.33 (±0.24)	0.945 (±0.112)	0.997	15.1 (±1.8)	0.975	40.5
Degraded office paper	40	1.83 (±0.05)	1.01 (±0.026)	0.999	72.6 (±2.4)	0.998	261
Fresh newsprint	29	1.45 (±0.09)	1.02 (±0.047)	0.999	31.7 (±1.4)	0.997	70.3
Degraded newsprint	30	1.87 (±0.12)	1.01 (±0.066)	0.997	78.6 (±2.6)	0.998	173
Fresh rabbit food	50	2.03 (±0.05)	0.955 (±0.032)	0.999	85.3 (±2.9)	0.999	202
Degraded rabbit food	40	2.03 (±0.06)	0.981 (±0.034)	0.999	96.0 (±3.6)	0.997	292

^a Number of observations.

^b K_F units are (μg/kg)(L/μg)ⁿ, 95% confidence interval of log K_F in parentheses.

^c Dimensionless Freundlich exponent, 95% confidence interval in parentheses.

^d Partition coefficient units are (μg/kg)(L/μg), 95% confidence interval in parentheses.

^e K_{oc} units are (μg/kg organic carbon)(L/μg).

^f Based on K_F, units are (μg/kg organic carbon)(L/μg)ⁿ.

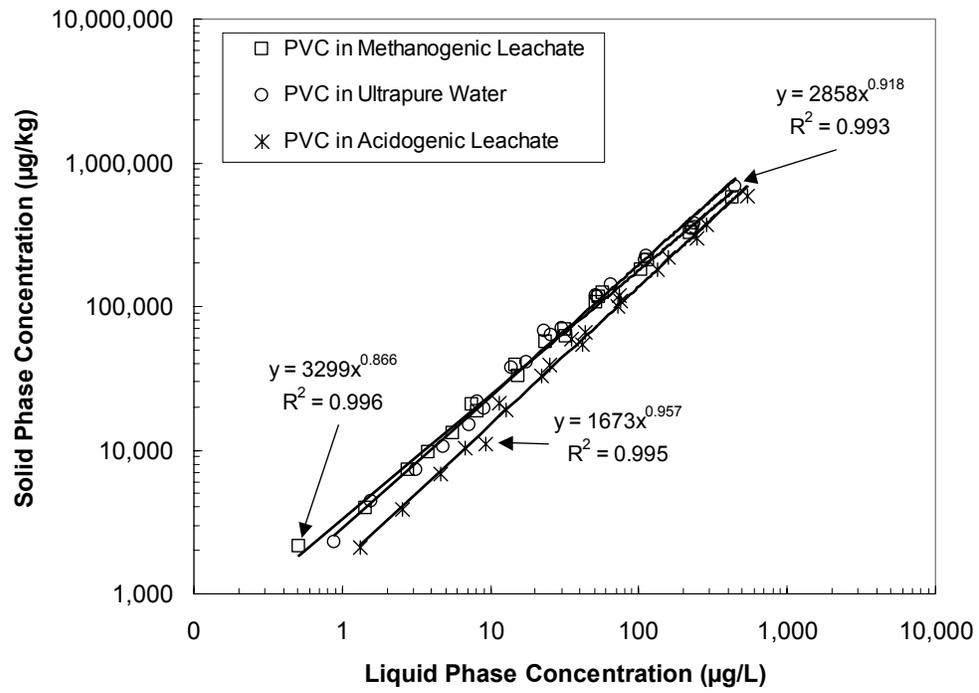


Figure 3-2. Effect of aqueous phase composition on PCE sorption to PVC.

Compared to single-solute K_p values, no consistent increases or decreases in K_p values were measured for the two leachate phases (compared to single-solute values, K_p values in leachates were 21% larger to 32% smaller). Therefore, leachate composition had little effect on PCE sorption to HDPE and biopolymer composites. Comparing PCE sorption to PVC in organic-free water, methanogenic leachate, and acidogenic leachate (Figure 3-2), a trend similar to that observed by Wu et al. (2001) became apparent, however. As observed by Wu et al. (2001), the isotherm in acidogenic leachate was more linear and the sorption capacity was lower when compared to the isotherm results obtained in ultrapure water and methanogenic leachate. Although the trend observed here for PCE followed that observed for toluene by Wu et al. (2001), it should be noted that it was not as pronounced. In particular, the n -value for the PCE isotherm in ultrapure water did not differ significantly from 1 ($p < 0.05$). It is likely that organic compounds in acidogenic leachate act as plasticizers that convert PVC from the glassy to rubbery state. Softening of glassy polymers by high concentrations of cosolutes in multisolute systems has been reported previously (Huang and Weber 1998, White and Pignatello 1999). Propionic and butyric acid in acidogenic leachate may have been the principal plasticizers of PVC because their solubility parameters [$\delta = 9.7$ and $9.1 \text{ (cal/cm}^3)^{1/2}$, respectively (Hanson, 2000)] fall into the range of δ values given above for PVC.

3.2 DCE Sorption Capacity of MSW Components

Sorption capacities for DCE (Table 3.4) were lower than for PCE (Table 3.1), toluene, and *o*-xylene (Wu et al. 2001).

Table 3.4. Single-solute isotherm parameters describing DCE sorption to MSW components

Sorbent	N ^a	log K _F ^b	n ^c	R ²	K _p ^d	R ²	K _{oc} ^e
Poly(vinyl chloride) ^f							
High density polyethylene	38	0.83 (±0.43)	0.963 (±0.172)	0.980	5.16 (±0.68)	0.954	5.9
Fresh office paper	N/A ^g	N/A	N/A	N/A	N/A	N/A	N/A
Degraded office paper	27	0.88 (±0.65)	0.839 (±0.267)	0.946	2.84 (±0.55)	0.892	10.2
Fresh newsprint	23	0.76 (±0.25)	0.948 (±0.105)	0.995	4.12 (±0.27)	0.993	9.1
Degraded newsprint	28	1.15 (±0.33)	0.915 (±0.142)	0.988	8.47 (±0.46)	0.995	18.6
Fresh rabbit food	26	0.90 (±0.36)	0.920 (±0.153)	0.986	4.84 (±0.45)	0.987	11.4
Degraded rabbit food	24	1.11 (±0.38)	0.934 (±0.163)	0.985	8.48 (±1.48)	0.949	25.8

^a Number of observations.

^b K_F units are (μg/kg)(L/μg)ⁿ, 95% confidence interval of log K_F in parentheses.

^c Dimensionless Freundlich exponent, 95% confidence interval in parentheses.

^d Partition coefficient units are (μg/kg)(L/μg), 95% confidence interval in parentheses.

^e K_{oc} units are (μg/kg organic carbon)(L/μg).

^f Not yet equilibrated

^g Not analyzed, sorption of DCE to fresh office paper is negligible

The reason for lower sorption capacities could not be explained by the solubility parameter since it is similar to those of the other HOCs (Table 3.5). However, the low DCE sorption capacities can be explained by the greater hydrophilicity of DCE, as expressed by K_{ow} or the aqueous solubility. An inverse relationship exists between aqueous solubility and sorption capacity (Chiou et al. 1979). The aqueous solubility of DCE is 3500 mg/L, which exceeds that of toluene, *o*-xylene, and PCE (Table 3.5). Similarly, sorption capacity increases with K_{ow} (Karickhoff et al. 1979, Schwarzenbach and Westall 1981), and the K_{ow} value of DCE is smaller than those of the other HOCs (Table 3.5).

3.3 Toluene Isotherms for Polyethylenes

Toluene isotherms for HDPE, MDPE, and LDPE revealed that sorbents that contain a higher amorphous fraction have higher sorption capacities (Table 3.6). Polymeric sorbents contain both crystalline and amorphous fractions, but sorption takes place solely in the amorphous fraction. LDPE contained the highest amorphous fraction of the polyethylenes tested while HDPE contained the lowest. As expected, therefore, LDPE exhibited the largest toluene sorption capacity while HDPE exhibited the lowest. When toluene sorption capacities of the polyethylenes were normalized by the amorphous fraction ($K_{amorphous}=K_p/f_{amorphous}$) it was expected that similar $K_{amorphous}$ values would result for the three polyethylenes. However, this was not the case (Table 3.6), which suggests that knowledge of the amorphous fraction alone is not sufficient to predict HOC sorption capacities for different polyethylenes.

Table 3.5. Sorbate characteristics

Sorbate	Log K _{ow} ^a	S _w ^b	δ ^c
Toluene	2.69	515	9.00
<i>o</i> -Xylene	3.12	175	8.90
<i>cis</i> -1,2 DCE	1.86	3500	9.29
PCE	2.88	150	9.09

^a Octanol/water partition coefficient (Mackay et al. 1995).

^b Aqueous solubility (mg/L) (Mackay et al. 1995).

^c Solubility parameter ((cal/cm³)^{1/2}) (Barton 1991)

Table 3.6. Isotherm parameters describing toluene sorption to HDPE, MDPE, and LDPE

Sorbent	N ^a	log K _F ^b	n ^c	R ²	K _p ^d	R ²	f _{amorphous} ^e	K _{amorphous}
HDPE	40	1.82 (±0.25)	1.04 (±0.102)	0.990	90.1 (±12.1)	0.965	0.195	462.7
MDPE	40	1.96 (±0.20)	1.02 (±0.080)	0.994	104.1 (±11.2)	0.978	0.340	306.2
LDPE	16	2.12 (±0.70)	0.985 (±0.264)	0.982	123.1 (±28.5)	0.964	0.495	248.7

^a Number of observations.

^b K_F units are (μg/kg)(L/μg)ⁿ, 95% confidence interval of log K_F in parentheses.

^c Dimensionless Freundlich exponent, 95% confidence interval in parentheses.

^d Partition coefficient units are (μg/kg)(L/μg), 95% confidence interval in parentheses.

^e Amorphous fraction (Peacock 2000)

3.4 Toluene Isotherms for Norman Landfill Newsprint

Isotherm parameters describing toluene sorption to newsprint samples from the Norman, OK, landfill (NLF) are summarized in Table 3.7. Partition coefficients in Table 3.7 show that the toluene sorption capacity was largest for the bottom layer sample (BNP) and smallest for the middle layer sample (MNP). Initially, it was anticipated that the extent of newsprint degradation would increase with increasing sampling depth in the landfill. However, the O-alkyl to alkyl ratios of the NLF newsprint samples increased in the order BNP<TNP<MNP (Table 2.3). Thus, the MNP sample was more polar, and thus less degraded, than the TNP sample. Therefore, residence time (or depth) is not the only factor that affects the extent of degradation of MSW components. Microbial activity in landfills varies spatially and is affected by factors such as pH and moisture content. The observation that TNP was degraded to a greater extent than MNP suggest that conditions for microbial growth were more favorable in the region from which the TNP sample was collected. For example, water that percolates through the cover soil may absorb primarily in the upper reaches of the landfill such that during certain periods (e.g. rain events), the moisture content in the region from which the TNP sample was collected could be greater than in the region from which the MNP sample was collected.

To compare toluene sorption capacities of NLF newsprint samples with those of fresh (FNP) and laboratory-degraded (DNP) newsprint samples, normalized sorption parameter [$\log(K_{oc}/K_{ow})$] values were plotted as a function of the sorbent O-alkyl/alkyl ratio in Figure 3-3. The data points in Figure 3-3 show that FNP, the most polar material, had the lowest toluene sorption capacity while BNP, the least polar material, had the largest.

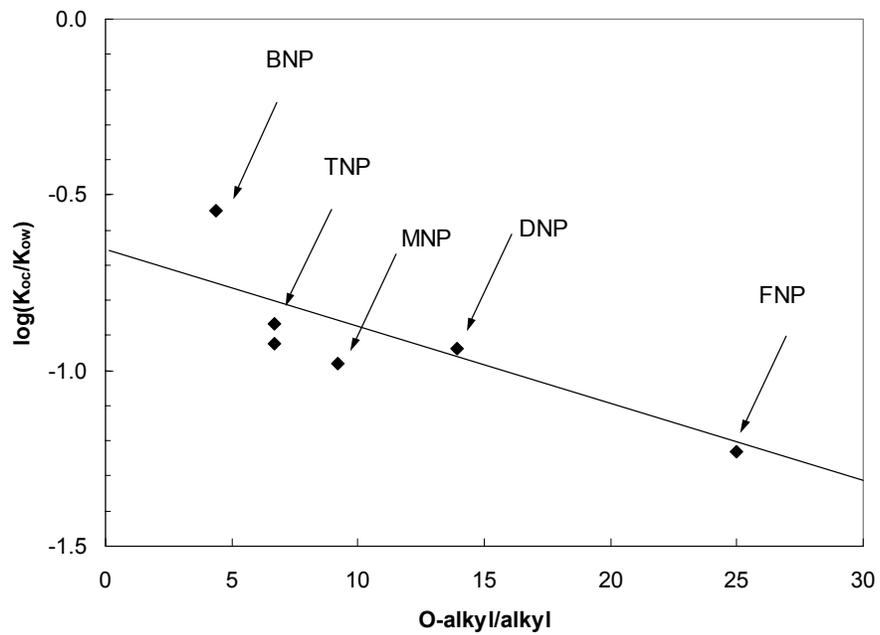


Figure 3-3. Dependence of normalized sorption parameter on O-alkyl/alkyl ratio for newsprint samples.

Table 3.7. Isotherm parameters describing toluene sorption to newsprint samples from the Norman, OK, landfill

Sorbent	N ^a	log K _F ^b	n ^c	R ²	K _p ^d	R ²	f _{oc}	K _{oc} ^e
Newsprint Top Layer (12'-16')	12	1.35 (±0.24)	1.02 (±0.174)	0.985	24.7 (±3.01)	0.979	0.371	66.6
Newsprint Middle Layer (20'-24')	10	1.20 (±0.57)	1.05 (±0.416)	0.953	20.8 (±2.40)	0.989	0.407	51.1
Newsprint Bottom Layer (32'-36')	12	1.64 (±0.10)	0.956 (±0.075)	0.997	37.6 (±2.79)	0.991	0.270	139.4

^a Number of observations.

^b K_F units are (μg/kg)(L/μg)ⁿ, 95% confidence interval of log K_F in parentheses.

^c Dimensionless Freundlich exponent, 95% confidence interval in parentheses.

^d Partition coefficient units are (μg/kg)(L/μg), 95% confidence interval in parentheses.

^e K_{oc} units are (μg/kg organic carbon)(L/μg).

Toluene sorption capacities of the materials with intermediate polarities (TNP, MNP, and DNP) were similar. Furthermore, Figure 3-3 depicts the trend line obtained by Wu et al. (2001) for six biopolymer composites. As shown in Figure 3-3, the normalized sorption parameter of the three NLF newsprint samples increased with decreasing sorbent polarity as expressed by a decreasing O-alkyl/alkyl ratio. Furthermore, toluene sorption capacities of TNP and MNP newsprint samples were predicted reasonably well by the trend line established for fresh and laboratory-degraded MSW components by Wu et al. (2001). In contrast, the sorption capacity of BNP, the most hydrophobic newsprint sample, was not predicted as well, suggesting that the trend line may not be valid for more hydrophobic sorbents (see section 3.6 for additional discussion).

3.5 Sorbate Effects on Sorption

It is well-established, that $\log(K_{oc})$ increases linearly with sorbate $\log(K_{ow})$ for soils and sediments (Karickhoff et al. 1979, Schwarzenbach and Westall 1981) as well as for mixed refuse and individual MSW components (Reinhart et al. 1990, Wu et al. 2001). Combining $\log(K_{oc})$ values obtained here for PCE and DCE with K_{oc} values obtained for other HOCs in previous refuse sorption studies (Reinhart et al. 1990, Wu et al. 2001) and plotting them against sorbate $\log(K_{ow})$ yields panel A in Figure 3-4. Overall, the trend depicted in panel A of Figure 3-4 shows that K_{oc} increases with increasing K_{ow} for an individual sorbent or MSW mixture. The irregularity for the two most hydrophobic compounds (PCE and *o*-xylene) primarily results from PCE sorption capacities being consistently larger than those of *o*-xylene despite PCE having a lower K_{ow} value than *o*-xylene (Table 3.5).

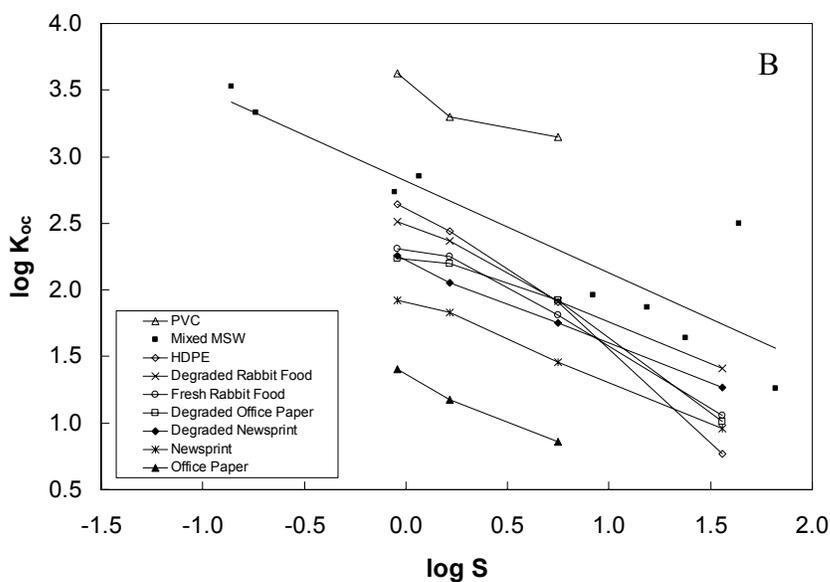
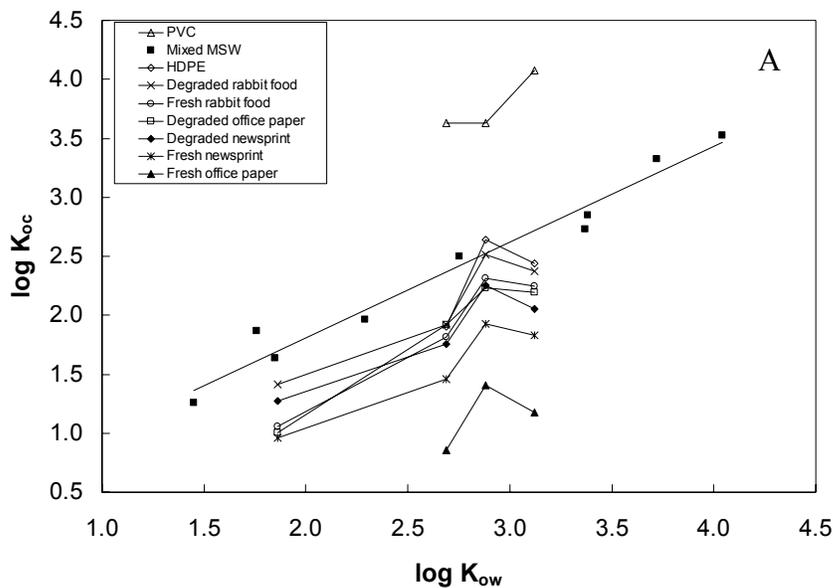


Figure 3-4. Dependence of $\log K_{oc}$ on $\log K_{ow}$ for individual MSW components and mixed MSW (A). Dependence of $\log K_{oc}$ on $\log S$ for individual MSW components and mixed MSW (B). PVC data represent K-values divided by f_{oc} and provide a valid comparison only at an equilibrium liquid-phase concentration of $1 \mu\text{g/L}$. Data for mixed MSW are from Reinhart et al. (1990). To obtain $\log S$, aqueous solubilities (in mmol/L) were used for HOCs that are liquids at isotherm temperature, and supercooled liquid solubilities (in mmol/L) were used for HOCs that are solids at isotherm temperature.

It should be noted that considerable uncertainty is associated with the K_{ow} value for PCE. For example, Hansch et al. (1995) list an experimentally determined $\log(K_{ow})$ value for PCE of 3.40 whereas Mackay et al. (1995) suggest a $\log(K_{ow})$ value of 2.88 (Table 3.5). Clearly, the K_{ow} value listed by Hansch et al. (1995) would have improved the correlations depicted in panel A of Figure 3-4. Apart from K_{ow} , the aqueous solubility of a sorbate is commonly used to predict K_{oc} values (Chiou et al., 1979, Grathwohl and Rahman, 2002). Generally, an improved relationship is obtained when $\log(K_{oc})$ values are plotted versus $\log(S)$ as shown in panel B of Figure 3-4. Supercooled liquid solubilities were used for all sorbates tested by Reinhart et al. (1990) that were solids at room temperature as suggested by Carmo et al. (2000). It should be noted that the point for 2,4-dichlorophenol in the data set of Reinhart et al. (1990) deviates from the trendline when $\log(K_{oc})$ values are plotted against $\log(S)$.

The aqueous solubility of an HOC can also be used to normalize isotherms when different sorbates are tested with a given sorbent (e.g. Kleineidam et al. 2002). To illustrate the effectiveness of this procedure, single-solute DCE and PCE isotherm data obtained in this research were plotted together with the single-solute toluene and *o*-xylene isotherm data of Wu et al. (2001). For the sorbent fresh rabbit food, panel A in Figure 3-5 depicts the isotherm data in traditional format, i.e. by depicting the equilibrium solid phase concentrations as a function of the equilibrium liquid phase concentration. The differences among the individual isotherm sets disappear when solid-phase concentrations are plotted against liquid phase concentrations normalized by the aqueous solubility of the HOC (C_e/S_w) as shown in panel B of Figure 3-5. Thus, HOC isotherms on a given sorbent can be predicted from a single isotherm if the aqueous solubility of the compound of interest is known.

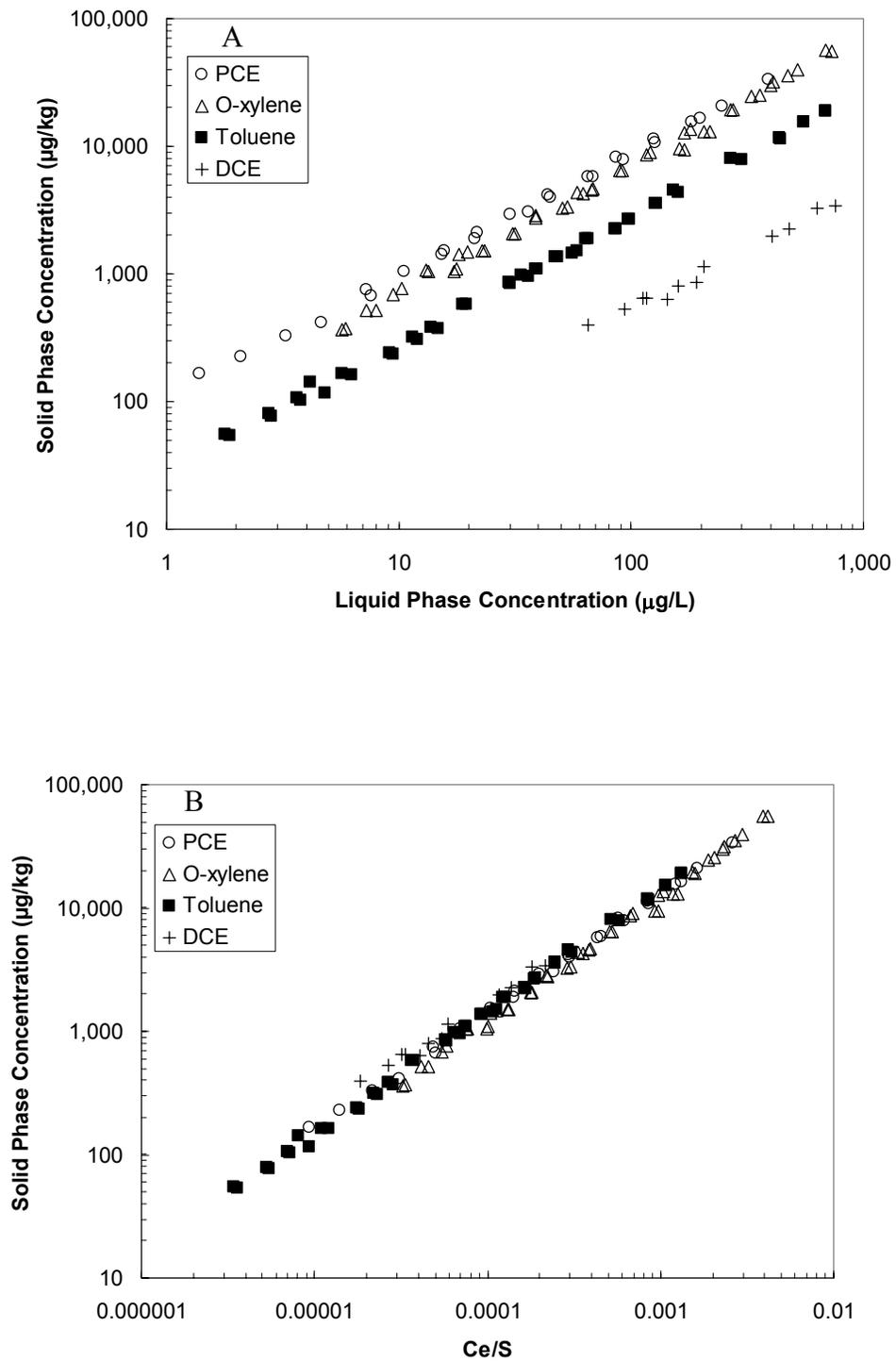


Figure 3-5. Single-solute HOC isotherms on fresh rabbit using liquid phase concentrations (A) or liquid phase concentrations normalized by HOC aqueous solubility (B) as abscissa.

It should be noted that supercooled liquid solubilities are required to normalize liquid phase concentrations of compounds that are solids at the temperature of interest.

3.6 Sorbent Effects on Sorption

As illustrated by the sorption capacity differences in Figure 3-4, sorbent characteristics strongly affect HOC sorption. To be able to predict HOC sorption capacities for individual sorbate/sorbent pairs, a suitable descriptor of one or more sorbent characteristics needs to be identified in addition to a suitable descriptor for the sorbate such as K_{ow} or S_w . The polarity of a sorbent is one important characteristic that affects HOC sorption. Traditionally, sorbent polarity is measured by the polarity index [(O+N)/C] (Rutherford et al. 1992, Xing et al. 1994a, b) or by the percentage of polar organic carbon determined from solid-state ^{13}C CP-MAS NMR spectra (Kile et al. 1999). As shown by Wu et al. (2001), the normalized sorption parameter [$\log(K_{oc}/K_{ow})$] describing HOC sorption to MSW components decreased as sorbent polarity increased, a trend that is consistent with that observed previously for individual biopolymers, soils, and sediments (Stuer-Lauridsen and Pedersen 1997, Kile et al. 1999). However, Wu et al. (2001) detected a fair amount of variability when plotting the normalized sorption parameter [$\log(K_{oc}/K_{ow})$] for MSW component data against the polarity index or the percentage of polar organic carbon. Wu et al. (2001) further showed that small amounts of lipophilic extractives (<5% of the sorbent mass) caused large differences in sorption capacity that were not captured well by measures such as the polarity index or the percentage of polar organic carbon. The ratio of O-alkyl to alkyl groups, determined from solid-state ^{13}C CP-MAS NMR spectra (Table 2.3), was therefore selected as a sorbent organic matter descriptor since it recognizes the importance of both sorbent polarity and

lipophilic extractives content on HOC sorption. O-alkyl groups are attributed to more polar regions of the sorbent; i.e., regions containing cellulose and hemicellulose, while alkyl regions are primarily non-polar aliphatic regions; i.e., regions containing poly(methylene) groups. Apart from Wu et al. (2001), the importance of aliphatic sorbent organic matter on HOC sorption has recently been recognized by a number of research groups (Chefetz et al. 2000, Salloum et al. 2002, Mao et al. 2002, Gunasekara and Xing 2003). Panel A in Figure 3-6 depicts the dependence of $\log(K_{oc}/K_{ow})$ on the O-alkyl/alkyl ratio for PCE and DCE data collected in this study as well as for literature data (Wu et al. 2001, Chefetz et al. 2000, Salloum et al. 2002). Panel A in Figure 3-6 shows that $\log(K_{oc}/K_{ow})$ decreases with increasing O-alkyl/alkyl ratio; in other words, the HOC sorption capacity decreases with increasing sorbent polarity and/or decreasing sorbent lipophilic extractives content. It should be noted that the abscissa in panel A of Figure 3-6 is presented on a logarithmic scale to illustrate more clearly the manner in which HOC sorption capacity increased for sorbents with O-alkyl/alkyl ratios of less than about 5, at which point $\log(K_{oc}/K_{ow})$ increased exponentially with decreasing O-alkyl/alkyl ratio. Panel A in Figure 3-6 suggests that the O-alkyl/alkyl ratio, as determined by ^{13}C CP-MAS NMR, is a suitable predictor for HOC sorption capacities down to an O-alkyl/alkyl ratio value of about 1. It is unclear at this point whether the O-alkyl/alkyl ratio does not affect HOC sorption at lower values, as suggested by the data of Salloum et al. (2002) or whether improved quantitative ^{13}C CP-MAS NMR data are needed to accurately determine the O-alkyl/alkyl ratio for relatively nonpolar sorbents (e.g. the kerogens studied by Salloum et al. 2002).

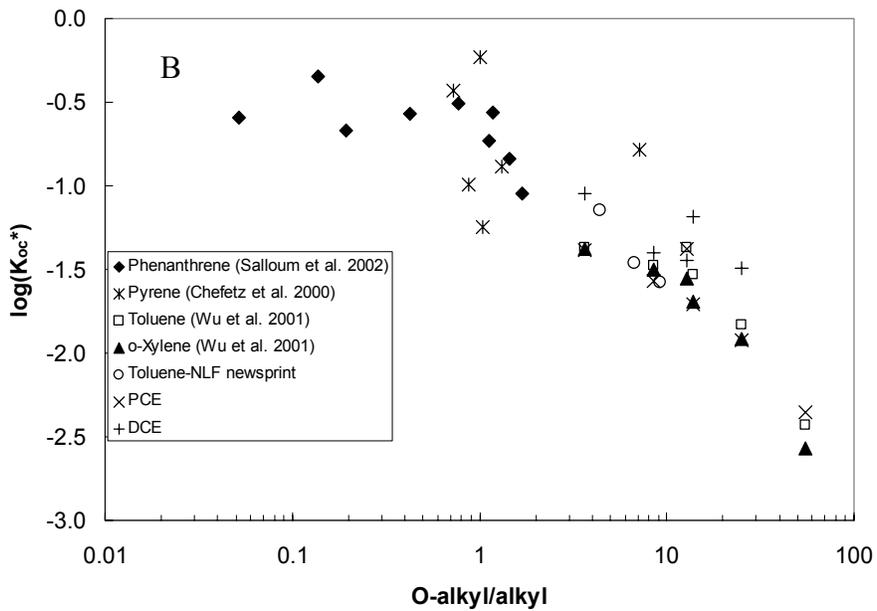
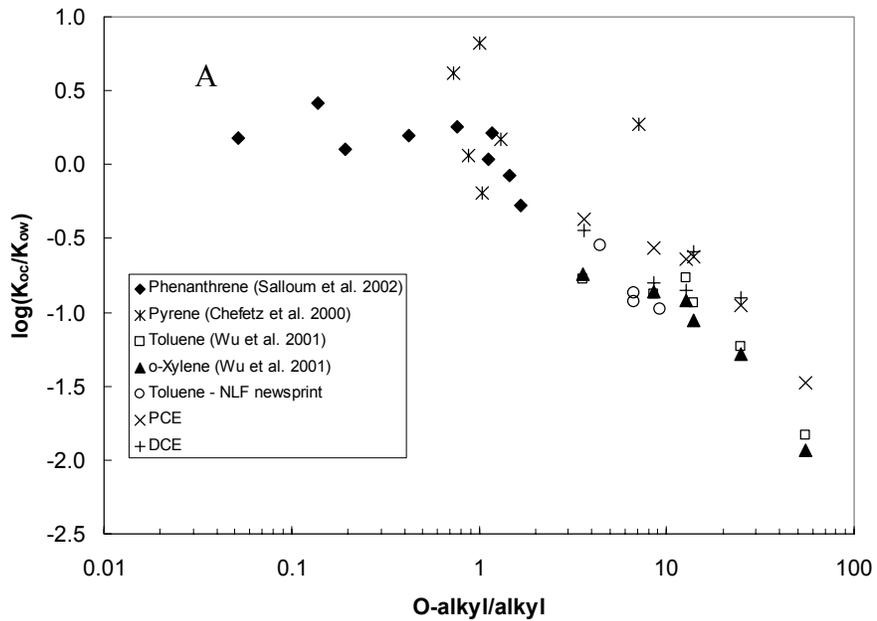


Figure 3-6. Dependence of normalized sorption parameter on O-alkyl/alkyl ratio (A) and dependence of unit-equivalent partitioning coefficient on O-alkyl/alkyl ratio (B).

In this study, another method of normalizing K_{oc} values was explored. As suggested by Grathwohl and Rahman (2002), a unit-equivalent partitioning coefficient (K_{oc}^* , unitless) is obtained when K_{oc} (L/kg) is multiplied by the aqueous solubility (S_w in units of kg/L) of the HOC (or the supercooled liquid-state solubility when the HOC is a solid at the temperature of the isotherm experiment, Carmo et al. 2000). In panel B of Figure 3-6, the unit-equivalent partitioning coefficient is plotted as a function of the O-alkyl/alkyl ratio for the same data shown in Panel A. Similar trends were obtained in panels A and B of Figure 3-6, which is not surprising given the close relationship that exists between aqueous solubility (or the supercooled liquid-state solubility) and K_{ow} (Chiou and Schmedding 1982).

4 Results and Discussion - Desorption

Desorption tests were conducted with model MSW components aged 30 days in three PCE-spiked liquid phases: ultra-pure water, acidogenic leachate, and methanogenic leachate. A one-compartment diffusion model was used to determine diffusion coefficients describing PCE desorption from HDPE and PVC while a two-compartment diffusion model was necessary for the biopolymer composites. Long-term (250 day) aging tests will be conducted in future work to assess the effect of aging time on PCE desorption rates.

4.1 Model Description

HOC diffusion models used in this study were described and results verified experimentally in previous research (Wu 2002). A one-compartment diffusion model was used to describe PCE desorption from HDPE and PVC since these sorbents are homogeneous materials in

which the HOC desorption rate is controlled by diffusion through a single polymer phase. The one-compartment model contains one adjustable parameter, the diffusion coefficient (D). PCE desorption rates from biopolymers composites (rabbit food, newsprint, and office paper) were described by a three-parameter biphasic polymer diffusion model. This model assumes the presence of a slow-desorbing compartment (Φ_s) and a fast-desorbing compartment ($\Phi_f=1-\Phi_s$) with separate diffusion coefficients for each compartment (D_s and D_r , respectively). Sorbent particle density and diameter play an important role in determining diffusion coefficients, and values used in determining desorption model parameters are listed in Table 4.1.

4.2 Effects of Sorbent Type on Desorption

For PCE desorption experiments conducted in methanogenic leachate, Figures 4-1 and 4-2 show the normalized PCE mass remaining in the solid phase as a function of time for homogeneous sorbents (HDPE and PVC) and heterogeneous biopolymer composites (office paper and newsprint), respectively. Uniform PCE desorption rates were observed for HDPE and PVC. In contrast, desorption curves for the biopolymer composites exhibited a fast initial desorption step that was followed by slow desorption of the remaining PCE fraction. Diffusion coefficients describing PCE desorption from HDPE and PVC are listed in Table 4.2 and compared with diffusion coefficients for toluene and *o*-xylene from Wu (2002). HDPE is a homogeneous rubbery polymer and therefore a linear isotherm model was used to describe the boundary condition at the external particle surface. The same linear model was used for PVC in acidogenic leachate since it was shown here and by Wu (2002) that PVC is plasticized by constituents in acidogenic leachate.

Table 4.1. Particle densities and diameters of model MSW components^a

Materials	Particle density (g/L)	Mean particle diameter (μm)
PVC	1.4	140
HDPE	0.962	500
Fresh office paper	1.44	278
Degraded office paper	2.13	210
Fresh newsprint	1.32	298
Degraded newsprint	1.81	213
Fresh rabbit food	1.50	320
Degraded rabbit food	1.78	289

^afrom Wu (2002)

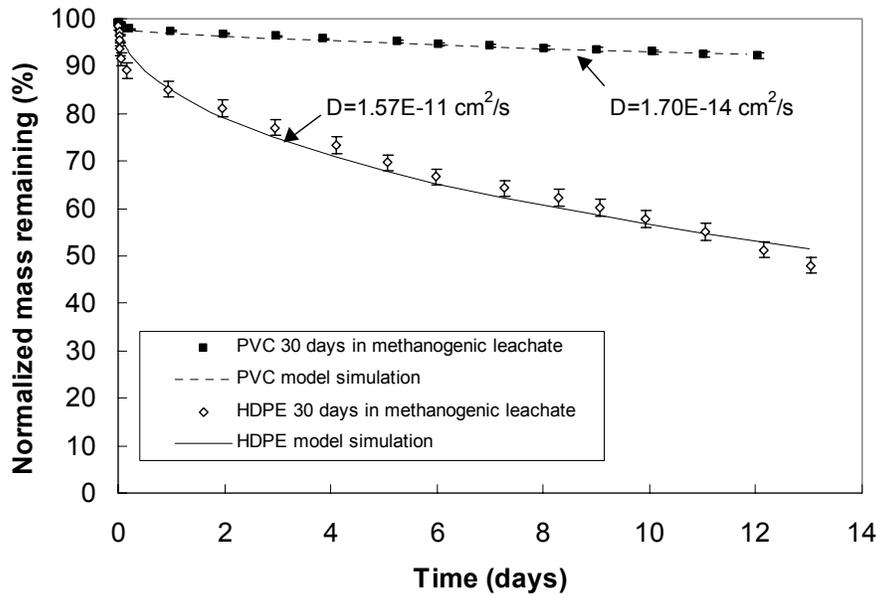


Figure 4-1. PCE desorption rates from PVC and HDPE in methanogenic leachate after 30 days of aging

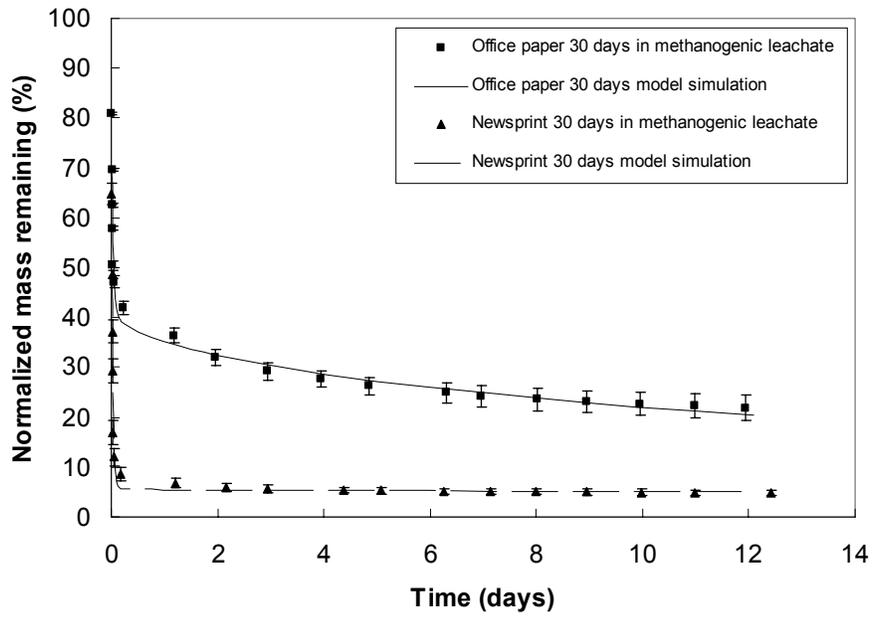


Figure 4-2. PCE desorption rates from representative biopolymer composites in methanogenic leachate after 30 days of aging

Table 4.2. Comparison of diffusion coefficients describing PCE, toluene, and *o*-Xylene desorption from HDPE and PVC

Sample	PCE ^a		Toluene ^{a,b}		O-xylene ^{b,c}	
	D (cm ² /s)	MSE ^d	D (cm ² /s)	MSE ^d	D (cm ² /s)	MSE ^d
HDPE (DI Water)	1.46E-11	0.007	N/A	N/A	N/A	N/A
HDPE (Acidogenic Leachate)	1.60E-11	0.005	4.72E-11	0.019	1.06E-11	0.011
HDPE (Methanogenic Leachate)	1.57E-11	0.005	4.53E-11	0.014	N/A	N/A
PVC (DI Water) ^c	2.25E-14	0.002	N/A	N/A	N/A	N/A
PVC (Acidogenic Leachate) ^e	9.61E-15	0.003	3.74E-14	0.003	1.39E-14	0.002
PVC (Methanogenic Leachate) ^e	1.70E-14	0.003	1.78E-14	0.004	N/A	N/A

^aaging time=30 days

^bfrom Wu (2002)

^caging time=250 days

^dmean square error

^e K_f and n values used for PVC were obtained from the appropriate 250-day isotherms

A non-linear isotherm model was used to describe the boundary condition at the external PVC particle surface when PCE desorption experiments were conducted in ultra-pure water and methanogenic leachate. Diffusion coefficients describing PCE, toluene, and o-xylene desorption from HDPE and PVC are on the order of 10^{-11} cm²/s and 10^{-14} cm²/s, respectively. These values are consistent for HOC diffusion coefficients in glassy and rubbery polymers (Berens and Huvard 1981, Rogers et al. 1960). HOC diffusion in glassy polymers is slower than in rubbery polymers because the glassy polymer matrix is more rigid and contains internal nanovoids that provide strong adsorption sites, both of which reduce HOC desorption rates.

Diffusion coefficients describing PCE desorption from biopolymer composites are listed in Table 4.3. For PCE, diffusion coefficients ranged from 10^{-8} to 10^{-9} cm²/s for the rapidly desorbing compartment and from 10^{-11} to 10^{-13} cm²/s for the slowly desorbing compartment. The rapid diffusion coefficient range is similar to that reported for soils and sediments using a one-compartment diffusion model [10^{-8} to 10^{-10} cm²/s (Harmon and Roberts 1994a), 10^{-9} to 10^{-10} cm²/s (Werth and Reinhard 1997)]. For phenanthrene desorption from geosorbents, Johnson et al. (2001) reported rapid compartment diffusion coefficients (D_r/a^2) in the range of 0.00031 to 0.032 day⁻¹ and slow compartment diffusion coefficients (D_s/a^2) in the range of 0.000011 to 0.0010 day⁻¹. Table 4.4 shows D_r/a^2 and D_s/a^2 values for PCE desorption from biopolymer composites in acidogenic leachate after 30 days aging, where the diffusional length scale (a) is assumed to be equal to the mean sorbent particle radius (see Table 4.1 for sorbent diameter). D_r/a^2 values obtained for MSW components are 2 to 4 orders of magnitude larger than those obtained by Johnson et al. (2001).

Table 4.3 PCE and toluene desorption rate parameter estimates for the Two-Compartment Polymer Diffusion Model^a

Sample	Φ_r	Φ_s	PCE			Toluene ^b				
			Dr (cm ² /s)	Ds (cm ² /s)	MSE ^c	Φ_r	Φ_s	Dr (cm ² /s)	Ds (cm ² /s)	MSE
OP	0.6334	0.3666	4.73E-09	6.72E-11	0.0797	0.6119	0.3881	2.53E-09	1.13E-11	0.0396
DOP	0.7655	0.2345	1.37E-08	8.45E-11	0.0337	0.5351	0.4649	9.53E-09	5.27E-11	0.0092
NP	0.9582	0.0418	1.28E-08	4.64E-12	0.0196	0.9257	0.0743	1.24E-08	5.27E-16	0.0079
DNP	0.9294	0.0706	3.11E-09	8.62E-12	0.0600	0.7323	0.2677	1.77E-09	6.30E-12	0.0456
RF	0.7268	0.2732	4.38E-09	9.95E-11	0.0628	0.8845	0.1155	3.15E-09	1.26E-11	0.0388
DRF	0.8241 ^d	0.1758 ^d	5.27E-09 ^d	6.93E-13 ^d	0.0583	0.7633	0.2367	4.99E-09	4.10E-14	0.0252

^aparameters that resulted in the best model fit of acidogenic leachate data after an aging time of 30 days

^b from Wu (2002)

^cmean square error

^d parameters for methanogenic leachate desorption test

Table 4.4 D_r/a^2 and D_s/a^2 values for PCE desorption from biopolymer composites

Solid	D_r (cm^2/s)	D_s (cm^2/s)	D_r/a^2 (day^{-1})	D_s/a^2 (day^{-1})
Office paper	4.73E-09	6.72E-11	2.115	0.0301
Degraded office paper	1.37E-08	8.45E-11	6.126	0.0378
Newsprint	1.28E-08	4.64E-12	4.981	0.0018
Degraded newsprint	3.11E-09	8.62E-12	2.369	0.0066
Rabbit food	4.38E-09	9.95E-11	1.478	0.0336
Degraded rabbit food	5.27E-09	6.93E-13	2.181	0.0003

The D_s/a^2 value for degraded rabbit food was within the range reported by Johnson et al. (2001) while D_s/a^2 values for the other MSW components were up to about 2 orders of magnitude larger. Diffusion coefficients describing PCB desorption from glassy and rubbery sediment organic matter were also several orders of magnitude slower than those shown in Table 4.2 for PVC and HDPE (7.3×10^{-21} and 2.6×10^{-18} , respectively; Carroll et al. 1994). These differences may be due to sorbate size and properties since phenanthrene and PCBs are larger and more hydrophobic than the HOCs tested in this study. Similarly, Piatt et al. (1998) reported diffusion coefficients for phenanthrene and pyrene desorption from two soils that were two orders of magnitude smaller than diffusion coefficients for less hydrophobic compounds such as toluene. These findings demonstrate that larger and more complex molecules may become entangled in the sorbent organic matrix, thus reducing their diffusion rates. Because HOCs that are more hydrophobic have higher sorption capacities, decreases in HOC diffusion coefficients have also been correlated with the partition coefficient K_p , in which case an inverse relationship is seen (e.g. Karapanagioti et al. 2000).

Figure 4-3 compares the desorption rates of fresh and anaerobically degraded biopolymers. Differences between desorption rates for fresh and degraded materials were largest with rabbit food while results between fresh and degraded office paper were not significantly different (Figure 4-3). Since isotherm results indicate that lipophilic extractives and lignin control HOC sorption to rabbit food and newsprint, it can be assumed that they will also have an effect on desorption rates. Lipophilic extractives have a lower surface energy than lignin and HOC sorption affinity is inversely proportional to surface energy (Reinhart et al. 1990).

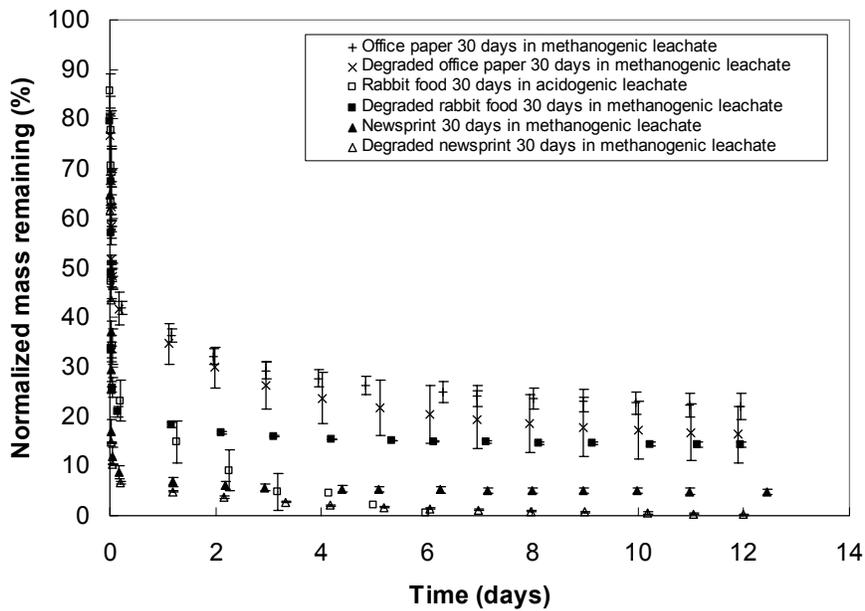


Figure 4-3. Effect of anaerobic sorbent degradation on PCE desorption rates

Rabbit food and degraded rabbit food have a higher proportion of lipophilic extractives than newsprint or degraded newsprint as seen in Table 2.1. This may cause a larger fraction of the sorbate to be associated with the lipophilic extractives in fresh and degraded rabbit food than in fresh and degraded newsprint leading to the larger fraction of slowly desorbing PCE from fresh and degraded rabbit food (Table 4.4). Fresh and degraded office paper have large slow desorption compartments, which may be due to two factors. The first is the possibility of a change in the sorbent organic matter matrix upon uptake of the HOC that would alter diffusive pathways and change the mass transfer rate (Barrer and Barrie 1957, Deitsch et al. 2000, Kan et al. 1997). The other possibility is that the HOCs are strongly associated with sizing agents in office paper. To evaluate these hypotheses, isotherm and desorption rate data were compared for office paper and filter paper (i.e., pure cellulose). The hypothesis that sizing agents in office paper control slow HOC desorption is supported by the filter paper isotherm data in Table 3.1 as well as the PCE desorption data shown in Figure 4-4. The PCE sorption capacity of filter paper (K_p) is approximately 11 times lower than that of office paper suggesting that a component in office paper other than cellulose was largely responsible for its sorption capacity. Given that sizing agents contain alkyl [i.e., poly(methylene)] groups, it is likely that they play an important role in HOC sorption to office paper. The PCE desorption data in Figure 4-4 further demonstrate that PCE quickly desorbed from filter paper with no sequestration whereas approximately 20% of the sorbed PCE remained on office paper after the rapidly desorbing PCE fraction was removed.

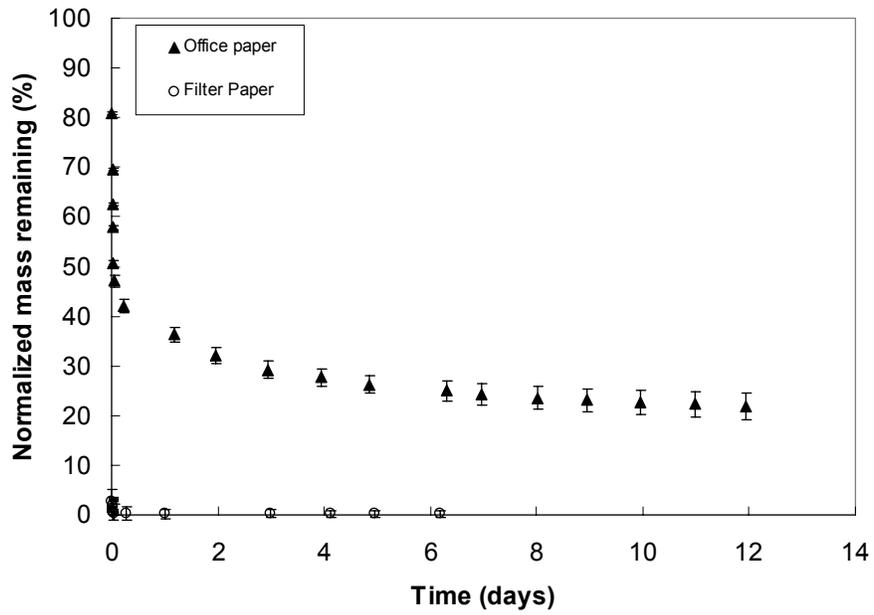


Figure 4-4. Comparison of PCE desorption rates from fresh office paper and fresh filter paper (cellulose). Aging time=30 days.

4.3 Sorbate effects

Table 4.2 compares the diffusion coefficients describing PCE, toluene, and *o*-xylene desorption from PVC and HDPE. Wu (2002) found that 30-day and 250-day aging times for HDPE and PVC yielded similar D values; therefore, diffusion coefficients describing *o*-xylene desorption from HDPE and PVC after 250 days of aging were used for comparison because 30-day data were not available for this sorbate. For HDPE, PCE diffusion coefficients were approximately 3 times slower than those for toluene and similar to those for *o*-xylene. For PVC, PCE diffusion coefficients were similar to the values for toluene and *o*-xylene. The effect of the lower diffusion coefficients describing PCE desorption from HDPE are easily observed in Figure B-10. The difference in diffusion coefficients between PCE and toluene that were obtained with HDPE are consistent with sorbate size and hydrophobicity. PCE has a larger molecular diameter than toluene [$d=0.72$ nm (Farrel and Reinhard 1994) versus $d=0.585$ nm (Baertsch et al. 1996), respectively] and is more hydrophobic [$S_w=150$ mg/L versus $S_w=515$ mg/L, respectively (Mackay et al. 1995)]. Similar diffusion coefficients for PCE and *o*-xylene may be due to similar solubilities and molecular diameters [$d=0.68$ nm (Baertsch et al. 1996), $S_w=175$ mg/L for *o*-xylene (Mackay et al. 1995)]. As the desorption rate parameter estimates in Table 4.3 show, D_r values for PCE were either similar to those of toluene or somewhat larger. In contrast, D_s values describing PCE desorption were always larger than those describing toluene desorption (Table 4.3). Figure B-11 through B-16 also illustrate that PCE desorption rates from biopolymer composites were either similar to or larger than toluene desorption rates. Two factors may explain this somewhat unexpected result: (1) desorption tests were conducted by separate individuals such that the results are not easily comparable and/or (2) compared to

the chlorinated aliphatic compound PCE, the aromatic nature of toluene led to stronger interactions with the biopolymer composites.

4.4 Leachate effects

Batch desorption tests were conducted in three liquid phases to determine whether leachate composition would change PCE desorption rates. Figure 4-5 compares PCE desorption data from HDPE in both acidogenic and methanogenic leachate phases and illustrates that leachate effects were negligible. Figure 4-5 does show a large difference in PCE desorption rates from office paper between methanogenic and acidogenic leachate, however. D_r and D_s values for office paper in the two leachates were similar but the slow desorption compartment was larger for methanogenic leachate than for acidogenic leachate ($\Phi_s=0.4237$ and $\Phi_s=0.3666$, respectively, Table C.1 in the Appendix). Desorption tests with toluene and office paper using phosphate-buffered DI water at pH 5 and pH 7 (representative of acidogenic and methanogenic leachates, respectively, Table 2.4) by Wu (2002) were conducted to test pH effects on HOC desorption rates from office paper. The desorption data obtained for the pH 5 sample were nearly identical to toluene desorption data from office paper in acidogenic leachate while the desorption data for the pH 7 sample matched methanogenic leachate data. This test shows that differences in toluene desorption rates from office paper in the two leachates were primarily due to pH, and this pH effect likely explains the PCE desorption data from office paper in Figure 4-5 as well. Previous research has shown that acidic conditions may cause cellulose and hemicellulose hydrolysis (Esteghlalian et al. 1997, Maloney et al. 1985, Lipinsky 1979). The acidogenic leachate may therefore alter the organic matrix of the office paper, thus enhancing desorption rates.

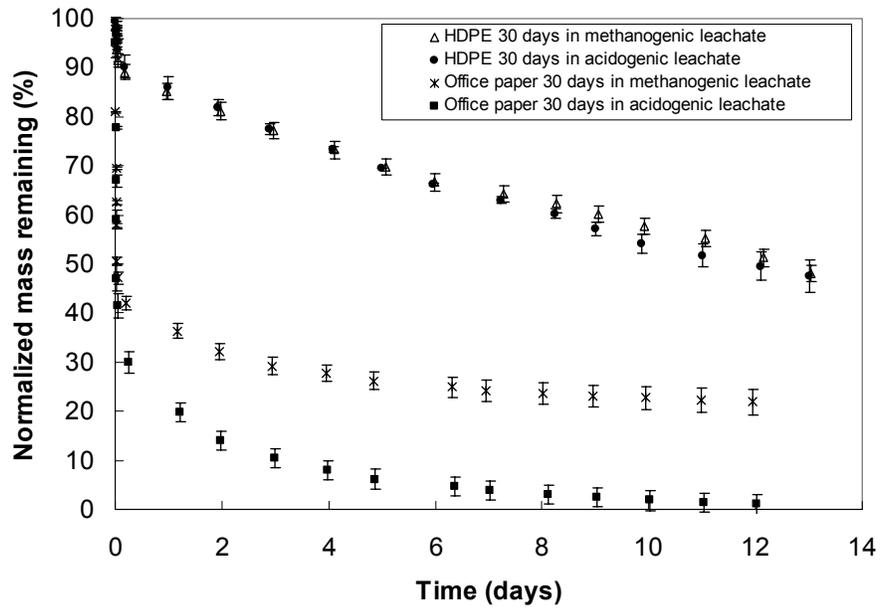


Figure 4-5. Leachate effects on PCE desorption rates from HDPE and fresh office paper

Based on PCE isotherm results in different liquid phases and based on the data of Wu (2002), enhanced PCE desorption rates were also expected from PVC in acidogenic leachate since constituents in the acidogenic leachate plasticize PVC from a glassy polymer to a rubbery state as mentioned above. Figure B-1 and Table 4.2 show little difference between the PCE desorption data and rate parameters in the three liquid phases, however. Improved estimates of leachate effects on PCE desorption rates from PVC are expected once sorption equilibrium is established during a longer aging period. Leachate effects were small for fresh and degraded newsprint (Figures B-4 and B-7, respectively). Results for degraded office paper were too scattered to reliably determine a leachate effect (Figure B-8), and experimental difficulties (loss of sorbent) precluded the assessment of leachate effects for fresh and degraded rabbit food.

4.5 Mass Balances

Mass balances were conducted using benzyl alcohol extractions to determine whether PCE losses occurred in the experimental procedure used to quantify desorption kinetics. Table 4.5 shows PCE recoveries for desorption tests conducted with HDPE, rabbit food, newsprint, and degraded newsprint. PCE recoveries ranged from 94.5-98.7% indicating that PCE losses were negligible and experimental procedures were reliable. Base extraction and combustion of benzyl alcohol extracted solids would have increased recoveries as shown by Wu (2002).

Table 4.5. Mass balance analysis

Solid	Desorbed fraction (%)	Benzyl alcohol extractable fraction (%)	Total mass recovered(%)
HDPE Sample 1 ^a	58.1	36.4	94.5
HDPE Sample 2 ^b	55.2	40.8	96.0
Rabbit Food Sample 1 ^a	96.0	1.1	97.1
Rabbit Food Sample 2 ^b	93.3	2.4	95.7
Newsprint Sample 1 ^a	86.1	12.1	98.2
Newsprint Sample 2 ^b	85.2	12.3	97.5
Degraded Newsprint Sample 1 ^a	89.4	9.2	98.7
Degraded Newsprint Sample 2 ^b	88.2	9.2	97.4

^aThe liquid phase was ultrapure water

^bThe liquid phase was acidogenic leachate

4.6 Model Predictions for Simulated MSW Mixtures

Using isotherm data and desorption rates for PCE obtained in this study and for toluene (Wu 2002), HOC desorption rates from mixed MSW can be predicted. Two scenarios were evaluated. In the first scenario, a MSW composition from 1960 was assumed; at that time, the percentage of plastics entering the landfill was much smaller than today. The second scenario assumes MSW composition data from 1997, at which time a much higher percentage of plastics entered a landfill. Sorbent organic matter compositions and HOC distributions are listed in Tables 4.6 and 4.7 for the 1960 and 1997 scenarios, respectively (US EPA 1998). Model predictions for toluene and PCE desorption from mixed MSW along with experimental data for toluene are shown in Figure 4-6. Experimental results for the 1960 scenario showed that the model prediction closely matched the experimental data. Additional experiments are required to verify the model prediction for simulated mixed refuse with a 1997 composition. Figure 4-6 further illustrates that predicted toluene and PCE desorption rates from simulated MSW mixtures are similar. Overall, the results of the desorption tests for simulated MSW mixtures illustrate that the greater percentage of plastics in the 1997 scenario greatly decreased HOC desorption rates.

5 Conclusions and Future Research

5.1 Conclusions

The objectives of this research were to measure the sorption capacity of PCE and DCE to model MSW components [i.e., high-density polyethylene (HPDE), poly(vinyl chloride) (PVC), model food and yard waste, office paper, and newsprint] and to determine the factors that control HOC sorption to MSW.

Table 4.6. Composition of sorbent organic matter and HOC distribution in simulated municipal solid waste (1960) after an aging time of 30 days

Waste category	Mass percentage (%) ^a	Fraction of sorbed toluene (%)	Fraction of sorbed PCE (%)
Total newsprint	20.64	13.85	13.23
Total office paper	22.68	3.17	4.71
Glassy plastics	0.21	1.39	1.28
Rubbery plastics	0.507	1.86	3.43
Food + yard waste	55.95	79.72	77.35

^afrom Wu (2002)

Table 4.7. Composition of sorbent organic matter and HOC distribution in simulated municipal solid waste (1997) after an aging time of 30 days

Waste category	Mass percentage (%) ^a	Fraction of sorbed toluene (%)	Fraction of sorbed PCE (%)
Total newsprint	18.58	9.21	6.78
Total office paper	20.42	2.10	2.41
Glassy plastics	5.86	28.77	20.30
Rubbery plastics	14.11	37.89	54.03
Food + yard waste	41.03	22.03	16.48

^afrom Wu (2002)

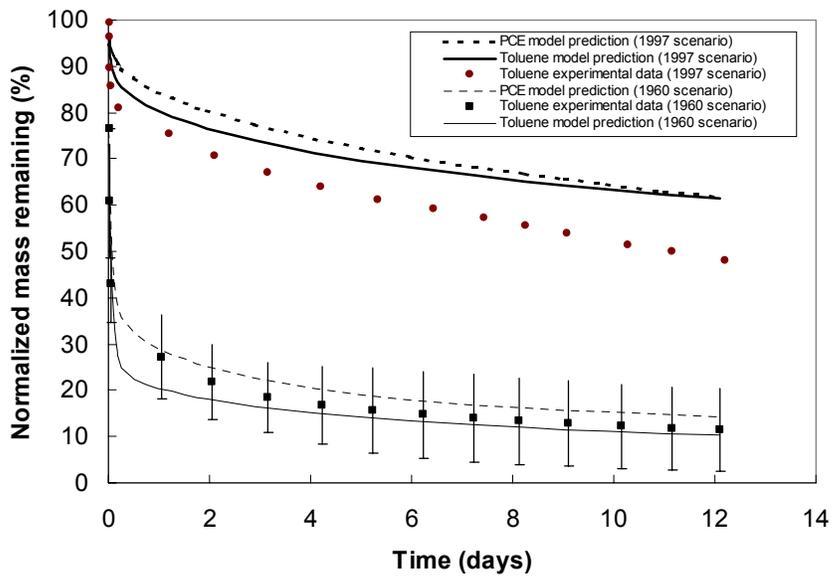


Figure 4-6. Toluene and PCE desorption rate predictions for simulated MSW mixtures after an aging time of 30 days. Toluene predictions are compared to experimental toluene desorption rate data obtained with simulated MSW mixtures.

Isotherms tests were also conducted with toluene and polyethylenes to determine the importance of amorphous regions in sorbent organic matter on sorption capacity. Toluene sorption capacities of newsprint samples collected from three depths in the Norman, OK, landfill were also measured and compared with those of fresh and-laboratory degraded newsprint samples. Finally, batch PCE desorption kinetics were measured after an aging time of 30 days. The conclusions of this study include:

- 1) Uptake of PCE by MSW components occurred primarily by linear partitioning into sorbent organic matter. A non-linear PCE isotherm was obtained for PVC in methanogenic leachate, which was expected because PVC is a glassy polymer.
- 2) DCE sorption capacities were lower than those for PCE and alkylbenzenes. This can be explained by the higher aqueous solubility of DCE and the inverse relationship between aqueous solubility and sorption capacity.
- 3) A small leachate effect was observed for PCE isotherms collected with PVC, where the isotherm data in acidogenic leachate was more linear and exhibited a smaller sorption capacity. PCE isotherm data were not affected by the leachate composition for the other MSW components.
- 4) Polyethylenes with higher amorphous fractions showed higher sorption capacities. Normalization of K_p using the amorphous fraction did not yield similar values, however, suggesting that knowledge of the amorphous fraction alone is not sufficient to predict the HOC sorption capacity of polyethylenes.
- 5) Toluene sorption capacity of NLF newsprint samples increased in the order of $MNP < TNP < BNP$. The extent of MNP degradation was smaller than that of TNP,

suggesting that the extent of sorbent degradation is not necessarily related to residence time or sample depth in the landfill.

- 6) Although it has been established that HOC sorption capacity decreases with increasing sorbent polarity, small amounts of lipophilic extractives strongly influence HOC sorption capacity. The O-alkyl/alkyl ratio is therefore a better sorbent organic matter descriptor for the predictions of HOC sorption capacities because it recognizes the importance of both sorbent polarity and lipophilic extractives content for HOC sorption. The results of this study showed that the O-alkyl/alkyl ratio is a suitable predictor for the HOC sorption capacity of fresh and degraded MSW components as well as for natural organic materials.
- 7) Overall, HOC sorption to MSW is strongly influenced by plastics and lipophilic extractives. As biological degradation of sorbent organic matter in the landfill proceeds, the affinity of the remaining organic matter for HOCs increases because of (a) a reduction in sorbent polarity, (b) an increase in lipophilic extractive content, and (c) the recalcitrance of plastics.
- 8) PCE desorption rates from plastics was slower than from biopolymer composites. The PCE desorption rate from PVC was slowest while it was fastest from newsprint and degraded office paper. PCE desorption rates from plastics were described well by a one-compartment diffusion model while a two-compartment diffusion model was required for biopolymer composites.
- 9) Using the model developed by Wu (2002), toluene desorption rates were predicted well for mixed simulated refuse with a 1960 waste composition. Additional experiments are

required to verify the prediction of toluene desorption from simulated mixed refuse with a 1997 composition.

5.2 Future Research

To enable a more complete interpretation of the data obtained in this thesis, the following tests should be conducted:

- 1) Determine the DCE sorption capacity of PVC.
- 2) Test whether aging time affects PCE desorption rates from MSW components by conducting desorption experiments after longer aging times.
- 3) Test whether aging time affects HOC desorption rates from MSW mixtures and whether the model developed by Wu (2002) adequately predicts these effects.

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Appendices

A. Isotherms

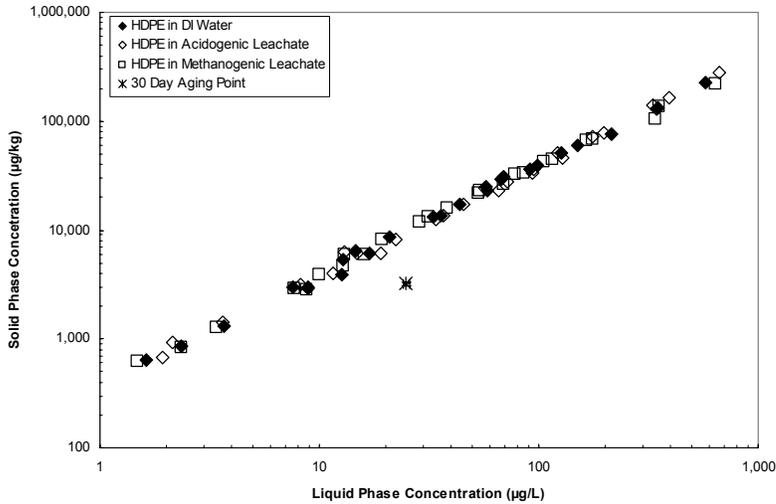


Figure A-1. PCE isotherms with HDPE in DI water, acidogenic leachate, and methanogenic leachate. The 30-day aging point represents the mean value of solid and liquid phase concentrations for the three liquid phases. Error bars represent one standard deviation of the mean for both liquid and solid phase concentrations.

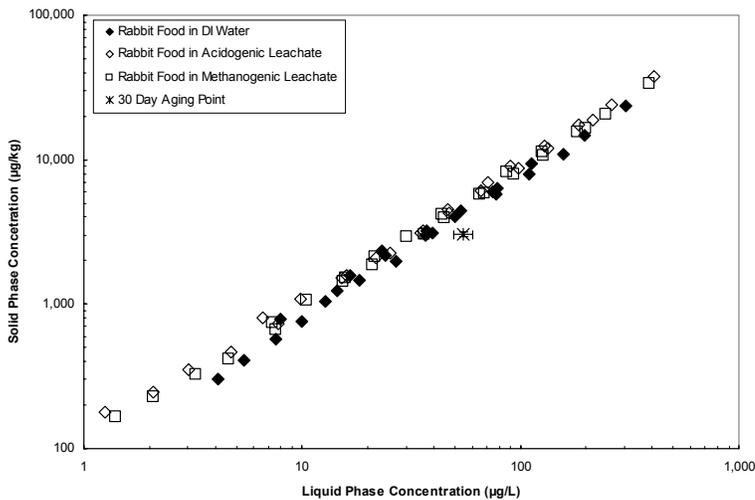


Figure A-2. PCE isotherms with rabbit food in DI water, acidogenic leachate, and methanogenic leachate. The 30-day aging point represents the mean value of solid and liquid phase concentrations for the three liquid phases. Error bars represent one standard deviation of the mean for both liquid and solid phase concentrations.

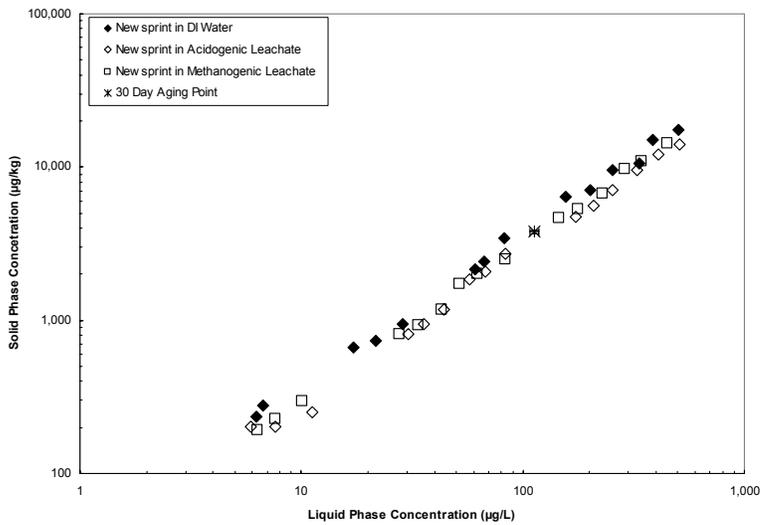


Figure A-3. PCE isotherms with newsprint in DI water, acidogenic leachate, and methanogenic leachate. The 30-day aging point represents the mean value of solid and liquid phase concentrations for the three liquid phases. Error bars represent one standard deviation of the mean for both liquid and solid phase concentrations.

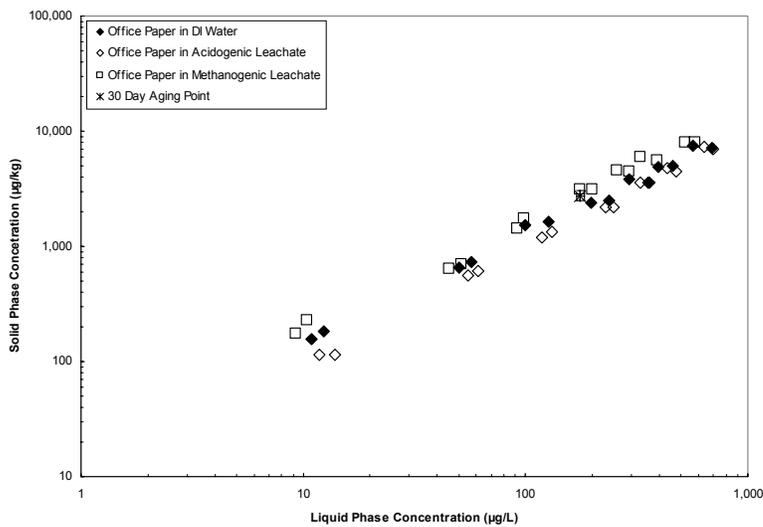


Figure A-4. PCE isotherms with office paper in DI water, acidogenic leachate, and methanogenic leachate. The 30-day aging point represents the mean value of solid and liquid phase concentrations for the three liquid phases. Error bars represent one standard deviation of the mean for both liquid and solid phase concentrations.

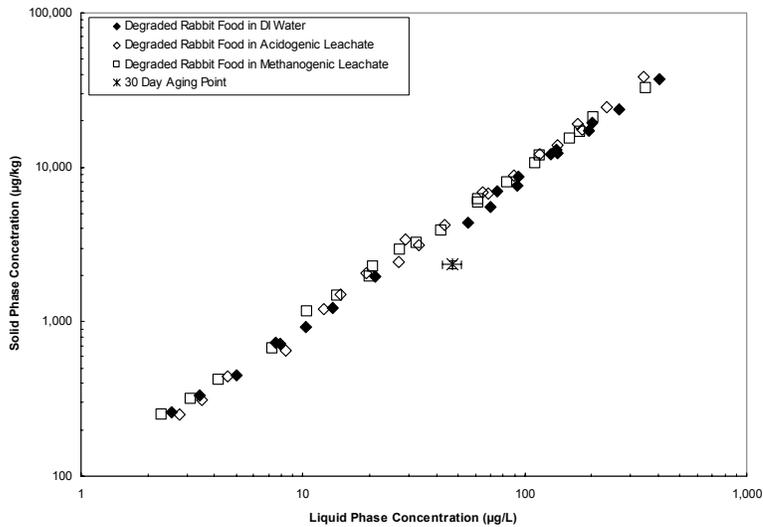


Figure A-5. PCE isotherms with degraded rabbit food in DI water, acidogenic leachate, and methanogenic leachate. The 30-day aging point represents the mean value of solid and liquid phase concentrations for the three liquid phases. Error bars represent one standard deviation of the mean for both liquid and solid phase concentrations.

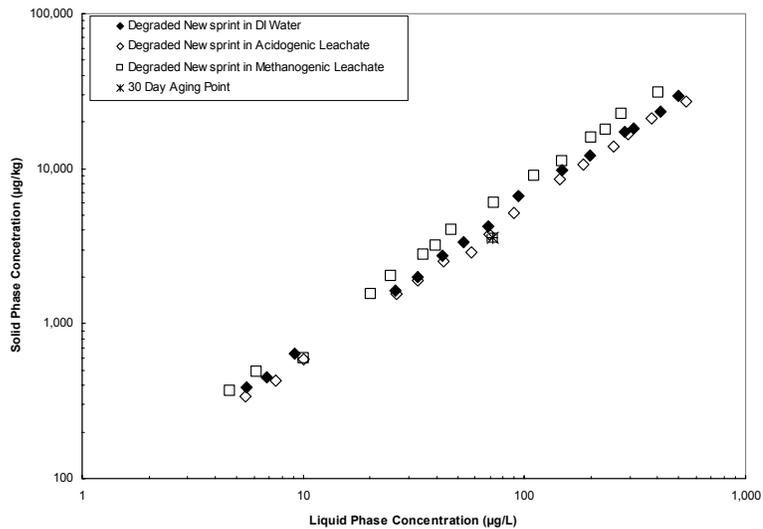


Figure A-6. PCE isotherms with degraded newsprint in DI water, acidogenic leachate, and methanogenic leachate. The 30-day aging point represents the mean value of solid and liquid phase concentrations for the three liquid phases. Error bars represent one standard deviation of the mean for both liquid and solid phase concentrations.

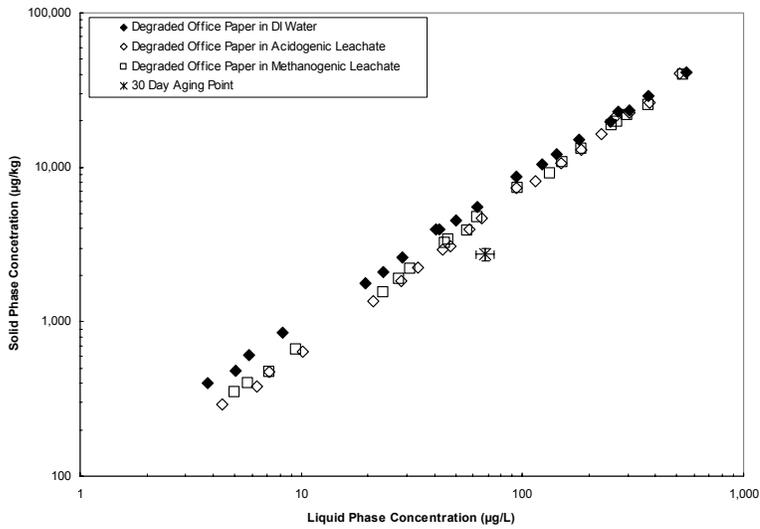


Figure A-7. PCE isotherms with degraded office paper in DI water, acidogenic leachate, and methanogenic leachate. The 30-day aging point represents the mean value of solid and liquid phase concentrations for the three liquid phases. Error bars represent one standard deviation of the mean for both liquid and solid phase concentrations.

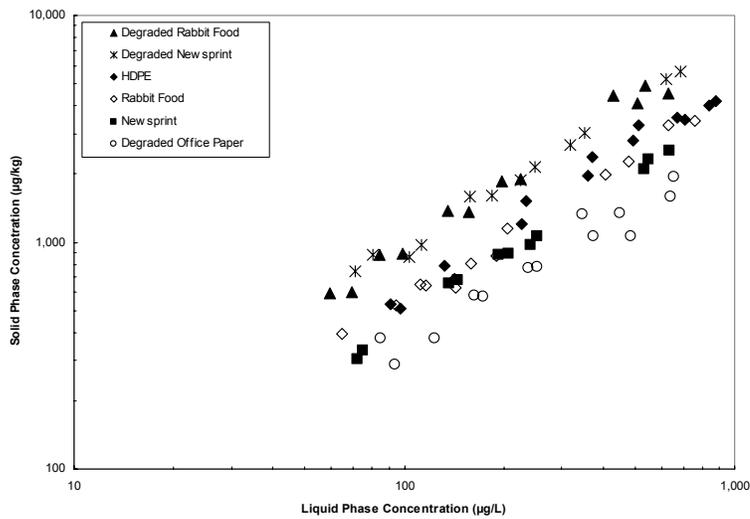


Figure A-8. DCE isotherms with MSW components in DI water.

B. Desorption Rate Data

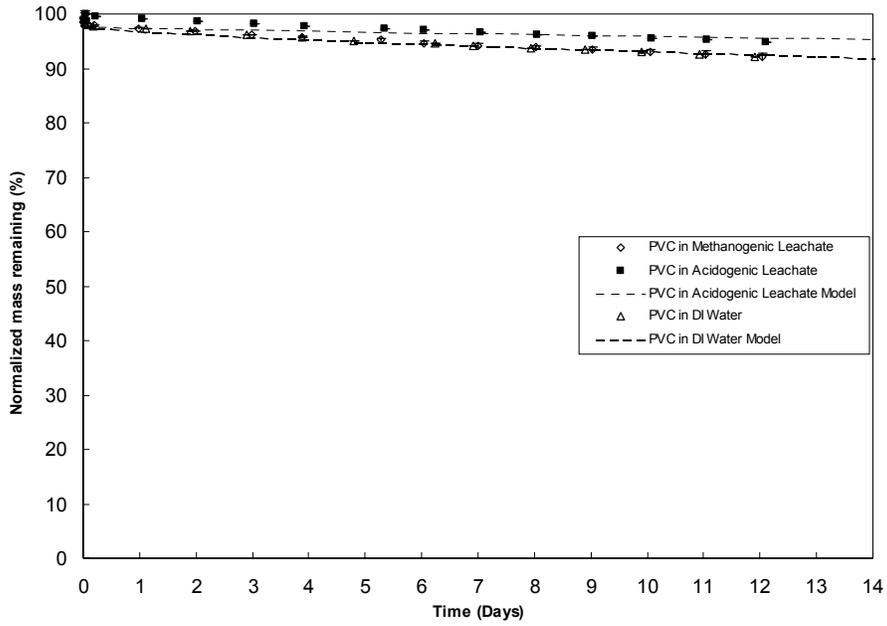


Figure B-1. PCE desorption rate from PVC in DI water, acidogenic leachate, and methanogenic leachate

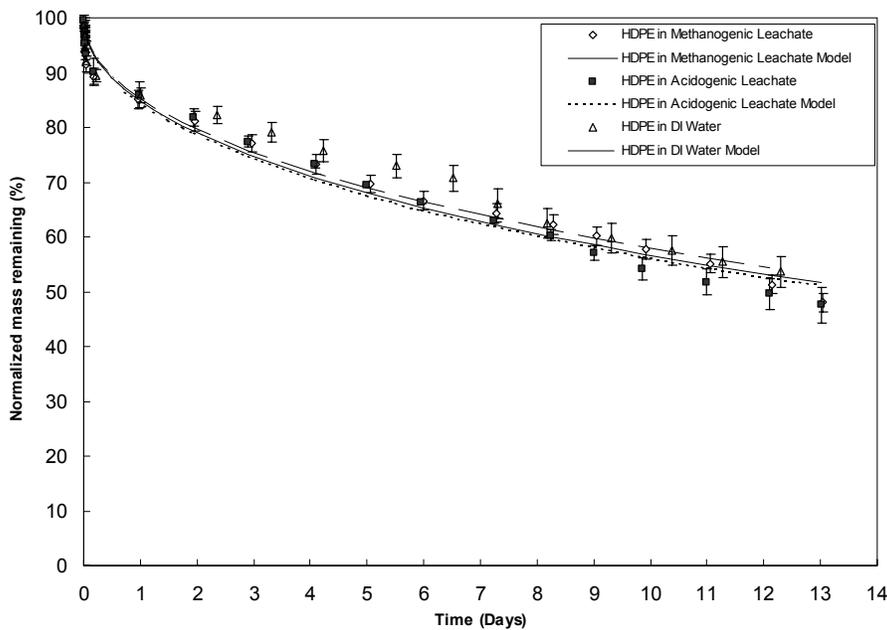


Figure B-2. PCE desorption rate from HDPE in DI water, acidogenic leachate, and methanogenic leachate

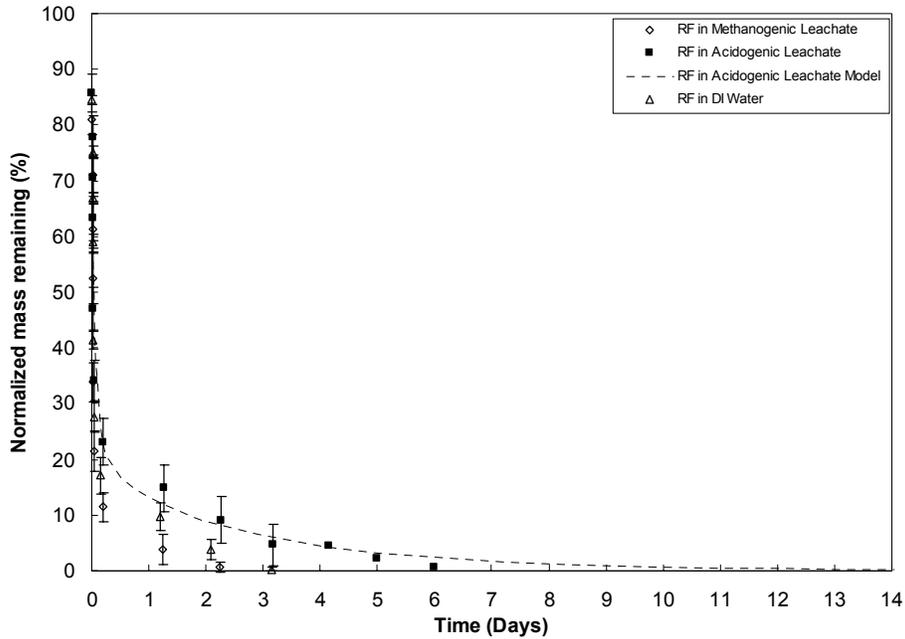


Figure B-3. PCE desorption rate from rabbit food in DI water, acidogenic leachate, and methanogenic leachate. Methanogenic leachate and DI water desorption tests are unreliable due to loss of liquid phase during purging process.

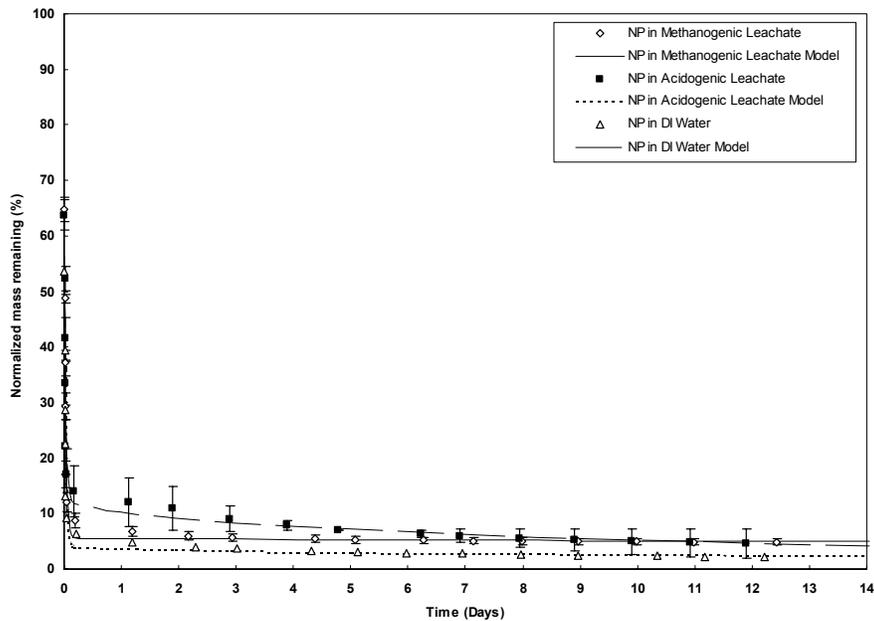


Figure B-4. PCE desorption rate from newsprint in DI water, acidogenic leachate, and methanogenic leachate

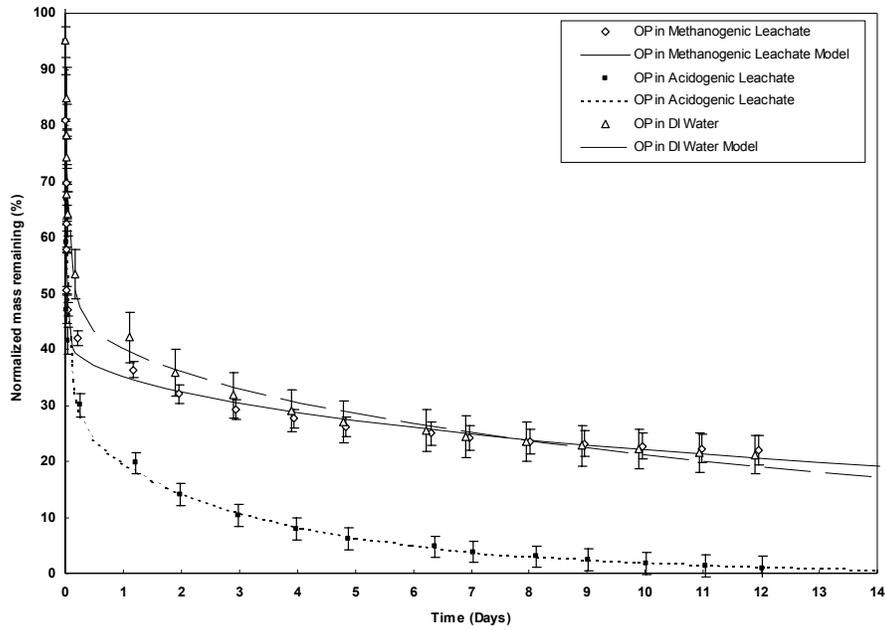


Figure B-5. PCE desorption rate from office paper in DI water, acidogenic leachate, and methanogenic leachate.

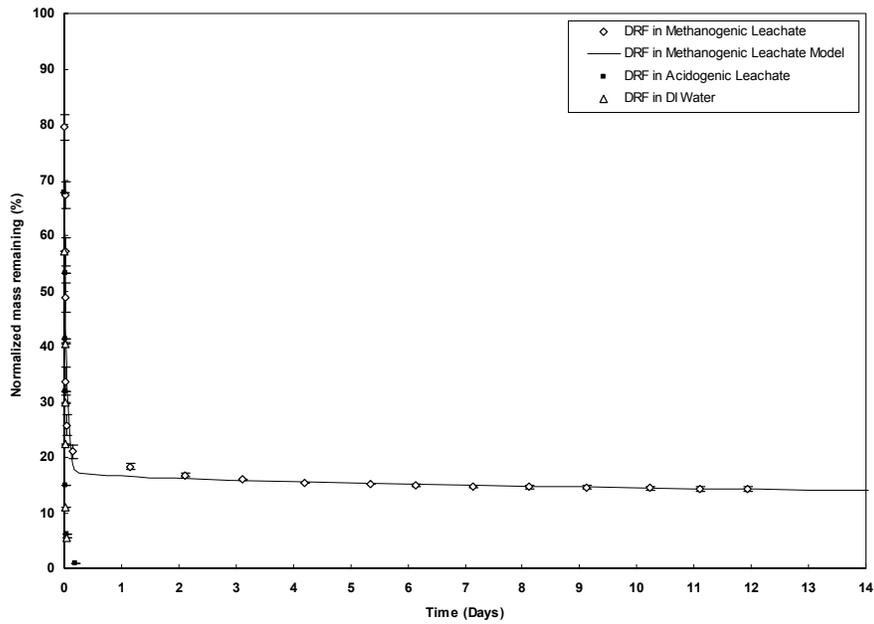


Figure B-6. PCE desorption rate from degraded rabbit food in DI water, acidogenic leachate, and methanogenic leachate. Acidogenic leachate and DI water desorption tests are unreliable due to loss of liquid phase during purging process.

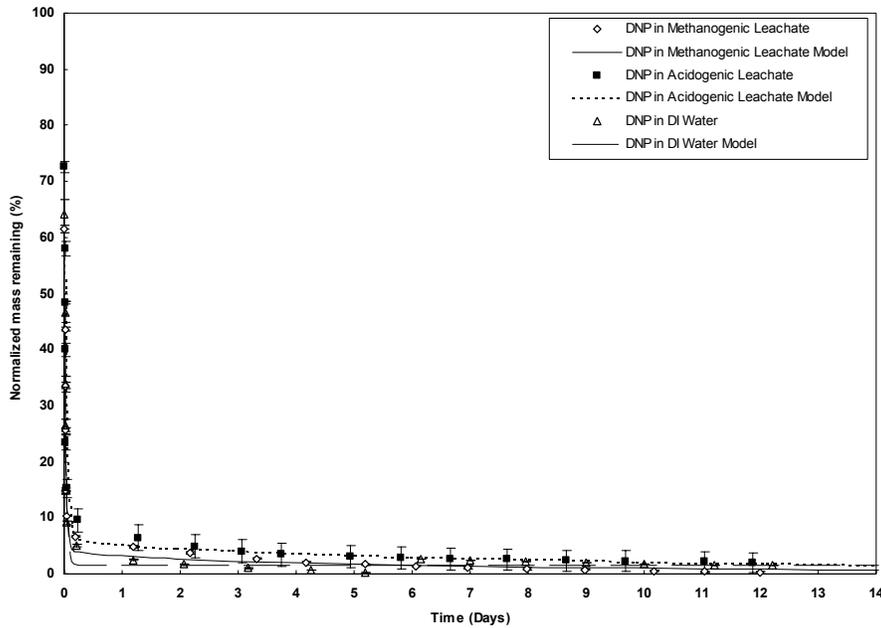


Figure B-7. PCE desorption rate from degraded newsprint in DI water, acidogenic leachate, and methanogenic leachate.

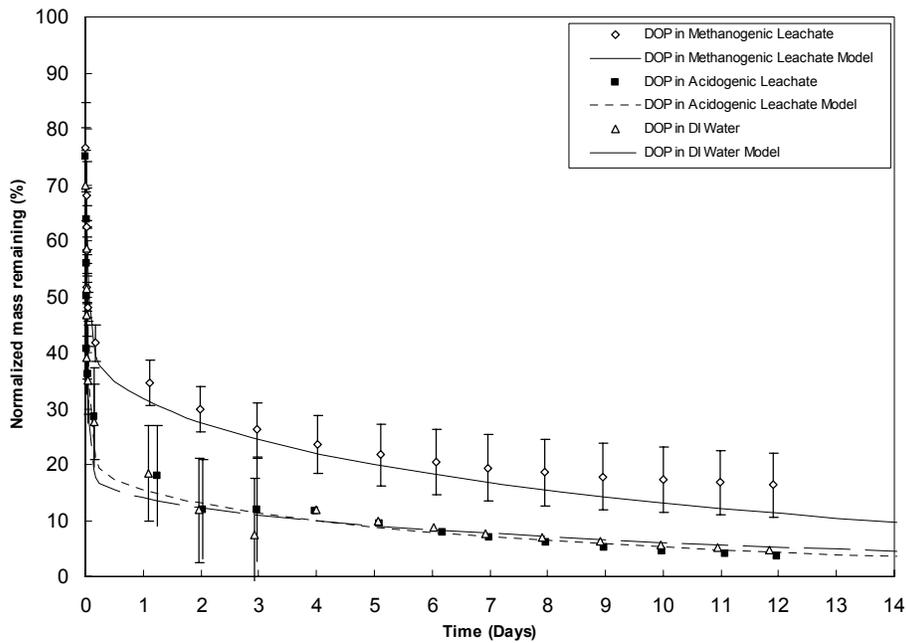


Figure B-8. PCE desorption rate from degraded office paper in DI water, acidogenic leachate, and methanogenic leachate.

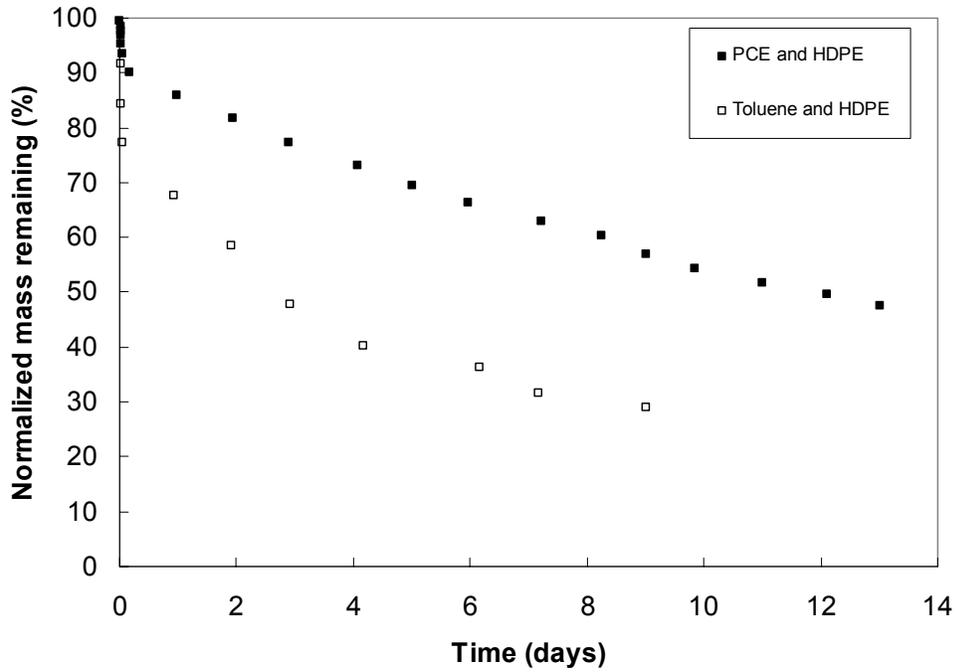


Figure B-9. Comparison of PCE and toluene desorption rates from HDPE in acidogenic leachate after an aging time of 30 days.

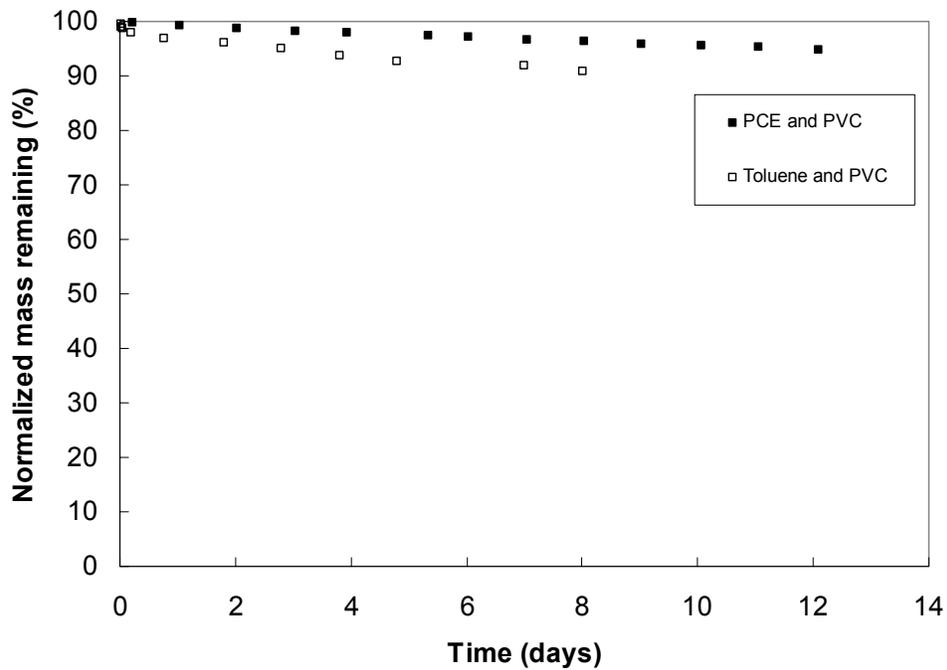


Figure B-10. Comparison of PCE and toluene desorption rates from PVC in acidogenic leachate after an aging time of 30 days.

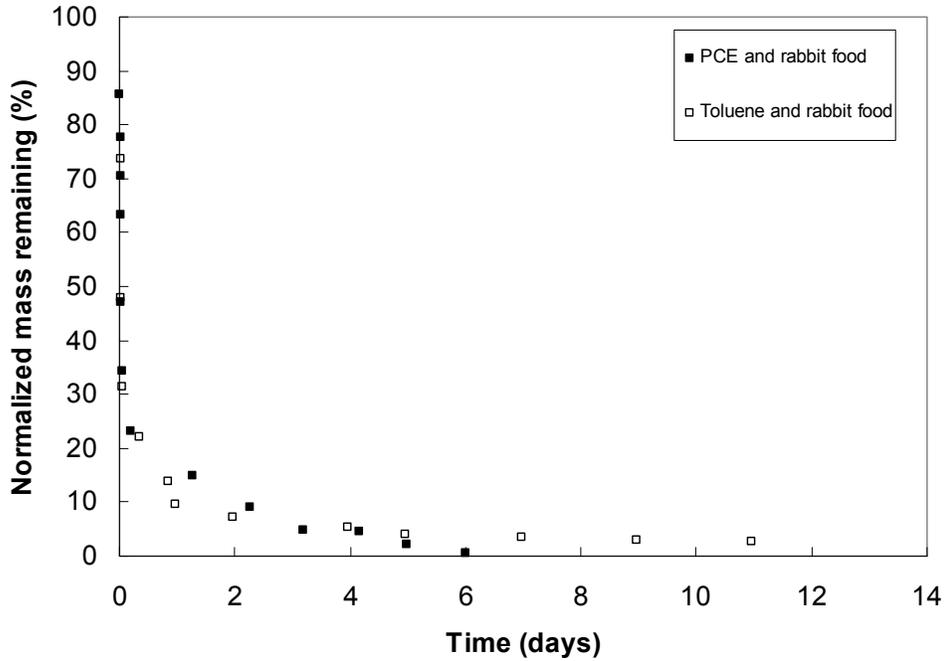


Figure B-11. Comparison of PCE and toluene desorption rates from rabbit food in acidogenic leachate after an aging time of 30 days.

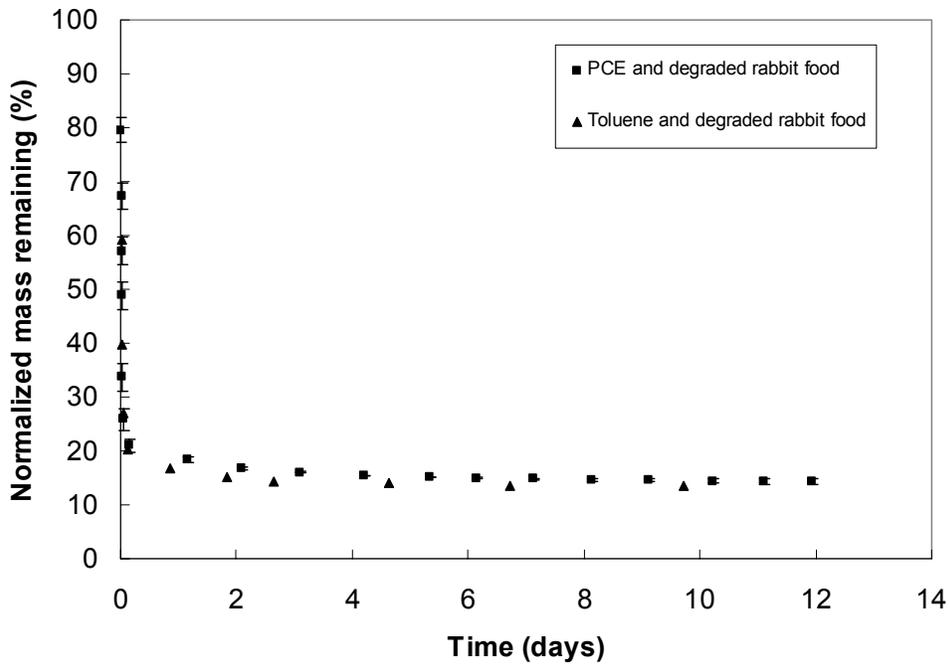


Figure B-12. Comparison of PCE and toluene desorption rates from degraded rabbit food after and aging time of 30 days. Liquid phase for PCE was methanogenic leachate, liquid phase for toluene was acidogenic leachate. The methanogenic leachate data were used for PCE because acidogenic leachate data were unreliable due to liquid losses during purging.

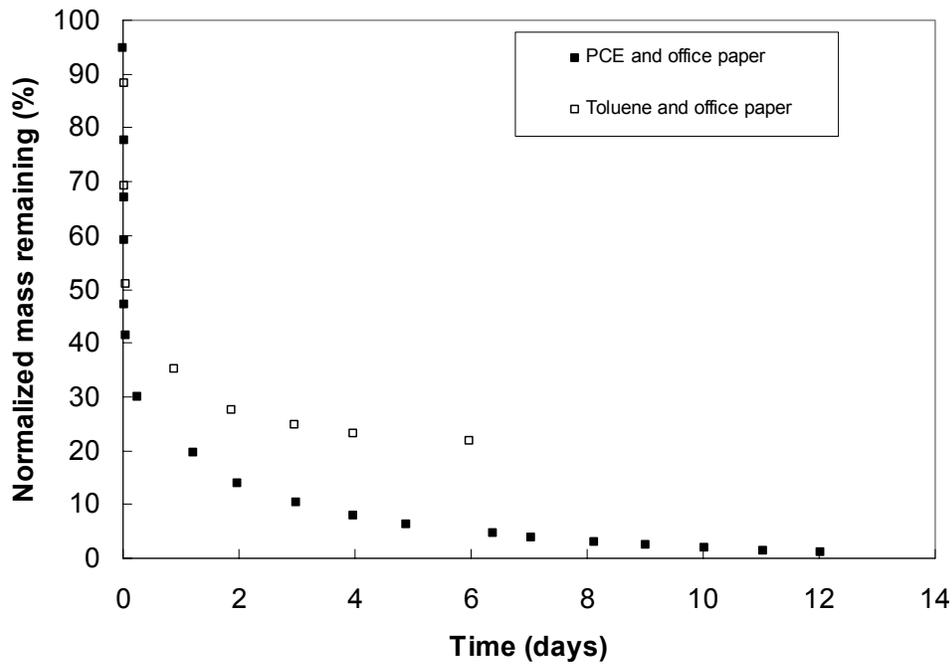


Figure B-13. Comparison of PCE and toluene desorption rates from office paper in acidogenic leachate after an aging time of 30 days.

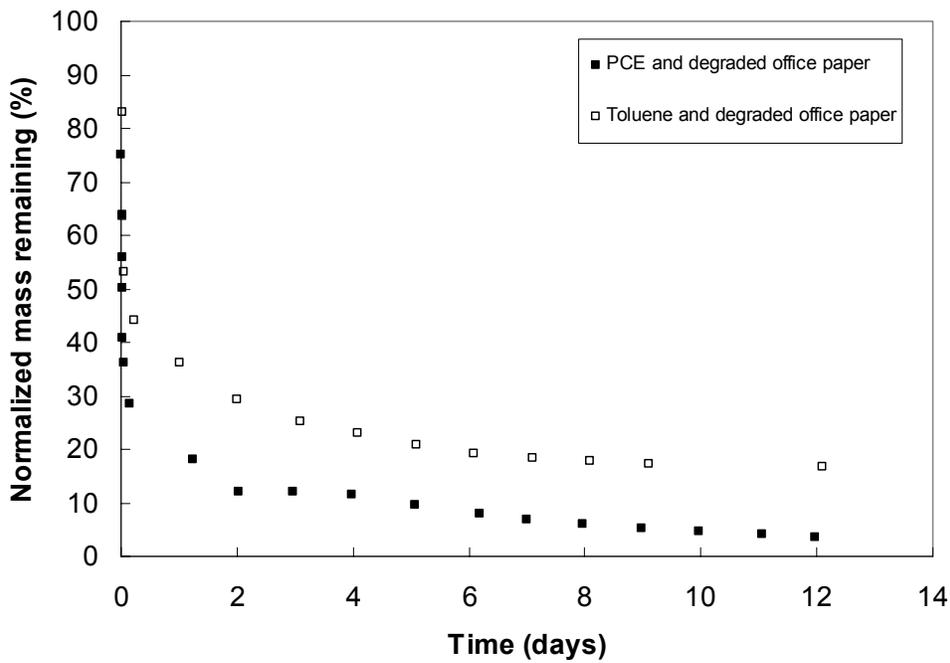


Figure B-14. Comparison of PCE and toluene desorption rates from degraded office paper in acidogenic leachate after an aging time of 30 days.

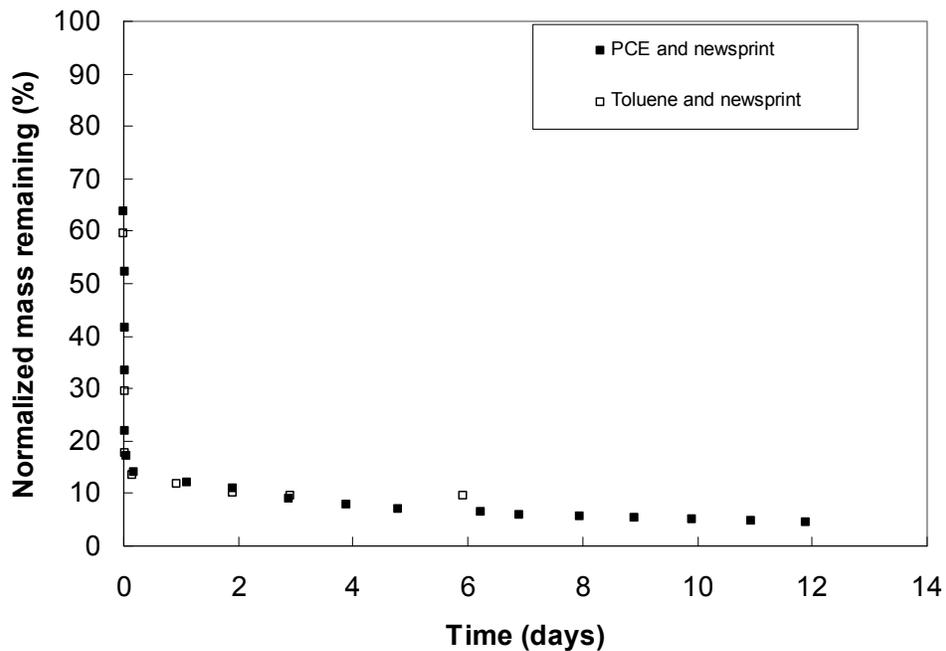


Figure B-15. Comparison of PCE and toluene desorption rates from newsprint in acidogenic leachate after an aging time of 30 days.

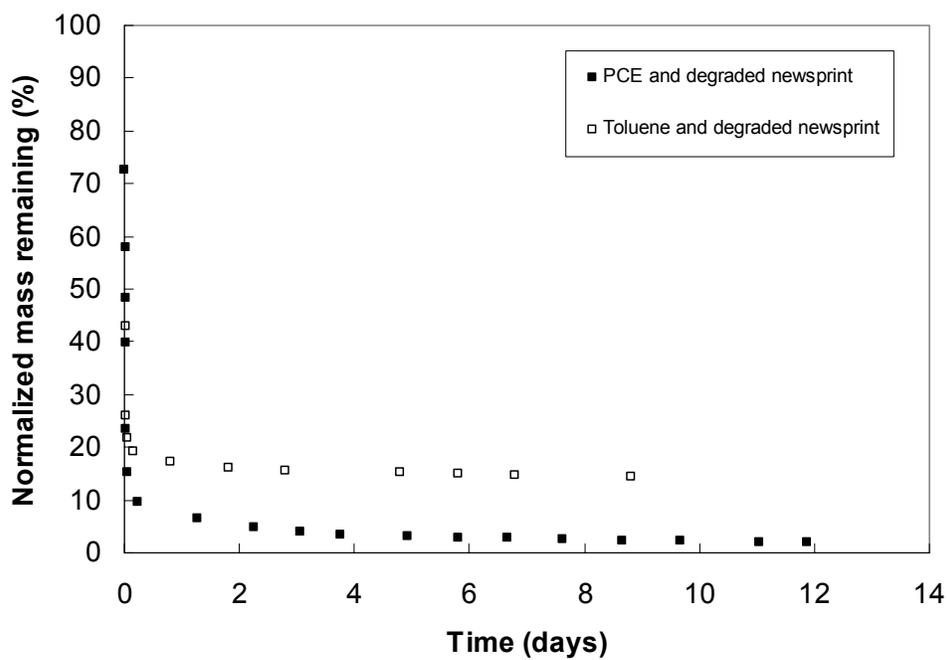


Figure B-16. Comparison of PCE and toluene desorption rates from degraded newsprint in acidogenic leachate after an aging time of 30 days.

C. Desorption Rate Parameters

Table C.1 PCE Desorption rate parameter estimates for the Two-Compartment Polymer Diffusion Model in three liquid phases. Aging time was 30 days.

Sample	Φ_r	Φ_s	PCE	
			Dr (cm ² /s)	Ds (cm ² /s)
OP (DI Water)	0.4903	0.5097	1.48E-09	6.36E-12
OP (Methanogenic Leachate)	0.5762	0.4237	4.34E-09	3.90E-12
OP (Acidogenic Leachate)	0.6334	0.3666	4.73E-09	6.72E-11
DOP (DI Water)	0.8107	0.1892	1.60E-08	4.97E-11
DOP (Methanogenic Leachate)	0.5672	0.4327	1.27E-08	5.32E-11
DOP (Acidogenic Leachate)	0.7655	0.2345	1.37E-08	8.45E-11
NP (DI Water)	0.8690	0.1309	1.03E-08	1.30E-11
NP (Methanogenic Leachate)	0.9436	0.0564	9.72E-09	2.82E-13
NP (Acidogenic Leachate)	0.9582	0.0418	1.28E-08	4.64E-12
DNP (DI Water)	0.9842	0.0157	4.26E-09	5.27E-16
DNP (Methanogenic Leachate)	0.9539	0.0461	4.82E-09	1.35E-11
DNP (Acidogenic Leachate)	0.9294	0.0706	3.11E-09	8.62E-12
RF (Acidogenic Leachate)	0.7268	0.2732	4.38E-09	9.95E-11
DRF (Methanogenic Leachate)	0.8241	0.1758	5.27E-09	6.93E-13