Abstract

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The overall goal of this research was to determine desorption rates of hydrophobic organic contaminants (HOCs) from municipal solid waste (MSW). Toluene and o-xylene, two alkylbenzenes that frequently occur in landfill leachates, served as model HOCs. HOC desorption rates were measured for individual MSW components expected to contribute to HOC sorption [high density polyethylene (HDPE), and poly(vinyl chloride) (PVC), newsprint, office paper, and degraded rabbit food as a model food and yard waste]. To quantify effects of MSW decomposition on HOC desorption rates, newsprint and office paper were tested in both fresh and anaerobically degraded forms. Effects of aqueous phase composition were evaluated by comparing HOC desorption rates in both acidogenic and methanogenic leachates to those obtained in ultrapure water. To determine the effects of aging (i.e., contaminant-sorbent contact time), desorption tests in ultrapure water were performed after aging times of 1 day, 1 week, 1 month, 6 months, and 9 months. Toluene desorption rates in acidogenic and methanogenic leachates and o-xylene desorption rates in ultrapure water were measured after aging times of 1 week and 6 months.

To compare HOC desorption rates in a quantitative manner, experimental data were described by polymer diffusion models. A single-parameter polymer diffusion model was used to describe HOC desorption rates from PVC and HDPE, while a three-parameter biphasic polymer diffusion model was implemented to describe HOC desorption rates from biopolymer composites. Desorption tests showed that HOC desorption rates varied greatly with sorbent characteristics. HOC desorption rates from plastics were rapid for rubbery polymers such as HDPE and slow for glassy polymers such as PVC. For biopolymer composites, an initial phase of rapid HOC desorption was followed by an extended period of slow HOC desorption.

In general, HOC desorption rates in acidogenic or methanogenic leachates were similar to those observed in ultrapure water. Exceptions were experiments conducted with PVC and fresh office paper in acidogenic leachate, in which cases enhanced HOC desorption rates were obtained. Volatile fatty acids such as propionic or butyric acids, which are important constituents of acidogenic leachate organic matter, may have plasticized PVC and thus enhanced HOC desorption rates. For fresh office paper, prior work by Wu (2002) showed that the lower pH of acidogenic leachate was primarily responsible for enhanced HOC desorption rates.

Regarding sorbate characteristics, desorption rates for toluene were generally faster than those of *o*-xylene, a larger more hydrophobic molecule. For biopolymer composites, the HOC fraction associated with the slowly releasing sorbent organic matter fraction increased with increasing aging time, and, compared to toluene, this trend was more pronounced for *o*-xylene.

Model predictions for simulated MSW mixtures showed that both waste composition and HOC characteristics greatly affect HOC desorption rates. Predicted half-lives for toluene and *o*-xylene were <1 and ~7 days, respectively, for a MSW mixture typical of the year 1960 and ~600 and 1525 days, respectively, for a MSW mixture typical of the year 2000. The principal changes in MSW composition that occurred between 1960 and 2000 was a decrease in food and yard waste and an increase in plastics. In particular, the greater presence of glassy polymers, such as PVC, in the newer MSW mixture led to slower alkylbenzene desorption rates. These predictions suggest that the mineralization rate of alkylbenzenes in old landfills may be controlled by biological processes while desorption processes may control alkylbenzene biodegradation rates in newer landfills.

Factors Controlling Desorption Rates of Hydrophobic Organic Contaminants from Municipal Solid Waste

By

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Biography

Lisa Mitchell was born on December 3, 1980 in Hinsdale, Illinois. She spent the majority of her youth in Charlotte, North Carolina. In 2003, she graduated with a B.S. in Environmental Engineering from North Carolina State University. Later that same year, she began work on her M.S. in Civil Engineering at the same university. Her research interests include water and wastewater treatment as well as solid waste management.

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1 Introduction and Objectives

Most municipal solid waste (MSW) is disposed of in landfills. Prior to 1980, few constraints existed regarding the codisposal of MSW with industrial wastes. Many older landfills are unlined and are thus a potential source of groundwater contamination. Indeed, alkylbenzenes are common groundwater pollutants found downgradient from old MSW landfills (Christensen et al. 1994). Furthermore, approximately 18% of the sites on the National Priority List of Superfund are landfills (US EPA 2005). Cost-effective and environmentally sound management strategies are needed to clean up these and many other sites. To develop such strategies requires information on contaminant fate in landfills.

To date, little research has been done to characterize sorption and desorption processes of hydrophobic organic contaminants (HOCs) in the MSW environment. In contrast, abundant literature is available for HOC sorption to/desorption from soils and sediments. However, these geosorbents typically have lower organic carbon contents than MSW and the surrounding aqueous phase (e.g., groundwater) has organic carbon concentrations that are two to three orders of magnitude lower than landfill leachate.

Sorption and desorption processes limit HOC transport and biodegradation in landfills (Sanin et al. 2000, Reinhart et al. 1991). Factors that influence the rate and extent of HOC sorption/desorption include sorbent properties, sorbate properties, aqueous organic matter composition, pH, and temperature. Sorbent decomposition reduces the mass of sorbent organic matter as well as the polarity/hydrophilicity of sorbent organic matter because more polar components such as cellulose and hemicellulose are preferentially degraded (Pichler and Kögel-Knabner 2000, Eleazer et al. 1997, Wu et al. 2001, Chen et al. 2004b). Increased sorbent hydrophobicity, as a result of biological sorbent degradation, has been shown to result in enhanced HOC sequestration (Guthrie et al. 1999). Chen (2003) also suggested that the degradation of polar biopolymers in MSW, such as cellulose and hemicellulose, did not significantly alter alkylbenzene bioavailability or sorption capacity, which were controlled by more non-polar constituents such as lignin and lipophilic extractives. With increasing aging

(i.e. HOC-sorbent contact) time, HOC bioavailability tends to decrease as a result of continued HOC diffusion into glassy polymers (Hatzinger and Alexander 1995) or sorbent micropores (Pignatello et al. 1993).

A fundamental characterization of sorption and desorption processes specific to the MSW environment is critical to permit the prediction of HOC fate in MSW landfills. To improve knowledge about HOC sorption and desorption processes in MSW landfills, the experimental plan of this research was designed to meet the following objectives:

1. Evaluate the effects of aging time on HOC desorption rates
2. Assess the effects of anaerobic sorbent decomposition on desorption rates
3. Determine the effects of leachate composition on HOC desorption rates
4. Determine the effects of sorbate characteristics on HOC desorption rates
5. Describe HOC desorption rates with appropriate models
6. Predict HOC desorption rates from simulated MSW mixtures

2 Literature Review

2.1 Properties of Municipal Solid Waste Components

The primary components of municipal solid waste (MSW) are paper (29.2%), food waste (15.6%), plastics (14.4%), rubber/leather/textiles (8.5%), wood (7.5%), yard waste (7.4%), metals (7.2%), and glass (6.1%, US EPA 2002). Of these, the components expected to contribute significantly to hydrophobic organic contaminant (HOC) sorption are paper products, food and yard waste, and plastics. While plastics such as high density polyethylene (HDPE) and poly(vinyl chloride) (PVC) are synthetic polymers, paper products and food and yard waste are comprised of biopolymers such as cellulose, hemicellulose, lignin, protein, and lipids. The properties of common polymers in the MSW environment are summarized below.

2.1.1 Polymer States

Organic polymers are present either in an amorphous or in a crystalline state. The presence of loose, randomly arranged polymer molecules characterizes the amorphous state. The crystalline state is characterized by the presence of polymer molecules in a regularly arranged lattice structure. While it is possible to produce completely amorphous polymers, exclusively crystalline polymers cannot be manufactured. Most polymers contain both amorphous and crystalline regions (Tobolsky and Mark 1980).

Amorphous polymers are classified as either rubbery or glassy, and this classification is based on the magnitude of intermolecular forces between individual polymer molecules. In rubbery polymers, weaker forces lead to a malleable structure while stronger intermolecular forces in glassy polymers result in a more rigid structure. The properties of crystalline polymer regions are between those of rubbery and glassy polymers; i.e., crystalline regions are moderately hard yet flexible (Treloar 1974).

2.1.2 Cellulose and Hemicellulose

Cellulose, an unbranched polymer containing several thousand D-glucose monomers joined via β-1,4-glycosidic linkages, is the most abundant natural organic compound due to its abundance in plant cell walls. It contains both crystalline and amorphous regions, and the source of cellulose determines the degree of crystallinity. The crystallinity of cotton and algal celluloses is about 70%, while that of wood cellulose (more common in landfill components) is approximately 40% (Treloar 1974). The degree of crystallinity of cellulose can be increased with acid hydrolysis or moisture wetting that occurs during processing or decreased by fine grinding or ball-milling (Bertran and Dale 1985). Cellulose is an insoluble polymer, yet polyhydroxyl structures offer H-bonding sites that give cellulose its hydrophilic nature (Severtson and Banerjee 1996). Only the amorphous regions of cellulose absorb water and have any sorption capacity (Treloar 1974). An inherent sorbent property called the glass transition temperature (T_g) dictates whether a compound will be glassy or rubbery under certain environmental conditions; the higher the temperature, the more glassy a polymer is. The amorphous regions of cellulose behave as a glassy polymer when dry, with a T_g of 225 °C, and as a rubbery polymer when wet, with a T_g of -45 °C (Akim 1978, LeBoeuf and Weber 2000).

Hemicelluloses are polar, non-crystalline, low-molecular weight polysaccharides that are associated with cellulose and lignin (to which it can covalently bind) in plant cell walls (Gerasimowicz et al. 1984, Salmen and Olsson 1998, Helm 2000). Hemicellulose is more readily hydrolyzed by acids than cellulose. Dry hemicellulose is in the glassy polymer state ($T_g \sim 180$ °C); however, upon wetting, hemicellulose becomes rubbery at room temperature (Back and Salmen 1982). Both cellulose and hemicellulose can be degraded under aerobic and anaerobic conditions (Eleazer et al. 1997, Pichler and Kögel-Knabner 2000).

2.1.3 Lignin

Lignin, an aromatic alcohol polymer, is the second-most abundant naturally occurring polymer and is located primarily in the cell walls of vascular plants (Crawford 1981). Lignin is a glassy polymer in both dry (T_g = 250 °C) and wet forms (T_g = 115 °C) (Sakata and Senju 1975, Back and Salmen 1982). Unlike cellulose or hemicellulose, natural lignin is very resistant to biodegradation in anaerobic environments partially because lignin contains hydrophobic phenylpropane units (Odier and Monties 1983, Young and Frazer 1987, Pichler and Kögel-Knabner 2000, Chen 2003). In wood, lignin can physically block microorganisms from accessing cellulose and hemicellulose thus impeding complete degradation of the latter biopolymers (Young and Frazer 1987). Lignin can also covalently link to cellulose and/or hemicellulose creating bonds which cellulolytic organisms cannot degrade under methanogenic conditions (Tong et al. 1990).

2.1.4 Lipids and Proteins

Source of lipids and proteins in landfills are food waste and microbial resynthesis. Under fermentative conditions, lipids can be β-oxidized to acetate by H_2-producing bacteria. Also, lipids can be synthesized from carbohydrates or amino acids and incorporated into microorganisms (Demeyer et al. 1998). These higher-molecular weight lipids are not easily degraded by microorganisms due to their length and complexity compared to other lipids (Dinel et al. 1996).

Proteins occur in many naturally occurring substances and consist of amino-acid chains joined via peptide bonds that can be degraded under anaerobic conditions. Proteins are both broken down and resynthesized in the MSW environment, resulting in relatively constant protein contents (Pichler and Kögel-Knabner 2000). Under dry conditions, proteins are glassy polymers. As the moisture content increases, water begins to plasticize proteins (Green et al. 1994, Sochava 1997).

2.1.5 High-Density Polyethylene and Poly(vinyl chloride)

High density polyethylene (HDPE) consists of repeating ethylene monomers ($CH_2=CH_2$) and has no branches or side-chains that could interfere with crystallization. As a result, HDPE is approximately 80% to 95% crystalline. The interstitial spaces between polymer segments allow small molecules to diffuse into the sorbent matrix. HDPE is classified as a rubbery polymer at room temperature with a T_g of -68 °C (Brandup et al. 1989).

Polyvinyl chloride (PVC) consists of repeating vinyl chloride monomers ($-CH_2-CH-Cl$) and cannot be biodegraded. PVC has a crystallinity of approximately 5-10% and is thus less crystalline than HDPE (Tobolsky and Mark 1980). It is a glassy polymer at room temperature, but it becomes rubbery if a non-volatile liquid (also known as a plasticizer) is incorporated into its structure (Treloar 1974).

2.2 Bioavailability

When hazardous and/or toxic organic compounds are converted by microorganisms to benign end products, this process is known as bioremediation. Biological activity in landfills could be utilized to remediate contaminated landfill sites. However, little information is available on factors controlling HOC biodegradation in the MSW environment. Therefore, understanding how sorption/desorption processes affect HOC bioavailability in MSW landfills helps overcome an important knowledge gap.

Bioavailability is defined as the rate of mass transfer of a chemical to the cell relative to the chemical's rate of uptake and metabolism (Bosma et al. 1997). In the context of this research, this definition can be viewed as the rate of HOC desorption, or availability, relative to the rate of HOC biodegradation. If a pollutant is sorbed, then the rate of mass transfer may become limiting, making biodegradation rates dependent on desorption rates (Hatzinger and Alexander 1995, Scow and Alexander 1992, Shaw et al. 2000). If microorganisms are able to utilize sorbed organic pollutants, desorption rates would not be a controlling factor, however. Several studies showed that pollutants in the aqueous phase are more readily available for biodegradation (e.g. Sanin et al. 2000, Shaw et al. 2000, Ogram et al. 1985). Sorption could reduce the bioavailability of HOCs in landfills because of slow HOC desorption from glassy/hard organic matter (Pignatello and Xing 1996, Weber et al. 1995), adsorption in micropores (Nam and Alexander 1998), and/or encapsulation in humic and humin portions of sorbent organic matter (SOM) (Guthrie et al. 1999). Prolonged exposure of HOCs to landfill SOM can enhance HOC sequestration because HOC molecules move into glassy SOM sites from which desorption is retarded and/or because HOC molecules or their metabolites strongly associate with humic substances that form as MSW degrades (Chen 2003). This section will discuss the physical and chemical factors that control HOC bioavailability.

2.2.1 Bioavailability in the MSW Environment

Anaerobic biodegradation of toluene under simulated landfill conditions has been reported; nonetheless, toluene is frequently detected in methanogenic leachate, suggesting that biodegradation is not complete in landfills (Sanin et al. 2000). HOC biodegradation is a function of sorption processes, which in turn are controlled by the characteristics of SOM. Chen (2003) showed that toluene sorbed to a rubbery polymer (HDPE) was readily bioavailable. In contrast, toluene sorbed to a glassy synthetic polymer (PVC) was less bioavailable. For biopolymers, Chen (2003) also found that a fraction of the toluene not consumed by microorganisms was sequestered by and/or covalently bound to humic matter; these associations became increasingly important as aging time increased as evidenced by increased ^{14}C concentrations in humic substances (especially humin). Toluene may become more entrapped in humin over time because it represents a glassy SOM domain. Results of Wu et al. (2001), Chen (2003), and Chen et al. (2004a,b) further suggest that as MSW in a landfill degrades, SOM becomes increasingly hydrophobic.

2.2.2 Physical Factors

Reduced HOC bioavailability can occur as a result of HOC partitioning to glassy organic matter and/or adsorption in micropores or on nanovoid surfaces. Partitioning refers to HOC sorption to polymers by mechanisms such as van der Waals, dipole-dipole, and hydrogen bond interactions (Xing et al. 1994b). Different polymeric phases in MSW represent glassy and rubbery regions; both the rubbery and glassy regions act as partitioning media, but the glassy regions also contain closed internal nanoscale pore surfaces on which HOCs can adsorb. Homogeneous rubbery polymers, such as HDPE, exhibit linear isotherms and show no desorption hysteresis due to their relatively flexible arrangement of polymer molecules. Homogeneous glassy polymers, such as PVC, have a uniform distribution of adsorption sites within a more rigid arrangement of polymer molecules. As a result, linear partitioning takes place in the bulk polymer, and a hole-filling adsorption mechanism that exhibits Langmuir-

like behavior occurs concurrently at closed internal nanoscale pore surfaces (Xing et al. 1996). Sorption rates are limited by diffusion through the bulk polymer since pore adsorption was found to occur rapidly. Many geosorbents and biopolymers contain both rubbery and glassy polymer phases. When the rubbery domain has reached equilibrium with the sorbate, the glassy domain is accessed and a new equilibrium state is obtained over time (Weber and Huang 1996). Weber and Huang (1996) also reported that increasing aging times result in an increase of the HOC fraction associated with the glassy domain.

Reduction in bioavailability also occurs when HOCs adsorb in micropores of soils and sediments (Ball and Roberts, 1991). Small pores, less than 100 nm, allow HOC access while excluding most microbial activity. Contaminant release could be hindered by high adsorption energies in such pores. Nam and Alexander (1998) found that the bioavailability of HOCs can be decreased in the presence of particles containing micropores (< 400 nm) with hydrophobic surfaces. However, bioavailability was not reduced with nonpolar or polar sorbents without micropores. Also, adsorption sites in nanovoids of glassy polymers fill faster than they empty; therefore, HOC desorption from nanovoid surfaces can limit desorption (Pignatello and Xing 1996). While nanovoid surfaces are likely present in the glassy polymer components of MSW, micropores, as discussed by Nam and Alexander (1998), should not play an important role in MSW as shown by the sorbent characterization results of Wu (2002).

2.2.3 Chemical Factors

Hydrophobic interactions and humification are two chemical factors that contribute to reduced HOC bioavailability. Hydrophobic interactions describe the partitioning process by which organic pollutants sorb to organic matter through bonding mechanisms such as van der Waals forces and hydrogen bonding that involve both the sorbents' and sorbates' hydrophobic sites (Lerch et al. 1997). Hydrophobic interactions are the primary mechanism for the sorption of herbicide to soils (Karickhoff 1981). Hydrophobic interactions have also

been shown to control the sorption of hydroxylated atrazine degradation products (HADPs) to soil and pyrene to humin (Lerch et al. 1997, Guthrie et al. 1999).

Humification refers to an irreversible chemical reaction that incorporates HOCs or their biodegradation intermediates into humic substances by both biological and non-biological means (Michel et al. 1995). Lignin and its degradation products can play an important role in humification of organic matter. Lignin degradation by-products can react with nitrogen-containing compounds and aid in the formation of humus (Stevenson 1994). HOCs can covalently bond, adsorb, or be sequestered in humus (Park et al. 2000, Dec and Bollag 1997, Dec et al. 1997). The data of Chen (2003) also suggest that toluene or toluene metabolites strongly associated with the humic matter of MSW components, and that these associations decreased HOC bioavailability.

2.3 Factors Affecting Sorption

The extent of HOC sorption is affected by sorbent, sorbate, and solvent properties. Although previous sorption research in the landfill environment is limited, numerous studies exist in the soils and sediments field. From these and more recent landfill studies, it is possible to identify relevant sorption properties of MSW.

2.3.1 Sorbent Effects

The organic matter fraction of soils and sediments is typically the main contributor to HOC sorption (Karickhoff et al. 1979, Means et al. 1980). As a result, partition coefficients (K_p) are normalized by the organic matter fraction (f_{oc}), i.e. $K_{oc} = K_p/f_{oc}$, to compare HOC sorption capacities of soils and sediments.

Apart from f_{oc}, the hydrophobicity of organic matter in soils and sediments controls HOC sorption. Information about sorbent hydrophobicity can be obtained from elemental analysis of SOM (Garbarini and Lion 1989, Schwarzenbach and Westall 1981, Isaacson and Frink 1984, Kile et al. 1995, Grathwohl 1990). As the ratio of C/O or H/O in SOM increases, functional groups containing oxygen become less abundant, and the hydrophobicity of SOM increases. The polarity of sorbent organic matter is controlled by its oxygen and nitrogen contents (Grathwohl 1990, Kile et al. 1995). The polarity index, (O+N)/C, is the ratio of polar to nonpolar groups in SOM. As the polarity index of SOM increases, HOC sorption capacity, as measured by K_{oc}, decreases (Rutherford et al. 1992, Xing et al. 1994a, Wu et al. 2001). However, no correlation has been found between partition coefficients of organic compounds and H/C, O/C, or H/O atomic ratios of MSW samples (Öman and Spännar 1999). Stuer-Lauridsen and Pedersen (1997) found that sorption was independent of polarity index for organic materials that had undergone biological or chemical processing such as peat and muck soils or soil extracts (humic acid, fulvic acid, and extracted peat).

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In MSW, small amounts of lipophilic extractives caused differences in HOC sorption capacities that were not captured well by the polarity index (Wu et al. 2001). The O-alkyl to alkyl ratio was therefore used to develop an improved correlation between K_{oc} and SOM characteristics. The O-alkyl/alkyl ratio recognizes the importance of both sorbent polarity and lipophilic extractives content on HOC sorption. Polar carbohydrates, alcohols, esters, and amines comprise the O-alkyl regions while paraffinic carbon comprises the hydrophobic alkyl regions (Chefetz et al. 2000). Therefore, as sorbent degradation increases, the O-alkyl/alkyl ratio of biopolymers decreases (Chen et al. 2004b). Compared to elemental analysis methods, the O-alkyl to alkyl ratio is more sensitive to the extent of anaerobic degradation and may be a good predictor of the HOC sorption capacity of MSW components (Chen et al. 2004b).

HOC sorption capacities of MSW components decrease in the order PVC > HDPE > rabbit food > fresh newsprint > fresh office paper. PVC exhibited the greatest sorption capacity due in part to its nonlinear adsorption component where HOCs adsorb on the internal surface nanovoids in the glassy polymer (Wu 2002, Wagner 2003). All other MSW components exhibited linear partitioning as the primary sorption mechanism. Furthermore, in terms of individual biopolymers, HOC sorption capacities decreased in the order lipids > lignin > proteins > humic acids > fulvic acids > cellulose (Garbarini and Lion 1986). In general, cellulose and hemicellulose contribute very little to the overall sorption capacity of MSW. This was verified by Chen (2003) who found that cellulase and hemicellulase addition had no significant effect on toluene bioavailability. Rabbit food has a relatively high lipophilic extractives content that contributes to its HOC sorption capacity (Wu 2002). The lignin content of MSW components is an important factor in HOC sorption capacity due to lignin's hydrophobic nature and resistance to biodegradation. Lignin could completely explain the sorption behavior of both fresh and degraded newsprint, but not degraded office paper (Chen et al. 2004a). The low HOC sorption capacity of fresh office paper can be attributed to its high cellulose content (Chen 2003). In general, biopolymers exhibited lower HOC sorption

capacities than plastics because the content of highly HOC-compatible sorbent fractions, like lipophilic extractives, is small in biopolymer composites (Wu et al. 2001). Biopolymer composites degrade due to biological activity in landfills and the organic carbon content decreases as methane yields increase (Eleazer et al. 1997, Pichler and Kögel-Knabner 2000). During decomposition, a preferential degradation of polar biopolymers, such as cellulose and hemicellulose, occurs resulting in increased hydrophobicity of sorbent organic matter and a shift toward more recalcitrant compounds like lignin and resin acids (Eleazer et al. 1997, Pichler and Kögel-Knabner 2000, Chen et al. 2004b). Sorption capacity trends for degraded biopolymers were not the same as for fresh polymers. Degraded office paper had a higher sorption capacity than degraded newsprint. Wagner (2003), showed that pure cellulose exhibited negligible HOC sorption capacity. While lignin could explain the entire HOC sorption capacities of fresh and degraded newsprint, it could only explain 54% of HOC sorption to degraded office paper (Chen et al. 2004b). Two possible factors, both of which would increase the percentage of lipophilic extractives in SOM, may explain the higher HOC sorption capacity of degraded office paper: 1) as degradation proceeded, microbial synthesis could have produced lipids and proteins that contribute to HOC sorption and/or 2) hydrophobic sizing agents that are added during the paper making process to improve printing remained after cellulose and hemicellulose degradation and contributed to HOC sorption capacity (Chen 2003, Wagner 2003, Wu 2001).

Reinhart et al. (1990) reported that biopolymer degradation increased sorbent hydrophobicity, and this had little effect on K_{oc} values for refuse that was relatively hydrophobic prior to degradation. As a result, Reinhart et al. (1990) suggested that leachate HOC concentrations could increase over time due to reductions in organic matter mass over time. However, in landfills the HOC sorption capacity of polar compounds like cellulose and hemicellulose is relatively low compared to other more non-polar compounds such as lignin and lipophilic extractives. Chen (2003) suggested that the degradation of these compounds may not alter the overall sorption capacity of landfills or may actually decrease the bioavailability of sorbed HOCs as SOM becomes more hydrophobic.

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2.3.2 Sorbate Effects

Sorbate structure, size, and reactivity of functional groups affect sorption (Brusseau and Rao 1989). Increased sorbate hydrophobicity results in increased HOC sorption to organic matter (Karickhoff et al. 1985, Wu and Gschwend 1986). For soils and sediments, a linear correlation between $logK_{oc}$ and $logK_{ow}$, the sorbate octanol/water partition coefficient, was found (Karickhoff et al. 1979, Schwarzenbach and Westall 1981). This suggests that HOC sorption capacity increases with increasing K_{ow}, which is a measure of HOC hydrophobicity. A similar linear correlation was also found in a study evaluating the sorption capacity of MSW for HOCs (Reinhart et al. 1990, Wu 2002, Wagner 2003). Also, complex sorbate structure increase the time required for sorption to reach equilibrium (Brusseau and Rao 1989).

2.3.3 Solvent Effects

Solvent polarity and the presence of dissolved organic matter affect HOC sorption (Rao et al. 1990, Brusseau et al. 1991, Nkedi-Kizza et al. 1989). Organic cosolvents could increase HOC solubility, and thus HOC transport and bioavailability (Rao et al. 1990, Nanny and Ratasuk 2002). It is likely that some constituents of leachate organic matter function as organic cosolvents and affect HOC solubility.

Landfill leachates are rich in dissolved organic matter that is leached from degrading MSW components as rain water infiltrates landfills (Imai et al. 1995). Two types of leachate exist, acidogenic and methanogenic, which are present during different phases of waste fermentation. Composition of solid waste, rate of water infiltration, refuse moisture content, and landfill design affect leachate characteristics. Researchers have attempted to quantify the composition of organic compounds in leachate (Harmsen 1983, Schultz and Kjeldsen 1986, Nanny and Ratasuk 2002). Harmsen (1983) found that volatile fatty acids (VFAs) account for 95% of acidogenic leachate TOC. Schultz and Kjeldsen (1986) detected low

concentrations of aromatic hydrocarbons, including toluene and xylene isomers. Sampling leachate from landfills of varying ages, Nanny and Ratasuk (2002) found that fulvic acid comprised 51-66%. Wu (2002) reported that acidogenic leachate contained 40 – 50 times higher COD and DOC, respectively, than methanogenic leachate. VFAs constituted 63% of the acidogenic leachate COD, with the dominant VFA being butyric acid (Wu 2002). In methanogenic leachate, Wu found no humic acid while 57% of the organic matter was fulvic acid. In both leachates, low UV_{254} adsorbance values were found even though leachate DOC concentrations were high, suggesting that aromatic and unsaturated functionalities were largely absent.

HOC sorption can be affected by HOC binding to dissolved organic compounds in landfill leachate (Larsen et al. 1992, Bauer and Herrman 1998). Reinhart et al (1990) determined that acidogenic leachate with a high VFA concentration did not affect sorption of 1,4-dichlorobenzene to refuse. Larsen et al. (1992) showed that different methanogenic leachates had different effects on HOC sorption to aquifer materials. For instance, methanogenic leachates with high DOC concentration (about 600 mg/L) reduced the partition coefficient by approximately 50%, but other leachates led to increased contaminant sorption. Prior research more closely related to this study showed that acidogenic leachate swelled PVC, which decreased its sorption capacity. Most likely, acidogenic leachate constituents such as propionic and butyric acids served as plasticizers and transformed PVC from a glassy to a rubbery state (Wu 2002), a result that was supported by toluene isotherms that were linear in acidogenic leachate. For other MSW components, leachate composition did not affect toluene, *o*-xylene, and tetrachloroethene (PCE) sorption (Wu et al. 2001, Wu 2002, Wagner 2003).

2.4 Desorption

HOC desorption rates may be an important factor in developing timelines for site remediation. Sorbed HOCs could be slowly released from the solid into the aqueous phase, where they would become available for biodegradation. Desorption rates from glassy organic matter could be the rate-limiting step if biodegradation rates exceed desorption rates. Thus, HOC desorption rates may determine the persistence of HOCs in landfills. In contrast, if desorption rates exceed biodegradation rates, HOCs will likely be exported from unlined landfills as leachate seeps into the subsurface.

2.4.1 Desorption Hysteresis

Desorption hysteresis occurs when the desorption isotherm is not the same as the sorption isotherm (Brusseau and Rao 1989, Kan et al. 1994). Hysteresis can become more pronounced with aging time as HOCs sorb to increasingly desorption-resistant SOM phases. Hysteresis is often attributed to either non-equilibrium conditions or the inherent properties of the sorbent-solute pair.

If desorption hysteresis occurs because equilibrium was not reached, the sorption isotherm, the desorption isotherm, or both may not have been in equilibrium. Insufficient contact times of several hours to several days can cause this effect (DiToro and Horzempa 1982, Kan et al. 1994, Huang et al. 1998). Also, experimental errors can contribute to non-equilibrium or loss of sorbate. Sorbate could be lost to the reactor system itself if inadequate materials are used or radiochemical impurities could be mistaken for the compound of interest, causing calculation errors (McCarthy et al. 1986).

Entrapment of sorbed molecules within the SOM matrix, irreversible chemical bonding of the solute to SOM, and/or adsorption within sorbent micropores are inherent properties of the sorbent-solute pair that could cause desorption hysteresis. HOC entrapment, and thus the

formation of a desorption-resistant fraction, could result from the slow diffusion of organic compounds within condensed organic matter (Brusseau and Rao 1989, Carroll et al. 1994). Carroll et al. (1994) observed both a rapidly desorbing labile fraction and a slowly desorbing resistant fraction of PCBs in Hudson river sediment, and they concluded that a condensed phase of sediment organic matter contributed to the slowly desorbing PCB fraction. Burgos et al. (1996) found similar two-phase desorption rates when studying naphthalene release from soils. They attributed the slowly desorbing fraction to entrapped HOC within soil micropores. It has also been suggested that sorbate-sorbent interactions may account for some desorption resistance (Isaacson and Frink 1984, Bhandari et al. 1996, McGroddy et al. 1996). Recently, the concept of a desorption-resistant fraction resulting from slow diffusion from soils and sediments has been questioned. Sharer et al. (2003) found that a desorption-resistant fraction of chlorobenzene in four soil types rapidly formed (after only 24 hours), suggesting that a specific sorbate-sorbent interactions may be responsible.

With respect to the landfill environment, Wu (2002) and Wagner (2003) found that HOCs sorbed to biopolymers exhibited two-phase desorption while HOCs sorbed to plastics experienced more homogeneous release rates. Similar trends were exhibited in toluene bioavailability tests performed by Chen (2003). Toluene desorption rates were slowest from glassy PVC and fastest from rabbit food and fresh newsprint (Wu 2002). Results for toluene bioavailability tests were somewhat different and showed that toluene mineralization was slowest in tests involving PVC and fastest in tests involving HDPE (Chen 2003). One explanation for the difference results between Wu (2002) and Chen (2003) is that Wu (2002) used an intermediate purging technique in abiotic desorption tests while Chen (2003) utilized an aerobic toluene degrader that continuously removed toluene from the aqueous phase. For PVC and HDPE, Wu (2002) obtained toluene diffusivities of about $4*10^{-14}$ and $4*10^{-11}$ cm^2/s, respectively. For biopolymer composites, toluene diffusivities in the rapid desorbing compartments were $10^{-10} - 10^{-9}$ cm^2/s while those in the slow desorbing compartment were $10^{-14} - 10^{-11}$ cm^2/s. Small diffusivities for the slow compartments suggest that mass transfer processes may control the long-term fate of HOCs in MSW landfills.

Anaerobic degradation of MSW resulted in increased HOC migration into the desorption-resistant fraction (Wu 2002). These results agreed with those of Guthrie et al. (1999), who showed that biological sorbent degradation increased sorbent hydrophobicity and thus enhanced HOC sequestration. Desorption rate limitations could also arise in soils and sediments due to the rearrangement of the flexible humic polymer chains of SOM after solute sorption. This mechanism may block diffusion pathways causing desorption resistance. Kan et al. (1997) studied this phenomenon with naphthalene and tetrachlorobiphenyl sorbed to sediments and determined that irreversibility may be due to the occlusion of pollutants by conformational changes of SOM during the sorption process.

Longer aging times also increased the slowly desorbing HOC fraction in biopolymers (Wu 2002). Wu (2002) attributed this observation to incomplete HOC penetration into the condensed SOM of biopolymers at shorter aging times. These results are consistent with the work of Chen (2003), who suggested that as aging time increased, HOCs were to an increasing extent physically sequestered in or covalently bonded to the humic matter component of SOM. Chen (2003) showed that the humin fraction of biopolymers played an important role in toluene sequestration. Humin represents a glassy domain of SOM and has a more condensed structure than humic acids (White et al. 1999, de Jorge et al. 2000). No aging effects were observed in toluene desorption and bioavailability tests involving HDPE, a homogenous rubbery polymer (Wu 2002, Wagner 2003, Chen 2003). Since sorption equilibrium was not obtained in all desorption tests involving PVC, it is difficult to ascertain any definitive information regarding aging effects. Wu (2002) did not observe any aging effects, but bi-directional diffusion may have affected toluene desorption rates from PVC following short aging times (Wu 2002). Chen (2003) noted, however, that ^{14}C toluene moved into physically remote sites within PVC as aging time increased.

Brusseau et al. (1991) determined that branched HOCs diffuse more slowly than unbranched sorbates such as benzene and theorized that this occurs due to an increased potential for sorbate entrapment in SOM. Diffusion coefficients also decreased exponentially with

increasing molecular weight, or size of the sorbate (Brusseau and Rao 1989). In the MSW environment, Wu (2002) and Wagner (2003) found similar results with respect to sorbate hydrophobicity in some instances but not in others. For example, Wu (2002) found similar toluene and *o*-xylene desorption rates from fresh and degraded newsprint. van Noort et al. (2002) suggested that planar compounds sorb more strongly than non-planar compounds. As a result, planar compounds were primarily associated with the very slow desorption domain of sediments (van Noort et al. 2002).

Others have found that interactions between the sorbent and the solvent could increase desorption rates. Brusseau et al. (1991) determined that desorption rates increased when organic cosolvents swelled SOM and reduced diffusive resistance. Sahoo et al. (1997, 1998) suggested that surfactants can swell SOM and thus increase HOC diffusion rates. Wu (2002) and Wagner (2003) found that PVC was plasticized in the presence of acidogenic leachate, which enhanced HOC release rates. Also, HOC desorption rates from office paper were enhanced in acidogenic leachate, and Wu (2002) showed that this phenomenon could be explained by the lower pH of acidogenic leachate. Leachate composition had no other effects on HOC desorption rates from MSW components (Wu 2002, Wagner 2003).

2.4.2 Desorption Models

Typically, models describing HOC desorption rates from homogenous polymers are one-compartment models, while models describing HOC desorption rates from biopolymer composites require the presence of two or more compartments. For complex sorbents such as geosorbents or MSW components such as paper products or food and yard waste, HOC desorption typically occurs in two stages, a fast desorbing stage where release occurs within hours and a slow desorbing stage that is associated with the desorption-resistant fraction (Wu and Gschwend 1986, Pavlostathis and Jaglal 1991, Pignatello and Huang 1991, Pavlostathis and Matharan 1992, Harmon and Roberts 1994, Carroll et al. 1994). To interpret desorption

rate data, models based on chemical kinetics and mass transfer concepts are used (Pignatello et al. 1993).

2.4.2.1 Chemical Kinetics

Slow release of pollutants from soils and sediments can be caused by chemisorption (Burgos et al. 1996). In chemisorption, covalent bonds or charge transfer complexes are formed between the contaminant and the sorbent. However, chemisorption is usually not a major factor for neutral HOCs (Brusseau et al. 1991, Kan et al. 1998).

2.4.2.2 Mass Transfer Limitations

Mass transfer resistances during HOC desorption from MSW components to the aqueous phase are film diffusion (external mass transfer), intraparticle diffusion, and intraorganic matter diffusion. Mass transfer limitations can produce apparent irreversible sorption and are used to explain the two-stage desorption process (Weber and Miller 1988, Ball and Roberts 1991, Harmon et al. 1994).

2.4.2.3 Film Diffusion

HOCs encounter external mass transfer resistance when sorbing or desorbing across the fluid boundary layer surrounding a sorbent particle. This film diffusion process is characterized by the following equation:

$$N = k_f (C - C_p(r = a)) \tag{2.1}$$

where, N is the flux of solute per unit area of external surface (M_x/L^2T), k_f is the film mass transfer coefficient (L/T), C is the solute concentration in the well-mixed bulk solution (M_x/L^3), and C_p(r=a) is the solute concentration at the particle surface (radius =a) (M_x/L^3).

Film mass transfer is generally not rate-limiting in comparison to the other mass transfer phenomena (Brusseau et al. 1991).

2.4.2.4 Intraparticle Pore Diffusion

Intraparticle pore diffusion is the aqueous-phase diffusion of solute within the (micro)pores of particles. The radial pore diffusion model is generally used to characterize this mas transfer mechanism. It assumes that each particle is a porous sphere where pore diffusion is the only transport mechanism present and sorption sites are homogeneously distributed over the pore walls.

Under transient conditions, a mass balance over the volume of the particle yields Fick's Second Law:

$$\rho_a \frac{\partial q}{\partial t} + \varepsilon_i \frac{\partial C_r}{\partial t} = \frac{\varepsilon_i D_p}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial C_r}{\partial r}\right) \tag{2.2}$$

where,

ρ_a = apparent density of the sorbent particle (M_s/L^3);

ε_i = intraparticle porosity;

C_r = intraparticle aqueous phase concentration (M_s/L^3);

D_p = effective pore diffusion coefficient (L^2/T);

r = radial coordinate (L);

t = time (T).

Assuming linear partitioning, $q=K_dC_r$ is the applicable isotherm equation, where, q is the equilibrium solid phase concentration (M_x/M_s), K_d is the partition coefficient (L^3/M_s), and C_r is the equilibrium aqueous phase concentration (M_x/L^3). Substituting this isotherm equation into Fick's Second Law yields:

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$$\frac{\partial C_r}{\partial t} = \frac{D_p}{r^2 R_g} \frac{\partial}{\partial r}\left(r^2 \frac{\partial C_r}{\partial r}\right) \qquad (2.3)$$

where R_g is the internal or grain retardation factor, which is defined as:

$$R_g = 1 + \frac{\rho_a K_d}{\varepsilon_i} \qquad (2.4)$$

The apparent diffusion coefficient is defined as:

$$D_a = \frac{D_p}{R_g} \qquad (2.5)$$

For nonlinear isotherms, the Freudlich isotherm expression ($q = K_f C_r^{1/n}$) is used, where K_f is the Freudlich capacity coefficient $(M_x/M_s)/(M_x/L^3)^{1/n}$ and $1/n$ is the Freudlich exponent.

The resulting diffusion model is similar to equation 2.3; however, the grain retardation factor is dependent on the aqueous phase concentration:

$$R_g = 1 + \frac{1/n}{\varepsilon_i} \rho_a K_f C_r^{1/n-1} \qquad (2.6)$$

The intraparticle diffusion model has been shown to adequately describe the uptake of HOCs by sediments and soils (Miller and Pedit 1992, Wu and Gschwend 1986). However, this model fails to capture the complex nature of many soils and sediments because it contains only one diffusion coefficient (Connaughton et al. 1993, Pedit and Miller 1994, Harmon and Roberts 1994). Harmon et al. (1994) showed that these models underestimated the observed desorption rate at early times and overestimated the observed desorption rate at later times.

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As a result, single-parameter, one-compartment desorption models were modified to include multiple compartments.

2.4.2.5 Intraorganic Matter Diffusion

Intraorganic matter diffusion models describe the transfer of sorbate within a polymeric SOM matrix. There are two major physical differences between intraparticle diffusion and intraorganic matter diffusion (Brusseau et al. 1991): (1) the pore-like structures associated with polymeric SOM have sizes similar to those of the sorbate molecules while the pores in porous particles are typically larger, and (2) porous particles have fixed, rigid pore networks, while polymeric SOM does not.

HOC diffusion into spherical polymer particles can be expressed using Fick's second law of diffusion:

$$\frac{\partial q_r}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial q_r}{\partial r}\right) \tag{2.7}$$

where D is the intraorganic matter diffusion coefficient (L^2/T), q_r is the intraparticle solid-phase concentration (M_x/M_s), r is the radial position (L), and t is time (T).

2.4.2.6 Two-Compartment Model

Two-compartment models can be divided into two categories: first-order mass transfer models that are based on a linear driving force approximation (Karickhoff et al. 1980, 1985, Cornelissen et al. 1997, Johnson et al. 2001) and diffusion models that are based on Fickian diffusion (Berens and Huvard 1981, Brusseau and Rao 1989, Carroll et al. 1994). Conceptually, two-compartment models describe the following process: $C \leftrightarrow S_1 \leftrightarrow S_2$, where

C is the solution-phase HOC concentration, and S_1 and S_2 are solid-phase HOC concentrations in the labile and nonlabile sorption compartments, respectively.

2.4.2.7 Three-Parameter Biphasic First Order Mass Transfer Model

To quantify the HOC fractions in the labile and resistant SOM compartments, first order rate equations have been implemented as follows:

$$\frac{q(t)}{q_o} = \phi_s \exp(-k_s t) + \phi_r \exp(-k_r t) \tag{2.8}$$

q(t) = solid-phase sorbate concentration at time t

q_o = initial solid-phase sorbate concentration

Φ_s = slowly desorbing HOC fraction

Φ_r = rapidly desorbing HOC fraction

k_s = apparent first-order rate constant for the slowly desorbing fraction

k_r = apparent first-order rate constant for the rapidly desorbing fraction

Despite the empirical nature, this model has been successfully used to describe HOC desorption data from geosorbents (Karickhoff et al. 1985, Cornelissen et al. 1997, Johnson et al. 2001).

2.4.2.8 Three-Parameter Biphasic Polymer Diffusion Model

A biphasic polymer diffusion model, as utilized by Carroll et al. (1994), is more mechanistic as it relies on Fick's second law of diffusion to describe intraparticle mass transfer.

$$\frac{q(t)}{q_o} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \left[\phi_r \exp\left(\frac{-4n^2 \pi^2 D_r t}{a_r^2} \right) + (1-\phi_r) \exp\left(\frac{-4n^2 \pi^2 D_s t}{a_s^2} \right) \right] \tag{2.9}$$

Φ_r = rapidly desorbing HOC fraction

D_r = diffusion coefficient for rapidly diffusing HOC fraction

D_s = diffusion coefficient for slowly diffusing HOC fraction

a_r = equivalent spherical diameter of rapidly releasing SOM

a_s = equivalent spherical diameter of slowly releasing SOM

This model assumes that organic matter has both swollen and condensed regions that are spherical in nature and that diffusion within these SOM regions controls HOC desorption rates. The swollen SOM compartment is equivalent to rubbery polymers capable of releasing HOCs quickly, while the condensed SOM compartment represents glassy polymers that release HOCs more slowly.

3 Experimental Design and Methods

3.1 Municipal Solid Waste Components

Of the major MSW components mentioned in section 2.1, paper, food and yard waste, and plastics are the principal organic components expected to sorb HOCs. To represent the range of papers found in landfills, both office paper and newsprint were chosen. Paper materials represent 29.2% of landfilled refuse (US EPA 2002). Office paper is a chemical pulp with most of the original lignin removed, making cellulose and hemicellulose the dominant biopolymer components. Fresh office paper (FOP) was obtained from the NC State University recycling center. Newsprint is a mechanical pulp containing most of the lignin, cellulose, and hemicellulose present in wood. Fresh newsprint (FNP) was obtained from The News & Observer Recycling Division (News & Observer Publishing Co., Garner, NC). Upon arrival, both newsprint and office paper were shredded into 2-cm squares. Rabbit food (Manna Pro® Corp., St. Louis, MO) was chosen to represent food and yard waste. It contains both simple and complex carbohydrates, lipids, and proteins (in the form of alfalfa, wheat, soy, and oat products), and it has been used previously to represent food and yard waste (Schwab et al. 1994). Food and yard wastes comprise 23% of landfilled refuse (US EPA 2002). High-density polyethylene (HDPE) and poly(vinyl chloride) (PVC) (Catalog numbers 42,799-3 and 18,958-8, Sigma-Aldrich, Milwaukee, WI) were used to represent rubbery and glassy plastics, respectively, and together comprise 14.4% of the MSW stream (US EPA 2002).

Anaerobically degraded forms of office paper (DOP), newsprint (DNP), and rabbit food (DRF) were prepared in laboratory-scale reactors with leachate recycle and neutralization as described by Eleazer et al. (1997). Reactors were seeded with anaerobic sewage sludge, however, rather with than well-decomposed refuse. Office paper and newsprint were degraded for 9 months, at which point they were significantly decomposed, as indicated by the methane yield. Rabbit food reactors were operated under semi-bath conditions to control

volatile fatty acid production. For 9 months, rabbit food was added on a daily to weekly basis, depending on the stability of methane production.

3.2 MSW Component Characterization

The characteristics of MSW components were measured by Wu (2002). Sorbents were analyzed for cellulose, hemicellulose, lignin, lipophilic extractives, crude protein, ash content, organic carbon fraction, and BET surface area. MSW component characteristics are summarized Table 3.1. MSW particle densities and diameters, which were inputs to the desorption models, are summarized in Table 3.2.

Table 3.1 Sorbent characteristics [a]

Sorbent	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Lipophilic Extractives (%)	Crude Protein (%)	Ash (Wt %)	f_{oc}	BET Surface Area (m^2/g)
PVC	N/A[b]	N/A	N/A	N/A	N/A	0.0	0.389	0.8
HDPE	N/A	N/A	N/A	N/A	N/A	0.01	0.876	0.6
Fresh Newsprint	48.3	18.1	22.1	1.6	0.44	2	0.451	2.6
Degraded Newsprint	35.1	16	32.3	1.4	3.74	6.4	0.455	3.4
Fresh Office Paper	64.7	13	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
Degraded Rabbit Food	7.1	5.7	25.2	4.5	20.6	34.5	0.329	0.05

a Values from Wu (2002)

b N/A: not applicable

Table 3.2 Properties of model MSW components[a]

Sorbent	Particle Density (g/cm^3)	Mean Particle Diameter (µm)
PVC	1.4	140
HDPE	0.962	500
Fresh Newsprint	1.32	298
Degraded Newsprint	1.81	213
Fresh Office Paper	1.44	278
Degraded Office Paper	2.13	210
Degraded Rabbit Food	1.78	289

[a] Values from Wu (2002)

3.3 Sorbates

Both toluene and *o*-xylene (alkylbenzenes with different polarities) were selected because they are frequently detected in landfill leachates (Christensen et al. 1994). These HOCs have been shown to sorb to refuse and to biodegrade under simulated MSW conditions (Sanin et al. 2000). ^{14}C-labeled compounds were used (Sigma-Aldrich). Stock solutions were prepared by dissolving neat HOCs into 6 mL of methanol (HPLC-grade, Fisher Scientific) and stored at -10°C. Concentrations of stock solutions were determined by liquid scintillation counting. Purity of alkylbenzenes was first assessed by gas chromatographic analysis which showed peaks corresponding to toluene and o-xylene only. Sparging tests were then used to determine the percentage of non-volatile ^{14}C impurities associated with each HOC. Non-volatile ^{14}C impurities were found to be 1.7% for toluene and 1% for *o*-xylene. Non-volatile ^{14}C impurities were non-sorbable, which was shown through the addition of HDPE to solutions containing non-spargable ^{14}C, and all data were corrected for this impurity. Table 3.3 lists selected sorbate characteristics.

Table 3.3 Sorbate properties

	Toluene	*o*-Xylene
Molecular weight (g/mol)	92.1	106.2
Molecular Diameter (nm)[a]	0.585	0.68
Aqueous solubility (mg/L)[b]	518	185
log K_{ow}[b]	2.69	3.12
Solubility parameter δ (cal/cm^3)$^{1/2}$ [c]	8.9	8.8

[a] Baertsch et al. (1997)
[b] Schwarzenbach et al. (1993)
[c] Barton (1975)

3.4 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 low pH and no gas production. Methanogenic leachate was produced by recirculating water through refuse in the methane-phase of decomposition which was, confirmed by near neutral pH close and methane gas production. Both leachates were vacuum-filtered through a series of glass-fiber filters before its final filtration step through a 0.45 μm cellulose acetate membrane filter. Anaerobic conditions were maintained for the methanogenic leachate by vacuum-filtering samples in an anaerobic hood or under argon gas. After filtration, acidogenic leachate was stored at 4°C in brown glass containers. To maintain minimum interaction with oxygen, the headspace of the methanogenic leachate container was filled with argon. The methanogenic leachate was stored in brown glass containers inside the anaerobic hood to minimize contamination with O_2.

Leachate characterization included measurements of pH, chemical oxygen demand (COD), and dissolved organic carbon (DOC) according to Standard Methods. Leachate characteristics are listed in Table 3.4.

Table 3.4 Leachate characteristics

Leachate	pH	COD (mg/L)	DOC (mg/L)
Acidogenic	5.2	20,800	6,470
Methanogenic	7.1	1,360	250

3.5 Desorption Tests

To determine the effects of aging time on HOC release rates, batch desorption tests were conducted with individual MSW components using a continuous purging system as shown in Figure 3.1. Tests were conducted with 20mL flame-sealed glass ampules. These ampules were baked at 550°C for 4 hours prior to being filled with individual MSW components. All components were oven-dried at 100°C for 24 hours and stored in desiccators until use. After the ampules were filled with the desired sorbent, sorbent-containing ampules were covered with Parafilm and sterilized with 2.2 Mrad of γ-irradiation from a ^{60}Co source. After γ-irradiation, ampules were injected 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 200 mg/L of sodium azide. Ampules containing methanogenic leachate were filled in an anaerobic hood to minimize oxygen effects. Immediately after filling the ampules with the desired liquid phase and sodium azide, toluene or o-xylene stock solution was spiked into the bottom of the ampule and the ampules were flamed-sealed and aged. All tools used during this process were autoclaved prior to use.

The desorption apparatus, as shown in Figure 3.1, consisted of four 20-mL glass ampules connected via stainless steel tubing. The first ampule was designated for the aged solid sample. The second ampule was empty to safeguard against possible sample leakage into downstream traps. The third and forth ampules contained 18 mL scintillation cocktail to capture any HOC released from the sorbent. The inlet tubing for each of these ampules was long enough to reach the bottom of the ampule while the outlet tubing was short enough to not interfere with the aqueous interface. After the forth ampule, exhaust tubing was directed into a 20 mL scintillation vial where any remaining HOC was trapped in 18 mL of scintillation cocktail.
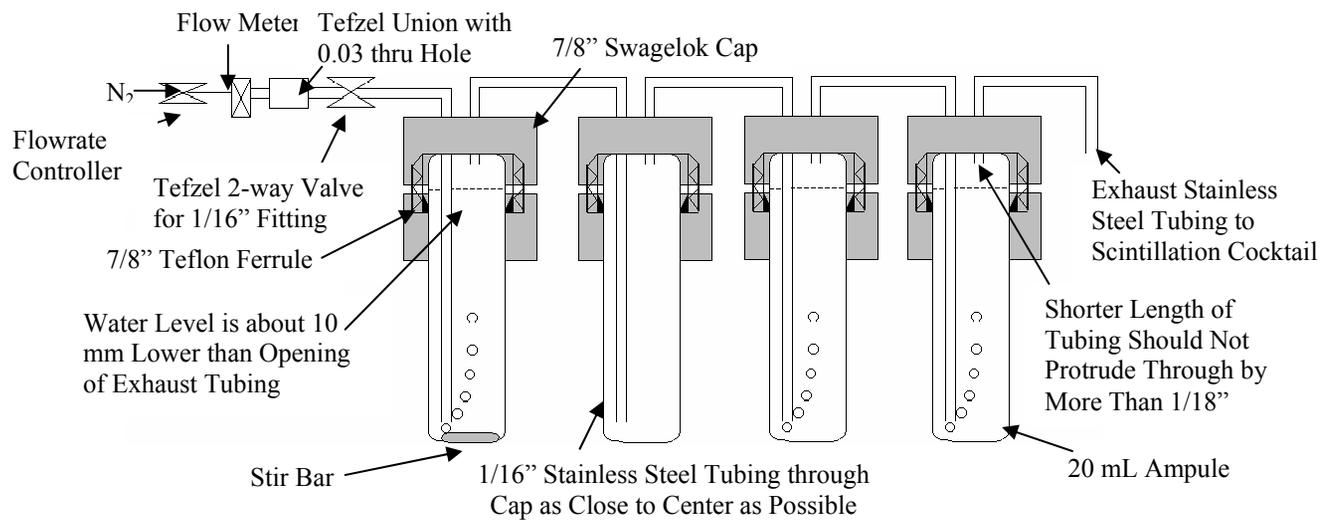
Figure 3.1: Desorption apparatus

Aging times of 1 day, 1 week, 1 month, 6 months, and 9 months were tested for toluene with phosphate-buffered ultrapure water. All other tests were conducted at aging times of 1 week and 6 months. During aging, ampules were tumbled end-over-end to assure effective mixing. Once the desired aging time was reached, ampules were centrifuged at 2000 rpm for 15 minutes.

Following centrifugation, desorption experiments included the following steps: 1) break ampule after desired aging time and remove 1.0 – 2.0 mL of liquid to quantify the aqueous phase HOC concentration, 2) add a stir bar to the sample ampule and attach the swagelok cap designated for the sample, 3) place sample on top of a magnetic stir plate, and 4) purge samples with water-saturated nitrogen gas at a flow rate of 15 mL/min. Ampules containing scintillation cocktail were switched for ampules containing fresh scintillation cocktail at predetermined times, and the HOC concentration in the cocktail was measured by scintillation counting to quantify the amount of HOC released from the solid. This occurred approximately 8 times on day one (enough to capture the rapid decrease in concentration). Day two consisted of two to three sample changes. Scintillation cocktail traps were changed once a day thereafter. Purging and stirring during desorption was continuous to maximize HOC release rates.

All tests were conducted in triplicate. Blank samples containing only liquid and sorbate were prepared to determine the initial HOC mass spiked into samples containing solids (M_o). The normalized HOC mass remaining on the solid during testing was calculated from:

$$\frac{q_t}{q_o} = \frac{q_o m_s - (M(t) - C_{eq} V_l)}{q_o m_s}$$

where $q_o = \dfrac{M_o - C_{eq} V}{m_s}$ 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. V_1 is the remaining liquid volume after the removal of 1.0 – 2.0 mL supernatant prior to the first purge. Both M_o and C_{eq} were corrected for non-sorbing, non-spargable impurities. See Appendix C for detailed calculations.

3.6 Mass Balances

Benzyl alcohol extractions were conducted to determine the remaining solid-phase HOC concentration at the end of testing. Solid samples were removed from the glass ampules and placed in 30-mL PTFE bottles and 15 mL benzyl alcohol was added. The PTFE bottles were centrifuged at 4000 rpm for 15 minutes after 5 days of agitation on a shake table. A 0.5-mL benzyl alcohol sample was added into 6 mL scintillation cocktail to quantify extracted HOC. The remaining supernatant volume was measured and discarded. Benzyl alcohol extractions were repeated until no additional ^{14}C was detected in the liquid phase.

3.7 Statistical Methods

To compare the effects of sorbent type, leachate characteristics, sorbate properties, and aging time on desorption model parameters, a 1-way ANOVA (p-value<0.05) was conducted using the mean value of the triplicate desorption data for each sorbent. When the F-Test indicated a significant difference (p-value <0.05), the means were compared using paired t-tests. Data analyses were performed using the general linear models (GLM) procedure in SAS/STAT software for Windows, Version 9.1 (SAS Institute Inc., Cary, NC).

4 Results and Discussion

To assess the effects of sorbate-sorbent contact time on HOC desorption rates, toluene desorption tests were performed with model MSW components in DI water after aging times of 1 day, 1 week, 1 month, 6 months, and 9 months. In addition, experiments with acidogenic or methanogenic leachate were conducted after aging times of 1 week and 6 months to evaluate the effects of aqueous phase characteristics on HOC desorption rates. To determine the effects of sorbate characteristics on desorption rates, *o*-xylene and toluene desorption rates were compared in ultrapure water after aging times of 1 week and 6 months. A one-compartment diffusion model was used to describe alkylbenzene desorption rates from HDPE and PVC while a two-compartment diffusion model was used for biopolymer composites.

4.1 Modeling Assumptions and Description

Diffusion models used in this study assumed that mass transfer was controlled by intraorganic matter diffusion; i.e. HOC diffusion through a polymeric matrix of sorbent organic matter (SOM). This assumption was verified by Wu (2002) to be an appropriate representation of tests performed in this study.

A one-compartment diffusion model was used to describe alkylbenzene desorption rates from HDPE and PVC. The manner in which this model was used assumed that the desorption rate is limited by diffusion through one polymer phase, sorbents are homogeneous polymeric spheres, the HOC concentration of the aqueous phase is always zero, and sorption equilibrium had been reached prior to initiation of desorption experiments. As shown in equation 2.7, this model has one adjustable parameter, the diffusion coefficient (D). If this model were used on heterogeneous biopolymers, the model would underestimate early HOC release rates and overestimate HOC later release rates.

A two-compartment model was used to describe HOC desorption from biopolymer composites. This model is a three-parameter biphasic polymer diffusion model, where the adjustable parameters are the HOC fraction residing in the slow compartment (Φs) and the diffusion coefficients describing HOC desorption rates from the slow and rapid compartments (Ds and Dr, respectively). The same assumptions listed for the one-compartment model apply to the two-compartment model.

Based on sorption kinetic data of Wu (2002), the equilibrium assumption could be wrong for shorter aging times (1day HDPE and biopolymer composites, < 6 months for PVC). In these cases, bi-directional diffusion could occur where sorption continues inward and desorption continues outward because internal sorption sites are not fully occupied. As a result, diffusion coefficient estimates could be larger than the true value if the HOC mass released is greater than if it were at equilibrium or smaller than the true value if inward HOC diffusion dominates. To facilitate the interpretation of modeling parameters, it was assumed that Ds and Dr values do not vary with aging time. Since the 6 months aging period was common to all trials, Dr and Ds values were determined for this aging time and used to describe desorption data at other aging times for the same sorbent-sorbate-solvent system. The effect of aging time on HOC desorption rates was therefore assessed by analyzing changes in Φs.

The diffusion models also require information about sorbent particle size and density, which are summarized in Table 3.3. Other inputs include isotherm parameters which are shown in Tables 4.1 and 4.2 for synthetic polymers and biopolymer composites, respectively.

Table 4.1 Isotherm parameters describing toluene and o-xylene sorption to HDPE and PVC[a]

| Material | Toluene | | | | | | o-Xylene | |
| | DI Water | | Methanogenic Leachate | | Acidogenic Leachate | | DI Water | |
	$K^{b,c}$	n^d	$K^{b,c}$	n^d	$K^{b,c}$	n^d	$K^{b,c}$	n^d
HDPE	70.7	-	72.4	-	76.1	-	244.1	-
PVC	1663	0.864	1309	0.873	483	1.043	4634	0.718

[a] Values from Wu (2002)

[b] K_p for HDPE, units are (µg/kg)(L/µg)

[c] K_F for PVC, units are (µg/kg)(L/µg)^n

[d] Dimensionless Freudlich exponent

Table 4.2 Partition coefficients (K_p) describing toluene and o-xylene sorption to biopolymer composites[a,b]

| Sorbent | Toluene | | | o-Xylene |
	DI Water	Methanogenic Leachate	Acidogenic Leachate	DI Water
Fresh Newsprint	13.0	13.3	13.4	31.1
Degraded Newsprint	25.8	22.8	20.5	52.7
Fresh Office Paper	2.7	2.4	2.0	5.7
Degraded Office Paper	23.4	20.8	19.9	44.4
Degraded Rabbit Food	27.3	24.5	31.7	79.3

[a] Values from Wu (2002)

[b] K_p units are (µg/kg)(L/µg)

4.2 Effects of Sorbent Type

Figure 4.1 shows the normalized toluene mass remaining on the solid as a function of desorption time for all MSW components after an aging time of 6 months in DI water. Solid lines represent model fits. Figure 4.1 indicates that toluene desorption rates were strongly influenced by sorbent type. Uniform desorption rates were observed for both synthetic polymers (HDPE and PVC), which was expected due to their homogeneity. For heterogeneous polymers, i.e. the biopolymer composites, a fast initial desorption step was followed by slow desorption of the remaining toluene. Similar trends for both plastics and biopolymers have been reported previously (Wu 2002, Wagner 2003). Across all solvent-sorbate pairings the following trends emerged. For the first ten hours of desorption, HOC desorption rates were fastest from biopolymer composites and slowest from PVC. Also, after the initial rapid-desorption stage from biopolymer composites, HOC desorption rates from HDPE surpassed those from biopolymer composites. During the period of slow HOC desorption from biopolymer composites, the extent of HOC desorption exhibited the following trend: fresh office paper < degraded office paper < fresh newsprint ~ degraded newsprint ~ degraded rabbit food. Trends observed in this study were not always consistent with those observed by Wu (2002); e.g., HOC desorption rates from HDPE were faster then those observed by Wu (2002). Inconsistencies can be explained by differences in the experimental protocol. Desorption experiments performed by Wu (2002) utilized an intermittent purging technique without constant stirring that led to HOC build-up within the bulk liquid. As a result, not as much HOC desorbed as with the continuous purging, continuous stirring technique implemented here. While trends in HOC desorption rates were largely similar to those in toluene bioavailability observed by Chen (2003) for the same MSW components, some differences were noted. For example, toluene release rates from PVC were faster in the bioavailability work of Chen (2003) because higher toluene concentrations (~300 mg/L) may have plasticized PVC in that study.

Diffusion coefficients describing toluene desorption rate data from HDPE and PVC are listed in Table 4.3. The linear partition model was used to relate solid-phase to liquid-phase alkylbenzene concentrations for HDPE. The same approach was used to model desorption rate data from PVC in acidogenic leachate since prior work showed that PVC is plasticized by constituents in acidogenic leachate, most likely propionic and butyric acids (Wu 2001, Wu 2002, Wagner 2003). For all other PVC trials the non-linear Freundlich isotherm was used. There was a significant difference between diffusion coefficients describing toluene desorption from HDPE and PVC (p-value = 1.76E-11). All toluene diffusivities in HDPE were on the order of 10^{-10} cm^2/s (Table 4.3), which is reasonably consistent with literature values. Wu (2002) found a diffusion coefficient of 3.85×10^{-11} cm^2/s for toluene desorption from HDPE. Joo et al. (2004) found the diffusion coefficient for toluene in HDPE geomembranes to be 3.27×10^{-9} cm^2/s. Similarly, Sangam and Rowe (2001) observed a diffusivity of 3.0×10^{-9} cm^2/s for toluene diffusion through an HDPE membrane. Toluene diffusivities in PVC were on the order of 10^{-13} cm^2/s for most trials (Table 4.3). One notable exception was the D value for toluene desorption from PVC in acidogenic leachate; this anomaly will be discussed below. Toluene diffusivity values through PVC are also consistent with literature values. Again, Wu (2002) obtained somewhat smaller toluene diffusion coefficients for PVC (D = 4.78×10^{-14} cm^2/s) as a result of intermittent purging and stirring. Berens (1989) reported a diffusion coefficient of 1.0×10^{-14} cm^2/s for toluene diffusion through PVC. The toluene desorption results from plastics are also consistent with the nature of HDPE and PVC. Since PVC is a glassy polymer with a rigid matrix, HOC diffusion in PVC would be slower than in a rubbery polymer with a more malleable matrix such as HDPE. Interstitial spaces between HDPE polymer segments allow small molecules to diffuse in and out of its sorbent matrix readily. On the other hand, PVC has two sorption mechanisms, partitioning into a more condensed polymer phase and adsorption on closed internal nanoscale pore surfaces. This dual-mode sorption mechanism could inhibit HOCs from desorbing from PVC as readily as from HDPE. The difference in HOC desorption rates from rubbery and glassy polymers is generally characterized with the ratio of $D_{rubbery}/ D_{glassy}$.

In this study, the ratio ranged from 10^2 to 10^3, which is in agreement with literature values that ranged from $10^2 - 10^8$ (Berens 1989, Carroll et al. 1994, Leboeuf and Weber 2000). Diffusion coefficients describing HOC desorption from biopolymer composites are listed in Table 4.4. Diffusion coefficients for the rapidly desorbing compartment ranged from 10^{-8} to 10^{-10} cm^2/s, with the majority being of the 10^{-9} cm^2/s magnitude. Statistically, the Dr value describing alkylbenzene desorption from degraded rabbit food was larger than those for the other biopolymer composites. For the slow desorbing compartment, Ds values ranged from 10^{-14} to 10^{-11} cm^2/s. The diffusion coefficients obtained for biopolymer composites fell within the ranges found in other literature. Wu (2002) observed ranges of 10^{-9} to 10^{-10} cm^2/s and 10^{-14} to 10^{-11} cm^2/s for Dr and Ds values, respectively. For polycyclic aromatic hydrocarbons (PAHs) with a wide range of hydrophobic properties, Dr values ranged from 10^{-12} to 10^{-10} cm^2/s and Ds values from 10^{-13} to 10^{-12} cm^2/s in soils and sediments (Shor et al. 2003). Carroll et al. (1994) reported polychlorinated biphenyls (PCBs) diffusion coefficients for rubbery ($7.3*10^{-21}$ cm^2/s) and glassy ($2.6*10^{-18}$ cm^2/s) regions of Hudson River sediment. The latter values were several orders of magnitude smaller than what is reported in table 4.4. Other soils and sediment literature contain diffusion coefficients that are similar to the Dr values reported here [10^{-8} to 10^{-10} cm^2/s for chlorinated alkenes in aquifer sediments (Harmon and Roberts 1994), 10^{-9} to 10^{-10} cm^2/s for volatile organics through sediment (Werth and Reinhard 1997)]. However, the latter studies all used a one-compartment intraparticle diffusion model. The differences between the values of Carroll et al. (1994) and this study can be attributed to sorbate size and polarity. For example, PCBs are larger more hydrophobic compounds compared to toluene. Larger and more complex compounds could become entangled in the SOM matrix, thus reducing their diffusion rates. Also, more hydrophobic compounds have higher sorption capacities, which typically correlate with smaller diffusion coefficients.

Table 4.5 shows Dr/a^2 and Ds/a^2 values for toluene desorption from biopolymer composites in DI after 6 months of aging time. This conversion assumes that diffusional length scales (a) are equal to the mean solid particle radius (Table 3.3). Johnson et al. (2001) reported

Dr/a^2 values in the range of 0.00031 to 0.032 day^{-1} and Ds/a^2 values in the range of 0.000011 to 0.001 day^{-1} for phenanthrene desorption from geosorbents. Dr/a^2 values from this study are two to three orders of magnitude larger while Ds/a^2 values are in the same range; again, the results are not directly compartable because phenanthrene is a more hydrophobic and larger molecule than toluene. More recently, Li and Werth (2004) reported D/a^2 values ranging from 0.097 to 16.7 day^{-1} for PCE and TCE desorption from natural soils. These one-compartment values are similar in magnitude to the Dr/a^2 values of this study, but one to six orders of magnitude larger than the Ds/a^2 values.
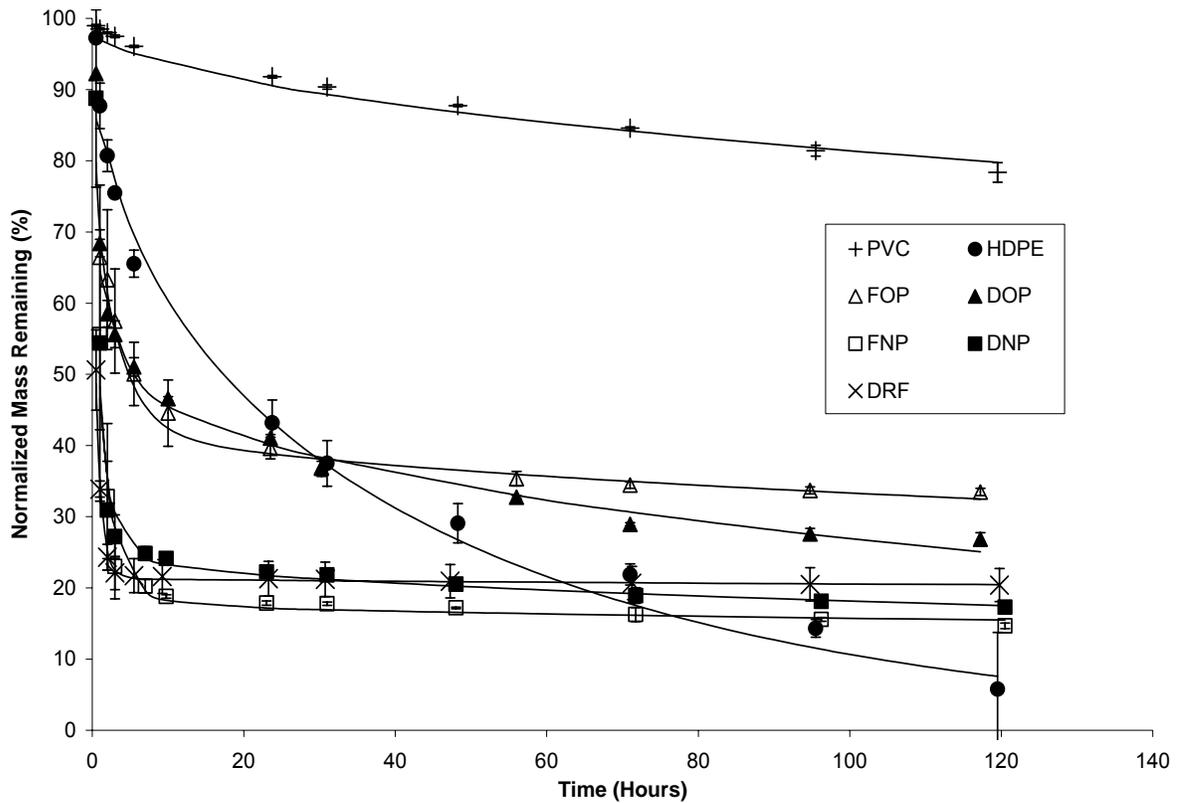
Figure 4.1: Toluene desorption rates from MSW components after 6 months of aging in DI water. Error bars represent one standard deviation of replicate samples.

Table 4.3 Effects of synthetic polymer type and aqueous phase composition on toluene diffusion coefficient estimates obtained from one-compartment polymer diffusion model at two aging times

Aging Time	Aqueous Phase	HDPE		PVC	
		D (cm²/s)	S[a]	D (cm²/s)	S[a]
1 week	DI	3.93E-10	8.94E-11	3.57E-13	3.54E-14
	Acidogenic Leachate	5.00E-10	4.99E-11	2.78E-12	4.83E-14
	Methanogenic Leachate	3.94E-10	3.26E-11	3.89E-13	3.30E-13
6 months	DI	2.95E-10	1.30E-11	4.40E-13	2.47E-14
	Acidogenic Leachate	3.64E-10	6.76E-11	1.55E-12	2.49E-13
	Methanogenic Leachate	5.24E-10	1.34E-10	3.76E-13	3.66E-14

[a] S = standard deviation

Table 4.4 Effects of sorbent type and aqueous phase composition on desorption rate parameter estimates obtained from two-compartment polymer diffusion model. Aging time was 6 months.

Sorbent	Aqueous Phase	Toluene				o-Xylene			
		Φ_r	Φ_s	Dr (cm²/s)	Ds (cm²/s)	Φ_r	Φ_s	Dr (cm²/s)	Ds (cm²/s)
Fresh Newsprint	DI	0.81 (±0.01)[a]	0.19 (±0.01)	3.68E-09 (±1.9E-09)	1.57E-12 (±1.6E-12)	0.65 (±0.06)	0.35 (±0.06)	2.67E-09 (±6.8E-11)	3.69E-13 (±2.1E-13)
	Acidogenic Leachate	0.80 (±0.04)	0.20 (±0.04)	4.81E-09 (±2.7E-09)	2.47E-13 (±2.8E-13)				
	Methanogenic Leachate	0.86 (±0.05)	0.14 (±0.05)	3.70E-09 (±2.1E-10)	1.47E-13 (±2.4E-15)				
Degraded Newsprint	DI	0.75 (±0.002)	0.25 (±0.002)	2.74E-09 (±1.9E-09)	2.68E-12 (±3.8E-13)	0.65 (±0.01)	0.35 (±0.01)	1.56E-09 (±4.0E-10)	6.17E-14 (±5.2E-14)
	Acidogenic Leachate	0.78 (±0.04)	0.22 (±0.04)	1.05E-09 (±2.0E-10)	1.49E-12 (±1.1E-12)				
	Methanogenic Leachate	0.79 (±0.02)	0.21 (±0.02)	1.75E-09 (±5.4E-10)	3.08E-12 (±4.8E-12)				
Fresh Office Paper	DI	0.56 (±0.001)	0.44 (±0.001)	1.61E-09 (±9.2E-10)	3.36E-12 (±4.3E-13)	0.44 (±0.02)	0.56 (±0.02)	8.72E-10 (±6.7E-10)	1.42E-12 (±5.3E-13)
	Acidogenic Leachate	0.61 (±0.16)	0.39 (±0.16)	1.05E-09 (±6.1E-10)	2.69E-11 (±2.1E-11)				
	Methanogenic Leachate	0.52 (±0.02)	0.48 (±0.02)	1.88E-09 (±5.0E-10)	4.22E-12 (±1.6E-12)				
Degraded Office Paper	DI	0.45 (±0.01)	0.55 (±0.01)	1.49E-09 (±5.3E-10)	9.96E-12 (±1.2E-13)	0.40 (±0.05)	0.60 (±0.05)	4.75E-10 (±2.1E-10)	1.69E-12 (±7.8E-13)
	Acidogenic Leachate	0.48 (±0.05)	0.52 (±0.05)	6.80E-10 (±3.7E-10)	3.45E-12 (±3.3E-12)				
	Methanogenic Leachate	0.46 (±0.01)	0.54 (±0.01)	1.78E-09 (±6.5E-10)	9.05E-12 (±5.0E-12)				
Degraded Rabbit Food	DI	0.78 (±0.03)	0.22 (±0.03)	7.60E-09 (±1.7E-09)	1.79E-13 (±2.0E-13)	0.70 (±0.03)	0.30 (±0.03)	5.14E-09 (±3.8E-10)	2.04E-13 (±1.6E-13)
	Acidogenic Leachate	0.82 (±0.02)	0.18 (±0.02)	5.75E-09 (±2.3E-09)	1.47E-13 (±1.5E-13)				
	Methanogenic Leachate	0.81 (±0.02)	0.19 (±0.02)	1.04E-08 (±1.9E-09)	4.80E-13 (±3.3E-13)				

a values in parentheses represent one standard deviation

Table 4.5 Dr/a² and Ds/a² values for toluene desorption from biopolymer composites[a]

Material	Dr (cm²/s)	Ds (cm²/s)	Dr/a² (1/day)	Ds/a² (1/day)
Fresh Newsprint	3.68E-09	1.57E-12	1.43	6.12E-04
Degraded Newsprint	2.74E-09	2.68E-12	2.09	2.04E-03
Fresh Office Paper	1.61E-09	3.36E-12	0.72	1.50E-03
Degraded Office Paper	1.49E-09	9.96E-12	1.17	7.80E-03
Degraded Rabbit Food	7.60E-09	1.79E-13	3.14	7.40E-05

[a] Calculated using 6 month in values obtained in DI water

Figure 4.2 compares toluene desorption rates for fresh and degraded biopolymer composites in DI water. Small differences were observed between toluene desorption rates from fresh and degraded forms of both office paper and newsprint. Somewhat more toluene was retained on degraded newsprint compared to fresh newsprint at the termination of desorption tests.

Biological activity in soils and sediments can lead to increased sorbent hydrophobicity over time and to increased HOC sequestration as a result (Guthrie et al. 1999). In general, Tables 4.4 and 4.6 suggest a trend where Φ_s values increase as biopolymer composites degrade, which indicates an increase in HOC sequestration in degraded polymers. Pairwise comparisons of all sorbate-solvent-sorbent systems at both 1-week and 6-month aging times yielded statistically significant difference only in approximately half of the comparisons, however. Aside from an increase in HOC sorption capacity due to increased hydrophobicity (Table 4.2), HOC releases from degraded components could also be slower because of increased associations with humic substances (humic acid, fulvic acid, humin). The latter was suggested by Chen (2003) who noted increased ^{14}C were levels associated with humic substances in degraded MSW components relative to fresh MSW components.

Fresh and degraded office papers both have large slow desorbing compartments, which was unexpected considering cellulose and hemicellulose have little sorption capacity. Previous research showed that a component other than cellulose controlled the HOC sorption capacity of and desorption rate from office papers (Wagner 2003). One explanation is that HOCs are strongly associated with sizing agents on office paper. This is a plausible theory considering sizing agents are hydrophobic compounds comprised of alkyl, or poly(methylene), groups which likely contribute to HOC sorption. Continuing with this theory, decomposition of fresh office paper could lead to the breakage of ester bonds between the cellulose and sizing agent, which in turn may increase the rapidly desorbing HOC fraction. However, the latter trend was not observed (Table 4.6). If, on the other hand, the hydrophobic regions of the sizing agent remain intact and associated with paper products during degradation, then the

HOC fraction associated with the slow-release compartment of office paper could increase with degradation. The latter trend is established in Table 4.6 and was confirmed by Wu (2002). In the course of this work, it was attempted to measure toluene sorption isotherms for the sizing agent alkenylsuccinic anhydride. Results were inconclusive, however, because the sizing agent formed an emulsion in water, and attempts to separate water and sizing agent phases at the termination of the sorption experiment were unsuccessful.
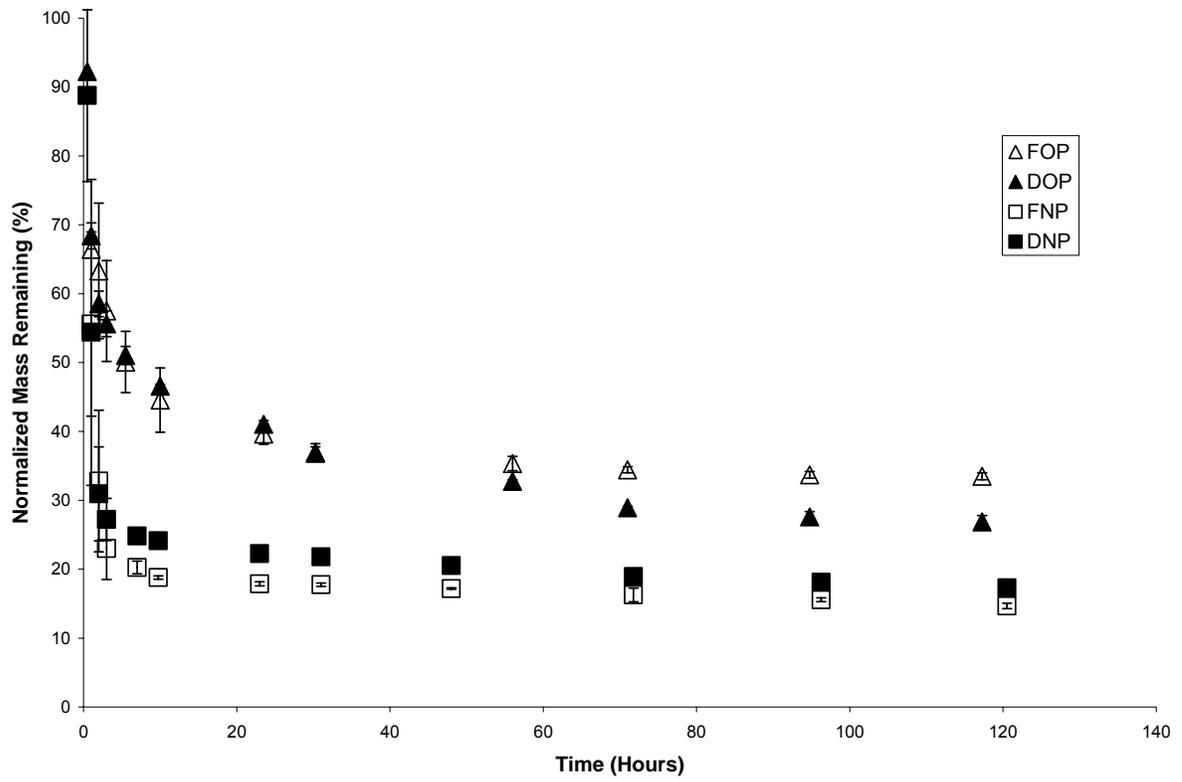
Figure 4.2: Effect of anaerobic sorbent degradation on toluene desorption rates after 6 months of aging in DI water. Error bars represent one standard deviation of replicate samples.

Table 4.6 Effects of sorbent aging time and aqueous phase composition on Φ_r and Φ_s estimates obtained from two-compartment polymer diffusion model[a]

Sorbent	Aging Time	DI Water		Acidogenic Leachate		Methanogenic Leachate	
		Φ_r	Φ_s	Φ_r	Φ_s	Φ_r	Φ_s
Fresh Newsprint	1 week	0.89	0.11	0.88	0.12	0.89	0.11
		±(0.02)	±(0.02)	±(0.02)	±(0.02)	±(0.04)	±(0.03)
	6 months	0.81	0.19	0.80	0.20	0.86	0.14
		±(0.01)	±(0.01)	±(0.04)	±(0.04)	±(0.05)	±(0.05)
Degraded Newsprint	1 week	0.80	0.20	0.85	0.15	0.80	0.20
		±(0.01)	±(0.01)	±(0.0)	±(0.0)	±(0.005)	±(0.005)
	6 months	0.75	0.25	0.78	0.22	0.79	0.21
		±(0.002)	±(0.002)	±(0.04)	±(0.04)	±(0.02)	±(0.02)
Fresh Office Paper	1 week	0.58	0.42	0.83	0.17	0.55	0.45
		±(0.05)	±(0.05)	±(0.04)	±(0.04)	±(0.06)	±(0.06)
	6 months	0.56	0.44	0.61	0.39	0.52	0.48
		±(0.001)	±(0.001)	±(0.16)	±(0.16)	±(0.02)	±(0.02)
Degraded Office Paper	1 week	0.60	0.40	0.63	0.37	0.57	0.43
		±(0.02)	±(0.02)	±(0.03)	±(0.03)	±(0.04)	±(0.04)
	6 months	0.45	0.55	0.48	0.52	0.46	0.54
		±(0.01)	±(0.01)	±(0.05)	±(0.05)	±(0.01)	±(0.01)
Degraded Rabbit Food	1 week	0.86	0.14	0.82	0.18	0.83	0.17
		±(0.06)	±(0.06)	±(0.07)	±(0.07)	±(0.002)	±(0.002)
	6 months	0.78	0.22	0.82	0.18	0.81	0.19
		±(0.03)	±(0.03)	±(0.02)	±(0.02)	±(0.02)	±(0.02)

[a] Diffusion coefficient estimates are the same for both aging times

4.3 Effects of Leachate Composition

Desorption test were conducted in three aqueous phases (acidogenic and methanogenic leachate and phosphate-buffered DI water) to assess the effects of leachate composition on alkylbenzene desorption rates. In general, leachates had no significant effect on HOC desorption rates, as exemplified for HDPE and degraded office paper in Figure 4.3. In the case of PVC and fresh office paper, however, faster toluene desorption rates (p-value < 0.004) were observed in acidogenic leachate (Figure 4.4).
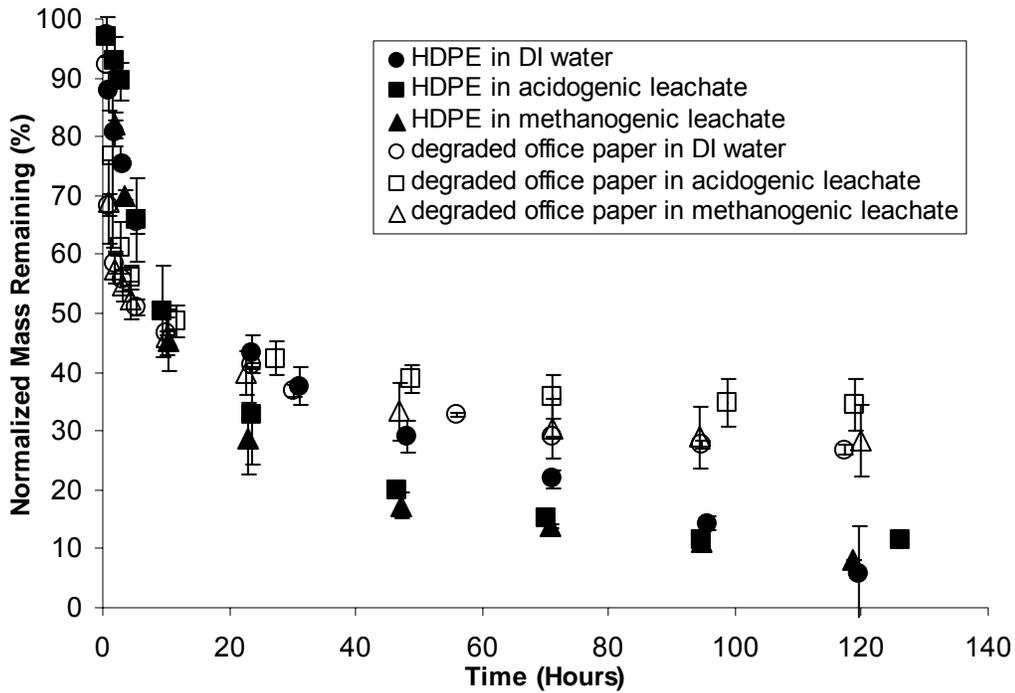
Figure 4.3: Leachate effects on toluene desorption rates from HDPE and degraded office paper after 6 months of aging. Error bars represent one standard deviation of replicate samples.
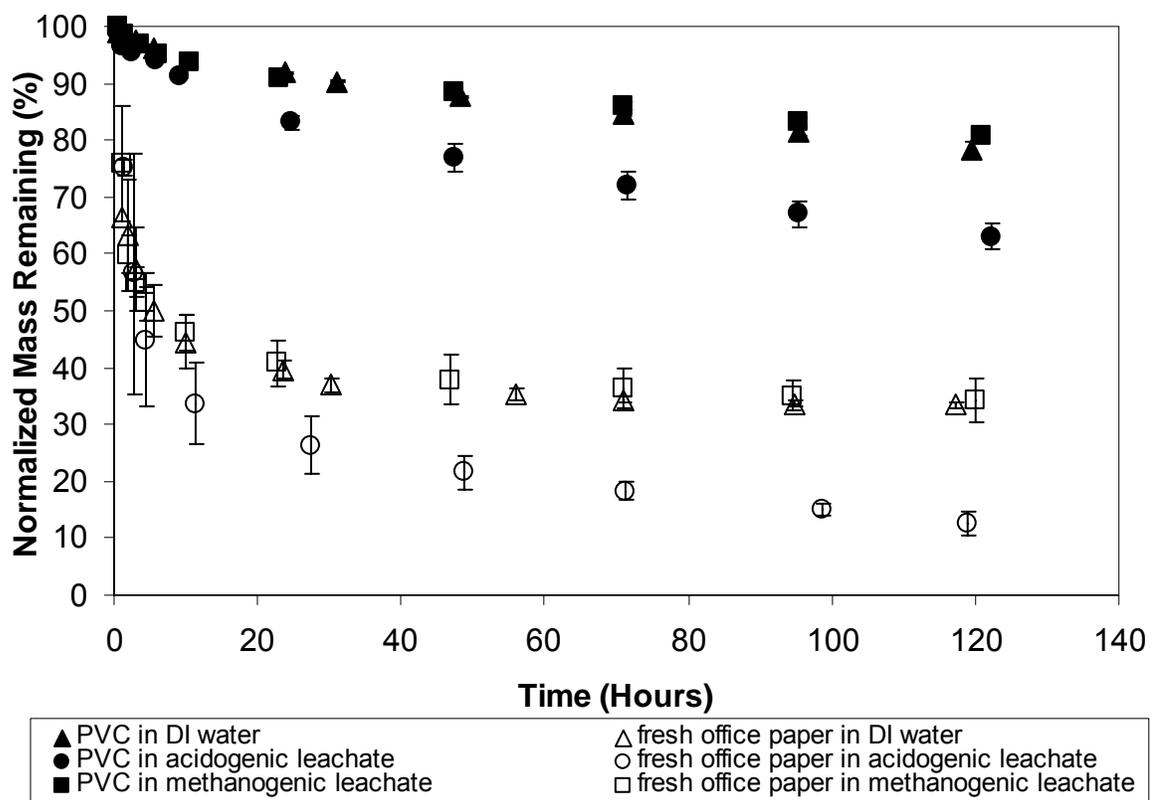
Figure 4.4: Leachate effects on toluene desorption rates from PVC and fresh office paper after 6 months of aging. Error bars represent one standard deviation of replicate samples.

Toluene diffusivities in PVC were an order of magnitude faster in acidogenic leachate than in either DI water or methanogenic leachate (Table 4.3). Previous research showed the same phenomenon (Wu 2002). One explanation for this result is that constituents in acidogenic leachate, such as propionic and/or butyric acids, could have plasticized PVC and converted it from a glassy to a rubbery state (Wu et al. 2001). This hypothesis is also supported by toluene sorption isotherm data which were linear in acidogenic leachate but non-linear in DI water and methanogenic leachate (Wu 2002).

Increased toluene desorption rates were also observed with fresh office paper in acidogenic leachate. While Dr values were approximately the same for all leachate types, Ds values were an order of magnitude greater in acidogenic leachate (Table 4.4). Wu (2002) showed that faster toluene desorption rates from office paper can be attributed to the lower pH of acidogenic leachate. Acidic conditions could cause cellulose and hemicellulose hydrolysis, which in turn could alter the SOM matrix and alter desorption rates (Maloney et al. 1985, Lipinsky 1979). However, Wagner (2003) showed that HOC sorption to pure cellulose is negligible and that HOC release rates are fast and complete within minutes. As a result, an alternative explanation is needed. For example, it is possible that prolonged exposure to low pH could have broken the ester bonds between cellulose and sizing agents, which may have led to enhanced toluene desorption rates.

4.4 Effects of Sorbate Properties

Both toluene and *o*-xylene were studied to determine the effects of sorbate properties on HOC desorption rates. Toluene is a smaller and less hydrophobic molecule than *o*-xylene. *o*-Xylene desorption rates were slower compared to those of toluene as exemplified by the data shown in Figure 4.5. Table 4.7 illustrates that *o*-xylene diffusivities in synthetic polymers were smaller than those of toluene (p-values ranged from 0.047 to 3.13E-05), and the difference was most noticeable with PVC after 6 months of aging. One exception to this trend was the result obtained with PVC after an aging time one week. Sorption equilibrium

would not have been reached between alkylbenzenes and PVC at this aging time; as a result, bi-directional diffusion could have taken place, making the validity of diffusion coefficient estimates questionable.

For biopolymer composites, Table 4.4 demonstrates a trend where Ds and Dr values for *o*-xylene are smaller than those for toluene. One exception is that the Ds value for *o*-xylene is larger for degraded rabbit food than the respective value for toluene. However, the standard deviation between these two numbers is too large to make the difference statistically significant. For all other biopolymers, Ds values for *o*-xylene were 2.3 to 42.3% of those for toluene while Dr values for *o*-xylene were 31.9 to 72.6% of those for toluene. Statistically, differences were significant for Ds values, but not for Dr values (p-value = 0.004 and 0.10, respectively). Wu (2002) observed similar trends but smaller differences. For biopolymer composites, Tables 4.8 to 4.10 show how the alkylbenzene fractions associated with the slow and rapid desorbing compartments changed with aging time for both toluene and *o*-xylene. Φs values for *o*-xylene were generally larger than those of toluene (exception: fresh office paper after a 1-week aging time), and changes in Φs with aging time were generally larger for *o*-xylene than for toluene. Both the trends in D and Φs values suggest that HOC sequestration in condensed, glassy SOM becomes more pronounced as sorbate hydrophobicity and size increases.

Table 3.3 summarizes toluene and *o*-xylene characteristics. There is an inverse relationship between molecular size and desorption rates. Since *o*-xylene is a larger molecule, its desorption rate should be slower than that of toluene. This effect can be attributed to the increased diffusional resistance larger molecules would experience (Ball and Roberts 1991, Berens 1989). With the addition of a methyl group, *o*-xylene also has a more complex structure, than toluene, which could aid in entanglement with the SOM matrix. The octanol-water coefficient (K_{ow}) is also greater for *o*-xylene, suggesting that it is more hydrophobic and thus has a greater affinity for SOM.
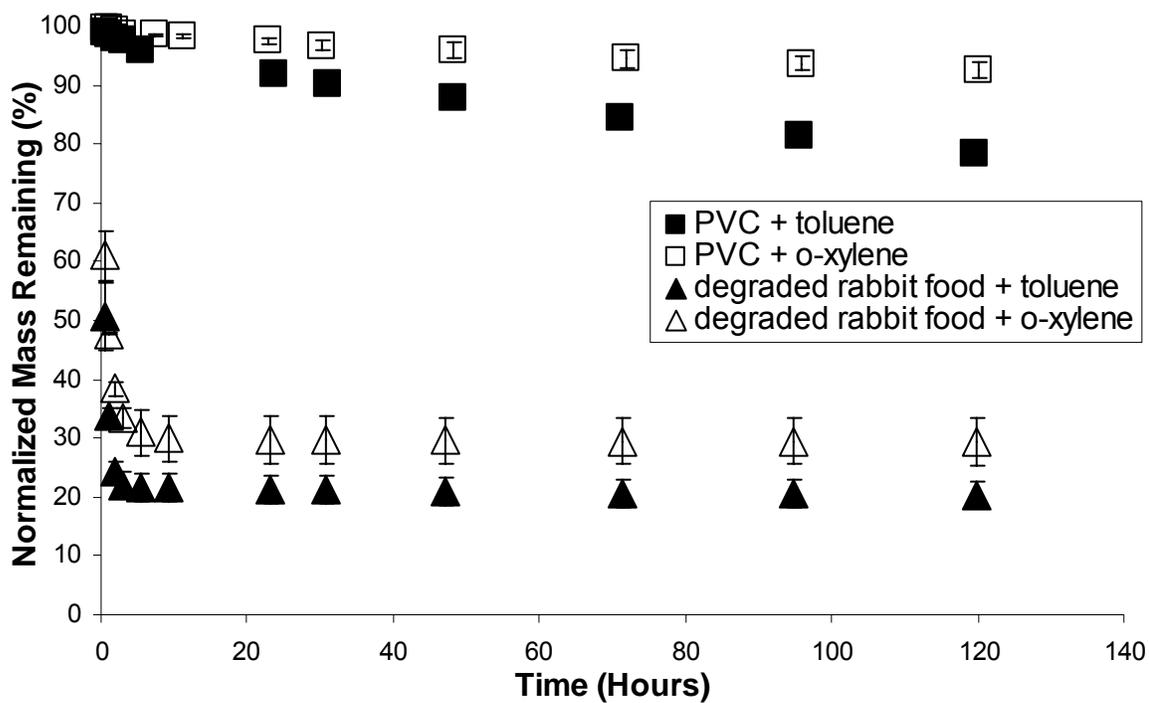
Figure 4.5: Toluene and o-xylene effects on desorption rates from PVC and degraded rabbit food after 6 months of aging. Error bars represent one standard deviation of replicate samples.

Table 4.7 Effects of aging time on diffusion coefficient estimates obtained from one-compartment polymer diffusion model. Experiments were conducted in DI water.

Aging Time	HDPE				PVC			
	Toluene		o-Xylene		Toluene		o-Xylene	
	D (cm²/s)	S	D (cm²/s)	S	D (cm²/s)	S	D (cm²/s)	S
1 week	3.93E-10	8.94E-11	1.89E-10	5.55E-11	3.57E-13	3.54E-14	5.01E-13	2.24E-13
1 month	5.04E-10	5.95E-11			3.09E-13	1.04E-13		
6 months	2.95E-10	1.30E-11	2.16E-10	2.70E-11	4.40E-13	2.47E-14	4.23E-14	2.20E-14
9 months	4.59E-10	2.97E-11			4.97E-13	4.12E-14		

Table 4.8 Effects of aging time, sorbent decomposition, and sorbate characteristics on Φr and Φs estimates. Sorbents: fresh and degraded newsprint; sorbates: toluene and o-xylene; aqueous phase: DI water

Aging Time	Fresh Newsprint				Degraded Newsprint			
	Toluene[a]		o-Xylene[a]		Toluene[a]		o-Xylene[a]	
	Φr	Φs	Φr	Φs	Φr	Φs	Φr	Φs
1 week	0.89	0.11	0.81	0.19	0.80	0.20	0.72	0.28
	(±0.02)[b]	(±0.02)	(±0.03)	(±0.03)	(±0.01)	(±0.01)	(±0.04)	(±0.04)
1 month	0.88	0.12			0.78	0.22		
	(±0.05)	(±0.05)			(±0.03)	(±0.03)		
6 months	0.81	0.19	0.65	0.35	0.75	0.25	0.65	0.35
	(±0.01)	(±0.01)	(±0.06)	(±0.06)	(±0.002)	(±0.002)	(±0.01)	(±0.01)
9 months	0.82	0.18			0.77	0.23		
	(±0.02)	(±0.02)			(±0.01)	(±0.01)		

[a] Diffusion coefficient estimates are the same for all aging times (see Table 4.4)

[b] Values in parentheses represent one standard deviation

Table 4.9 Effects of aging time, sorbent decomposition, and sorbate characteristics on Φr and Φs estimates. Sorbents: fresh and degraded office paper; sorbates: toluene and o-xylene; aqueous phase: DI water

| Aging Time | Fresh Office Paper | | | | Degraded Office Paper | | | |
| | Toluene[a] | | o-Xylene[a] | | Toluene[a] | | o-Xylene[a] | |
	Φr	Φs	Φr	Φs	Φr	Φs	Φr	Φs
1 week	0.58	0.42	0.60	0.40	0.60	0.40	0.58	0.42
	(±0.05)	(±0.05)	(±0.09)	(±0.09)	(±0.02)	(±0.02)	(±0.05)	(±0.05)
1 month	0.56	0.44			0.55	0.45		
	(±0.03)	(±0.03)			(±0.03)	(±0.03)		
6 months	0.56	0.44	0.44	0.56	0.45	0.55	0.40	0.60
	(±0.001)	(±0.001)	(±0.02)	(±0.02)	(±0.01)	(±0.01)	(±0.05)	(±0.05)
9 months	0.51	0.49			0.44	0.56		
	(±0.10)	(±0.10)			(±0.01)	(±0.01)		

[a] Diffusion coefficient estimates are the same for all aging times (see Table 4.4)
[b] Values in parentheses represent one standard deviation

Table 4.10 Effects of aging time and sorbate characteristics on Φr and Φs estimates. Sorbents: degraded rabbit food; sorbates: toluene and o-xylene; aqueous phase: DI water

| Aging Time | Toluene[a] | | o-Xylene[a] | |
	Φr	Φs	Φr	Φs
1 week	0.86	0.14	0.75	0.25
	(±0.06)	(±0.06)	(±0.005)	(±0.005)
1 month	0.83	0.17		
	(±0.03)	(±0.03)		
6 months	0.78	0.22	0.70	0.30
	(±0.03)	(±0.03)	(±0.03)	(±0.03)
9 months	0.77	0.23		
	(±0.05)	(±0.05)		

[a] Diffusion coefficient estimates are the same for all aging times (See Table 4.4)
[b] Values in parentheses represent one standard deviation

4.5 Effects of Aging Time

Tables 4.3 and 4.7 summarize alkylbenzene diffusivities in both HDPE and PVC for all tested solvent-sorbate pairs. There was no aging effect for HDPE as illustrated by similar D values and the absence of a correlation between D values and aging time. Chen (2003) found similar results for toluene bioavailability experiments with HDPE. The absence of an aging effect on HOC desorption rates can be attributed to the rubbery polymeric structure of HDPE. Figure 4.6 displays toluene desorption rates form HDPE and PVC after five aging times in DI water. Figure 4.6 also suggests that any differences in toluene desorption rates from HDPE were a result of random experimental error. Alkylbenzene diffusivities in PVC were similar after all aging times for a given solvent-sorbate pair (exception: o-xylene aged in DI water). However, this result could be misleading because, at shorter aging times (< 6 months), sorption equilibrium between alkylbenzene and PVC would not have been reached, making one of the modeling assumptions invalid (Wu 2002). Since sorption sites on the interior of PVC would not have been fully occupied, bi-directional diffusion most likely occurred at shorter aging times. Nonetheless, Figure 4.6 suggests that toluene desorption rates from PVC were very similar after all tested aging times. However, this trend did not hold for o-xylene aged in DI water. Even though there is an observable decrease in diffusivity for o-xylene from PVC (p-value = 0.03), it needs to be noted that the assumptions of the model are still invalid at earlier aging times.

Effects of aging time on alkylbenzene desorption rates from biopolymers were assessed by analyzing changes in Φs (and Φr). The adjustable parameters for the three-parameter, two-compartment diffusion model were determined from the data obtained after an aging time of 6 months. Data sets representing other aging times for the same sorbent-sorbate-solvent system were subsequently used to determine Φs while keeping Dr and Ds values fixed at the 6-month levels. Tables 4.6 and 4.8 through 4.10 show that Φs values increased with increasing aging time for all biopolymer composites. The same trend was observed by Wu (2002). Figure 4.7 displays an example of typical toluene desorption rates for biopolymer

composites after three aging times in DI water. The aging effect seen with both degraded office paper and degraded rabbit food suggests that the HOC had not fully penetrated the slow desorbing compartment during the earlier aging times or became increasingly associated with humic matter. Sharer et al. (2003) reported similar results for chlorobenzene desorption from soils, noting that the non-desorbing fraction increased with aging time.

Relative to toluene, aging effects appeared to be more pronounced for *o*-xylene, i.e., Φs values for o-xylene generally exhibited larger increases with aging time than those for toluene. This result suggests that more hydrophobic sorbates may form stronger associations with SOM over time. A study by Sharer et al (2003) observed a similar effect. The sorption and desorption behavior of chlorobenzene (K_{ow} = 500 mg/L) and ethylene dibromide (K_{ow} = 4250 mg/L) was studied in soil. Sharer et al. (2003) found that the nondesorbable fraction of ethylene dibromide increased more dramatically with aging time than that of chlorobenzene.
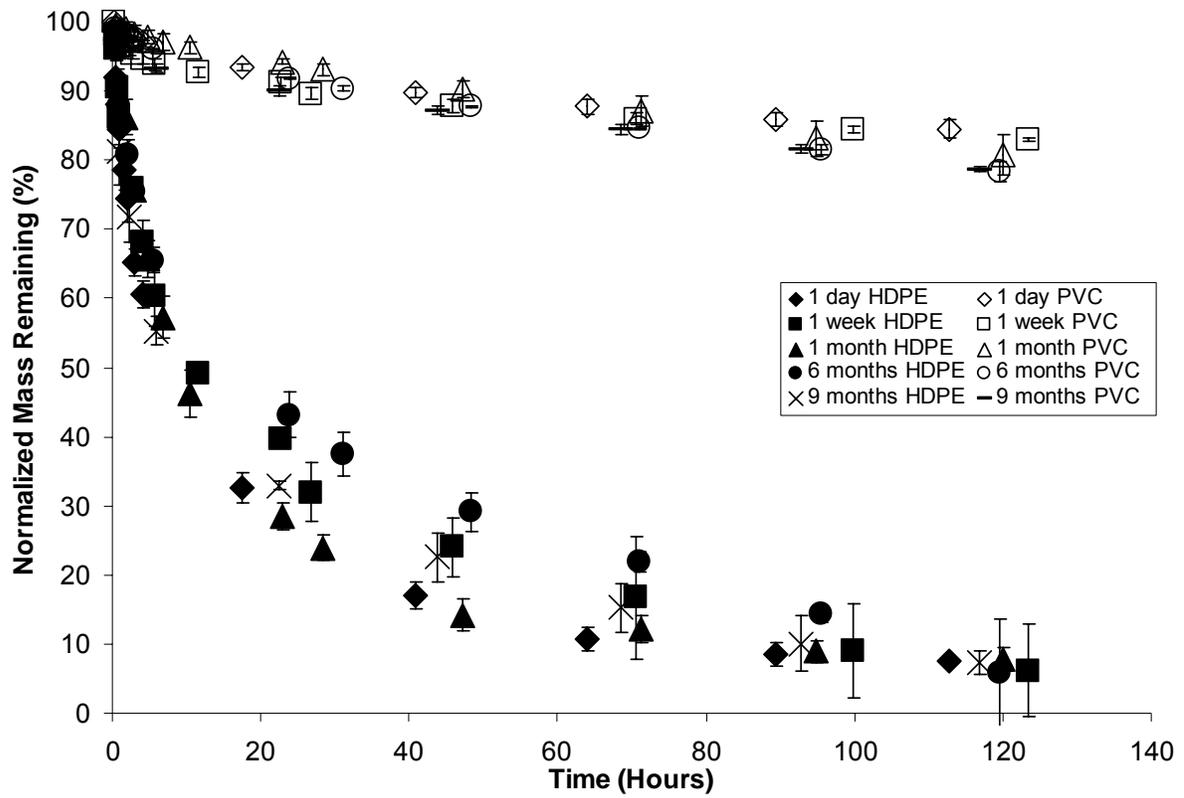
Figure 4.6: Toluene desorption rates from HDPE and PVC in DI water after five aging times. Error bars represent one standard deviation of replicate samples.
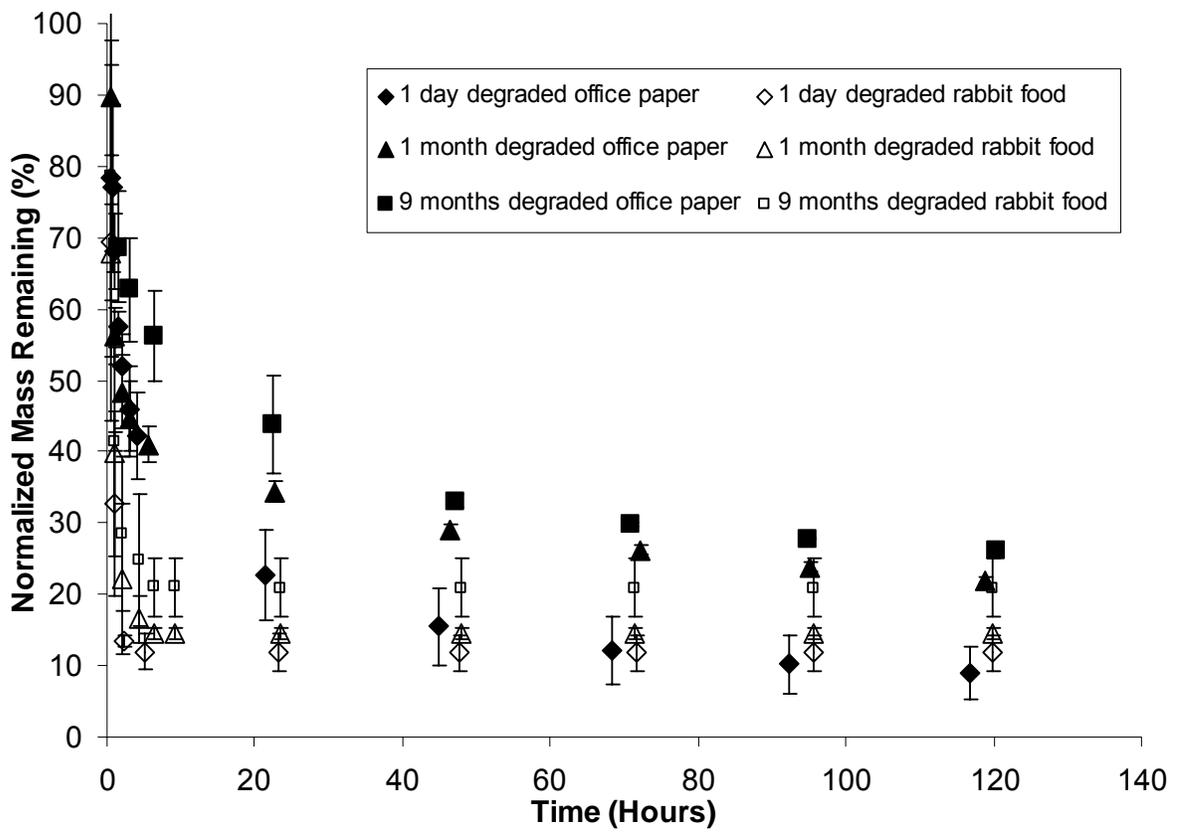
Figure 4.7: Toluene desorption rates from degraded office paper and degraded rabbit food in DI water after three aging times. Error bars represent one standard deviation of replicate samples.

4.6 Mass Balances

Mass balances were determined by conducting benzyl alcohol (BA) extractions of solids at the completion of desorption tests. This procedure helped confirm any experimental losses that may have occurred during testing. Extractions were performed with selected sorbate-sorbent-solvent systems as summarized in Table 4.11. Overall ^{14}C recoveries ranged from 91.8 – 103.8%. The highest recoveries were obtained with plastics. For plastics, complete ^{14}C recovery with BA was expected considering that they do not contain humic matter. Recoveries obtained with plastics show that ^{14}C losses from the reactors and/or to reactor components were negligible and that the experimental procedure was sound. Overall, lower recoveries were observed with biopolymers, and recoveries generally decreased as aging time time increased. This result indicates that more ^{14}C may have become associated with humic matter as aging increased. Further base extractions could have released HOCs associated with humic and fulvic materials, and the combustion of solids could have released HOCs associated with humins (Wu 2002, Chen 2003). Also, ^{14}C recovered from degraded MSW components was lower than from their respective fresh counterparts. This may indicate that anaerobic degradation enhanced the production of humic matter with which HOCs could associate. It should be noted that benzyl alcohol could have swelled the SOM and opened diffusive pathways (Deitsch and Smith 1999). Therefore, the recoveries shown for biopolymer composites in Table 4.11 cannot be used to calculate the percentage of ^{14}C associated with humic substances.

Table 4.11 ^{14}C recovery after desorption tests and benzyl alcohol extraction of sorbents

Sorbate	Solvent	Sorbent	Aging Time	[14]C Recovery (%)
Toluene	DI Water	HDPE	7 days	103.8 (±3.5)
Toluene	DI Water	HDPE	9 months	99.7 (±1.6)
Toluene	DI Water	PVC	7 days	100.6 (±1.9)
Toluene	DI Water	PVC	9 months	100.1 (±2.4)
Toluene	DI Water	Fresh Newsprint	7 days	97.8 (±1.9)
Toluene	DI Water	Fresh Newsprint	9 months	94.0 (±0.4)
Toluene	DI Water	Degraded Newsprint	7 days	95.7 (±1.2)
Toluene	DI Water	Degraded Newsprint	9 months	93.2 (±0.7)
Toluene	DI Water	Fresh Office Paper	1 month	96.9 (±2.0)
Toluene	DI Water	Fresh Office Paper	6 months	93.4 (±0.4)
Toluene	DI Water	Degraded Office Paper	1 month	92.4 (±0.8)
Toluene	DI Water	Degraded Office Paper	6 months	91.8 (±0.6)
Toluene	Acidogenic Leachate	Fresh Newsprint	7 days	98.3 (±0.9)
Toluene	Acidogenic Leachate	Fresh Newsprint	6 months	94.6 (±1.7)
Toluene	Acidogenic Leachate	Degraded Newsprint	7 days	93.5 (±0.1)
Toluene	Acidogenic Leachate	Degraded Newsprint	6 months	91.9 (±1.2)
Toluene	Acidogenic Leachate	Degraded Rabbit Food	7 days	96.7 (±0.5)
Toluene	Acidogenic Leachate	Degraded Rabbit Food	6 months	93.4 (±0.3)
Toluene	Methanogenic Leachate	Fresh Office Paper	7 days	97.4 (±0.2)
Toluene	Methanogenic Leachate	Fresh Office Paper	6 months	92.7 (±1.6)
Toluene	Methanogenic Leachate	Degraded Office Paper	7 days	92.9 (±1.7)
Toluene	Methanogenic Leachate	Degraded Office Paper	6 months	91.9 (±0.8)
o-Xylene	DI Water	HDPE	7 days	100.9 ±(3.6)
o-Xylene	DI Water	HDPE	6 months	101.3 ±(1.8)
o-Xylene	DI Water	PVC	7 days	95.1 (±2.9)
o-Xylene	DI Water	PVC	6 months	98.5 (±0.6)
o-Xylene	DI Water	Degraded Rabbit Food	7 days	94.8 (±0.8)
o-Xylene	DI Water	Degraded Rabbit Food	6 months	92.1 (±1.5)

4.7 Model Predictions of HOC Desorption Rates from Simulated MSW Mixtures

Desorption rates of alkylbenzenes from simulated MSW mixtures can be predicted once equilibrium (Wu 2002) and kinetic parameters are known for individual MSW components. In this study, toluene and o-xylene desorption rates were predicted for MSW mixtures that simulated MSW compositions in the years 1960 and 2000 (US EPA 2002). As shown in Table 4.12 and 4.13, the principal changes in MSW composition that occurred over the 40-year period are (1) an increase in the percentage of plastics, both rubbery and glassy, and (2) a decrease in the percentage of food and yard waste. Sorbent organic matter compositions and sorbed HOC distributions are listed in tables 4.12 and 4.13 for the 1960 and 2000 scenarios, respectively.

To predict alkylbenzene desorption rates from simulated MSW mixtures typical diffusion length scales associated with each category of discards needed to be assumed. Typical thicknesses of MSW components in landfills were used for this purpose and are listed in table 4.14. There are two common size categories of rubbery polymers, container wastes and thin films. Toluene desorption curves were obtained separately for each size classification and added according to the mass fraction of each size category. The same technique was used to address potential size differences in food and yard waste.

The distribution of sorbed alkylbenzenes in the simulated 1960 and 2000 MSW mixtures were predicted from the isotherm parameters of Wu et al. (2001) and Wu (2000). Tables 4.12 and 4.13 summarize sorbed alkylbenzene distributions for the 1960 and 2000 scenarios, respectively. A comparison of Tables 4.12 and 4.13 illustrates that almost 69.6-72.1% of alkylbenzene is predicted to sorb to food and yard waste in the 1960 scenario whereas more than 85% of alkylbenzene is predicted to sorb to plastics in the 2000 scenario.

Tables 4.12 Composition of sorbent organic matter in MSW (1960)

Waste Category[a]	Discards (tons*10^3)[b]	Category Mass Percent (%)	Sorption Capacity Parameter for Toluene[c]	Fraction of Sorbed Toluene in Hypothetical MSW (%)	Sorption Capacity Parameter for o-Xylene[d]	Fraction of Sorbed o-Xylene in Hypothetical MSW (%)
Rubbery Plastics	288	0.5	72.4	1.8	244.1	2.0
Glassy Plastics	102	0.2	1309	11.8	4634.5	13.3
Total Newsprint	12000	20.9	13.3	14.1	31.1	10.5
Total Office Paper	12910	22.5	2.4	2.7	5.7	2.1
Food Waste	12200	56	24.5	69.6	79.3	72.1
Yard Waste	20000					
Total[e]	57500	100		100		100

[a] assumes same discards ratio within each waste category as 2000 data (see Table 4.13)

[b] From EPA (2002)

[c] For glassy plastics, the Kf value (µg/kg)(L/µg)^n of PVC in methanogenic leachate was used, for other materials, the Kp values (µg/kg)(L/µg) in methanogenic leachate were used (Wu 2002)

[d] For glassy plastics, the Kf value (µg/kg)(L/µg)^n of PVC in ultrapure water was used, for other materials, the Kp values (µg/kg)(L/µg) in untrapure water were used (Wu 2002)

[e] Total for the waste categories considered here

Tables 4.13 Composition of sorbent organic matter in MSW (2000)

	Waste Category	Discards (tons $\times 10^3$)[a]	Individual Mass Percent (%)	Group Mass Percent (%)	Sorption Capacity Parameter for Toluene[b]	Fraction of Sorbed Toluene in Hypothetical MSW (%)	Sorption Capacity Parameter for o-Xylene[c]	Fraction of Sorbed o-Xylene in Hypothetical MSW (%)
Rubbery Plastics	HDPE	2677	2.6	13.8	72.4	11.6	244.1	11.4
	LDPE/LLDPE	2843	2.7					
	Polypropylene (PP)	2061	2					
	Plasticized Films (PVC, PS, PET)	6770	6.5					
Glassy Plastics	PVC	1102	1.1	4.9	1309	74.2	4634.5	76.3
	Polystyrene (PS)	2034	2					
	PET	1933	1.9					
Total Newsprint	Newsprint	6280	6	21.9	13.3	3.4	31.1	2.3
	Telephone Books	610	0.6					
	Corrugated Boxes & Magazines[d]	5150	5					
	Folding Cartons	5150	5					
	Tissue Paper and Towels[e]	2889	2.8					
	Other Paper[d]	2740	2.6					
Total Office Paper	Office Paper	3460	3.3	23.6	2.4	0.7	5.7	0.5
	Books	920	0.9					
	Standard (A) Mail	3790	3.6					
	Corrugated Boxes & Magazines[d]	5150	5					
	Commercial Printing	5390	5.2					
	Other Paper[d]	2740	2.6					
	Tissue Paper and Towels[e]	321	0.3					
	Paper Plates and Cups	1040	1					
	Milk Cartons	490	0.5					
	Bags and Sacks	1250	1.2					
Food & Yard Waste	Food Waste	25220	24.3	35.8	24.5	10.2	79.3	9.6
	Yard Waste	11960	11.5					
	Total[f]	103969	100	100		100		100

[a] From EPA (2002)

[b] For glassy plastics, the Kf value $(\mu g/kg)(L/\mu g)^n$ of PVC in methanogenic leachate was used, for other materials, Kp values $(\mu g/kg)(L/\mu g)^n$ in methanogenic leachate were used (Wu 2002)

[c] For glassy plastics, the Kf value $(\mu g/kg)(L/\mu g)^n$ of PVC in methanogenic leachate was used, for other materials, Kp values $(\mu g/kg)(L/\mu g)^n$ in methanogenic leachate were used (Wu 2002)

[d] Subcategory was divided into newsprint (50%) and office paper (50%) categories

[e] Subcategory was divided into newsprint (90%) and office paper (10%) categories

[f] Total for the waste categories considered here

Table 4.14 Thickness of MSW components used in model prediction

Waste Category	Representative Constituent(s)	Thickness (mm)	Mass Within Each Category (%)
Rubbery Plastics	HDPE - container	1.85[b]	52.8
	HDPE & PVC[a] - thin film	0.02[c]	47.2
Glassy Plastics	PVC - container	0.4[d]	100
Total Newsprint	Newsprint	0.27[e]	100
Total Office Paper	Office Paper	0.318[f]	100
Food & Yard Waste	Food Waste	5.0[g]	67.8
	Yard Waste	0.5[h]	32.2

[a] thin films were assumed to behave like rubbery polymers because of the inherent characteristics of the polymer (e.g. HDPE) or because of the presence of plasticizing agents (e.g. PVC)

[b] average thickness of typical containers: soda (1.33mm), milk (1.98mm), and orange juice (2.25mm) bottles

[c] estimated average film thickness from saran wrap and packaging films

[d] thickness of PET soda bottles

[e] assumes 3 sheets of newsprint (individual thickness = 0.09 mm) are stuck together when discarded

[f] assumes 3 sheets of office paper (individual thickness = 0.106 mm) are stuck together when discarded

[g] estimated average food waste thickness

[h] estimated average yard waste thickness (e.g. leaves and grass)

Alkylbenzene desorption curves were predicted for each waste category and then added according to the sorbed alkylbenzene distribution (Tables 4.12 and 4.13) to obtain an overall alkylbenzene desorption curves for simulated MSW mixtures. Figures 4.8 and 4.9 compare the model predictions for both the 1960 and 2000 scenarios for toluene and o-xylene, respectively.

Figure 4.8 shows that waste composition had a considerable effect on toluene desorption rates. For the 1960 scenario, it would take less than 1 day to release 50% of sorbed toluene. In contrast, it would take approximately 157 days to release 50% of sorbed toluene for the plastic-rich 2000 scenario. These predictions differ dramatically from those obtained by Wu (2002) who predicted toluene half-lives of approximately 5 days for the 1960 scenario and approximately 4 years for the 2000 scenario. The differences, especially for the new landfill scenario, are driven by new diffusion coefficient estimates for alkylbenzenes in plastics. The intermittent purge technique used by Wu (2002) yielded smaller diffusion coefficients, which greatly affected model predictions for simulated MSW mixtures.

Waste composition had a similar effect on o-xylene desorption rates as seen in Figure 4.9. Because of the greater hydrophobicity of o-xylene, increased half-lives were observed compared to toluene. It would take approximately 7 days to release 50% of sorbed o-xylene for the 1960 scenario and 1525 days (4.2 years) to release the same amount for the 2000 scenario.

To determine the model's sensitivity to diffusion length scale, thicknesses from each waste category were doubled one by one. The most significant effect was observed when the thickness of the glassy polymer category was doubled, in which case, the half-life of toluene increased from 157 days to 600 days for the 2000 scenario (Figure 4.10). Doubling the diffusion length scale for glassy polymers also affected toluene release rates for the 1960 scenario; however, the effect was not as pronounced because glassy polymers represent only 0.2% (wt/wt) in this scenario (Figure 4.10). Doubling the thickness of any other material had

little effect on toluene half-life. For all 1960 scenarios, toluene half-lives were less than 1 day, and the half-lives of the 2000 scenario increased from 157 to as much as 164 days.
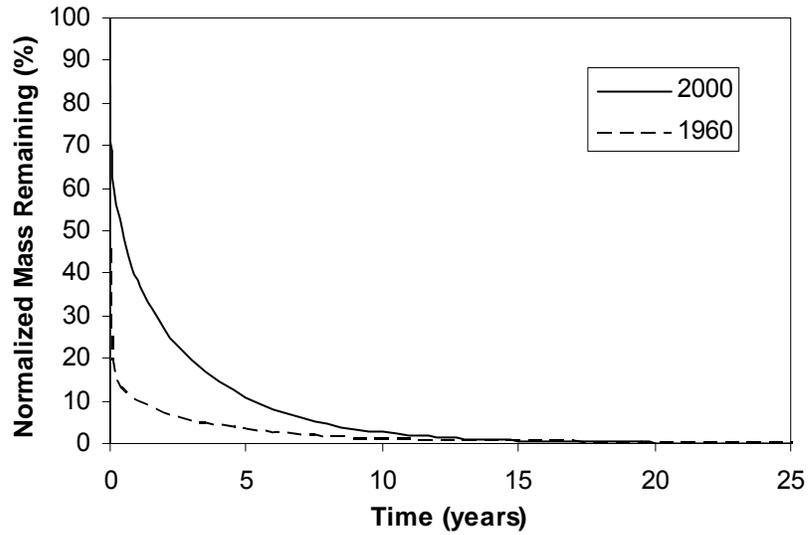
Figure 4.8: Predicted toluene desorption rates from mixed MSW
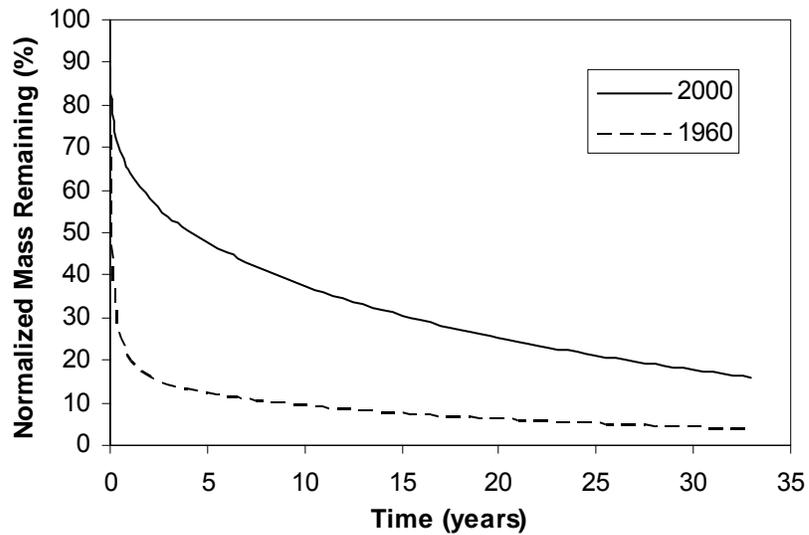
Figure 4.9: Predicted *o*-xylene desorption rates from mixed MSW
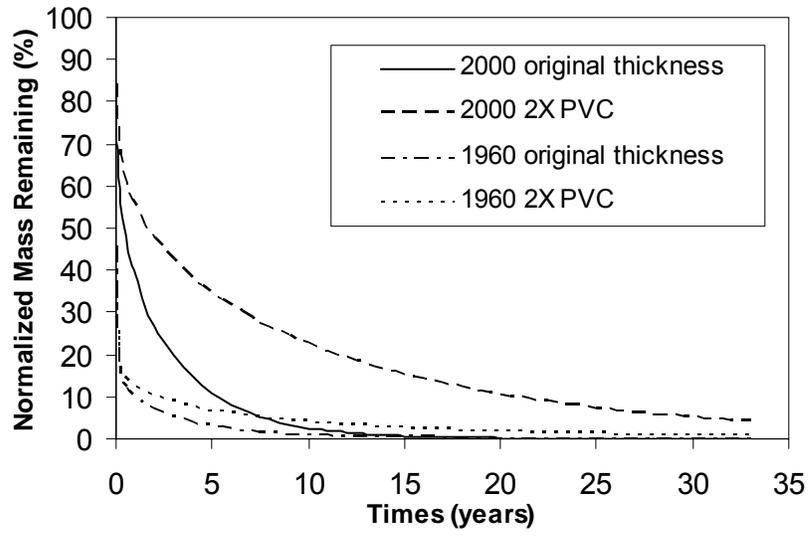
Figure 4.10: Model predictions for toluene desorption from mixed MSW as a function of PVC thickness

With *o*-xylene, a similar sensitivity to the diffusion length scale of glassy polymers was obtained. Doubling the PVC thickness increased the *o*-xylene half-life for the 2000 scenario to 5829 days (16 years). Unlike the toluene scenarios, doubling food and yard waste thicknesses also had a significant effect for the 1960 scenario. Doubling the food waste thickness increased *o*-xylene half-life to 17 days, and doubling the yard waste thickness increased *o*-xylene half-life to 10 days.

Additional desorption experiments are needed to verify model predictions. Overall, the results of the desorption predictions for simulated MSW mixtures illustrate that a greater percentage of plastics significantly decreases HOC desorption rates, potentially lessening the risk of groundwater contamination.

It should be noted that sorbent characteristics will not stay the same over time. The preferential degradation of polar SOM components like cellulose and hemicellulose will increase the hydrophobicity of the landfill SOM. This increased hydrophobicity could potentially sequester HOCs either within the SOM itself or in humic substances. Also, laboratory-degraded newsprints, such as the ones used in this study, may be less hydrophobic than degraded newsprint in actual landfills (Chen et al. 2004a). This could be because of continued cellulose/ hemicellulose degradation, biologically mediated changes in lignin characteristics, and/or the persistence of hydrophobic resin acids, all of which can contribute to an increased HOC sorption capacity of well-degraded landfilled newsprint (Chen et al. 2004a). Therefore, the predictions presented herein may overestimate HOCs release rates in a real-world scenario. On the other hand, predicted half-lives may not be sufficiently long for significant SOM decomposition to take place. Other environmental conditions such as rainfall and preferential flow paths could affect HOC behavior in landfills (Öman and Spännar 1999); e.g., aqueous HOCs may not be in equilibrium with surrounding SOM because they are transported by advection through different layers of waste in a landfill. As a result, the predictions presented herein may underestimate HOC release rates in a real-world scenario. For this reason, an advection-dispersion model that takes into account the

heterogeneity and geometry of landfills is needed to predict HOC transport in real landfills. A common remediation strategy for old municipal landfills on the National Priority List of Superfund is placement of a low permeability cover. This will minimize water infiltration into the landfill and reduce leachate generation. However, it has been shown that water stimulates toluene biodegradation (Sanin et al. 1999). Therefore, a balance must be considered between potential groundwater contamination due to increased infiltration and reduced HOC biodegradation within landfills.

5 Conclusions and Future Research

5.1 Conclusions

The objectives of this study were to measure desorption rates of toluene and *o*-xylene from model MSW components. The effects of sorbent characteristics, leachate composition, and sorbent/sorbate contact time (aging time) on alkylbenzene desorption rates were measured. The effects of sorbent decomposition on desorption rates were determined by studying two biopolymer composites (newsprint and office paper) in both their fresh and anaerobically degraded forms. The effects of solvent composition were examined by comparing alkylbenzene desorption rates in acidogenic and methanogenic leachates to those in DI water. The principal conclusions of this study were:

1. Desorption rates of HOCs varied greatly among MSW components. For plastics, HOCs were rapidly released from rubbery polymers such as HDPE and slowly released from glassy polymers such as PVC. For biopolymer composites, an initial phase of rapid HOC desorption was followed by an extended period of slow HOC desorption.

2. Leachate composition had little effect on alkylbenzene desorption rates; however, for PVC and fresh office paper, HOC release rates were enhanced in the presence of acidogenic leachate.

3. HOC desorption rates were slower for *o*-xylene than for toluene, suggesting that HOC desorption rates decrease with increasing sorbate size and hydrophobicity

4. The slowly desorbing HOC fraction in biopolymers increased with aging time, and this trend was more pronounced for *o*-xylene.

5. Predicted alkylbenzene desorption rates from simulated MSW mixtures showed that as the plastics content of MSW increased from <1% in 1960 to more than 18% in 2000, alkylbenzene half-lives increased from <1 to 600 days and from ~7 to 1525 days for toluene and *o*-xylene, respectively.

5.2 Future Research

The following tests should be performed to improve estimates of HOC transport and fate in MSW landfills:

1. Apart from alkylbenzenes, test other common HOCs to broaden our understanding of the effects of sorbate properties on sorption/desorption processes in MSW landfills.
2. Test the effects of aging time on HOC desorption rates from MSW mixtures to verify model predictions.
3. Perform isotherm experiments with sizing agents typically used in the production of office paper.
4. Examine the effects of a dynamic landfill environment on HOC transport by incorporating equilibrium and kinetic parameters describing HOC sorption to/desorption from MSW mixtures in an advection-dispersion model.

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Appendices

A. Experimental and Modeling Data

Table A.1 Toluene desorption data from HDPE in DI water after various aging times

1 Day			1 Week				
Data			Data			Model	
Time (hrs)	Average	S	Time (hrs)	Average	S	Average	S
0.25	98.84	0.79	0.25				
0.5	91.90	0.38	0.5	96.19	1.74	89.39	2.07
0.75	88.02	1.10	0.75	90.45	2.75	87.01	2.55
1	84.55	1.76	1	86.06	3.71	84.93	2.96
1.5	78.63	3.10	2.75	75.97	1.31	75.78	4.66
2	74.35	3.88	4	68.23	3.12	71.15	5.46
3	65.30	4.58	5.75	60.34	4.44	66.08	6.29
4	60.56	4.51	11.5	49.10	0.19	54.20	8.00
17.5	32.61	8.81	22.75	39.63	0.86	39.94	9.48
40.75	17.13	8.77	26.75	31.93	4.22	36.27	9.72
64	10.71	10.30	45.75	23.98	4.28	23.80	9.80
89.5	8.42	10.80	70.5	16.70	8.92	14.44	8.55
112.75	7.56	11.00	99.75	9.04	6.74	8.32	6.50
			123.5	6.18	6.63	5.44	4.94
% Sorbed:	77.19	(±0.045)	% Sorbed:	78.80	(±0.47)	MSE	0.011

1 Month					6 Months				
Data			Model		Data			Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.5					0.5	97.24	0.53	90.86	0.00
1.75	86.20	2.48	76.67	2.45	1	87.72	3.19	87.02	0.00
3	75.73	0.99	70.17	3.07	2	80.71	2.22	82.01	0.00
4.75	65.71	2.68	63.27	3.67	3	75.48	0.17	78.19	0.00
6.75	57.28	2.97	57.27	4.16	5.5	65.53	1.89	71.08	0.00
10.5	46.22	3.38	48.64	4.77	23.75	43.17	3.22	45.74	0.00
23	28.54	1.93	31.00	5.53	31	37.51	3.21	39.82	0.00
28.25	23.90	1.85	26.13	5.57	48.25	29.09	2.75	29.45	0.00
47.25	14.22	2.30	14.57	5.02	71	21.88	1.49	20.32	0.00
71.25	12.06	1.93	7.23	3.75	95.5	14.31	1.23	13.80	0.00
94.75	8.89	1.65	3.74	2.55	119.5	5.78	7.95	9.49	0.00
120	7.70	1.72	1.91	1.59					
% Sorbed:	79.96	(±0.39)	MSE	0.014	% Sorbed:	78.42	(±0.46)	MSE	0.011

Table A.1 (continued)

9 Months				
Data			Model	
Time (hrs)	Average	S	Average	S
1	81.21	4.78	83.66	0.89
2.25	71.70	3.61	76.11	1.27
6	55.33	2.09	62.66	1.89
22.5	32.93	0.54	35.99	2.69
43.75	22.54	3.45	20.27	2.66
68.5	15.26	3.51	10.80	2.15
92.75	10.06	3.94	5.90	1.57
116.75	7.24	1.67	3.27	1.07
% Sorbed:	77.92	(±1.00)	MSE	0.010

Table A.2 Toluene desorption data from HDPE in acidogenic leachate after various aging times

1 Week					6 Months				
Data			Model		Data			Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.25					0.75	97.05	3.43	86.46	0.00
0.5					1.75	92.93	4.15	79.49	0.00
1	91.71	0.27	82.63	2.33	2.75	89.38	3.27	74.75	0.00
2	82.51	1.48	76.01	3.17	5.5	65.89	7.04	65.31	0.00
4.25	67.17	2.97	66.11	4.31	9.5	50.31	7.76	56.04	0.00
10.75	45.84	4.06	49.51	5.88	23.5	32.73	8.25	36.87	0.00
23	27.85	2.05	32.59	6.78	46.5	19.81	0.78	20.74	0.00
31.25	21.23	1.53	25.36	6.78	70	15.34	0.54	11.90	0.00
48.25	14.77	0.58	15.57	6.10	94.75	11.61	0.49	6.69	0.00
72.5	13.46	0.02	8.04	4.51	126.25	11.41	0.44	3.24	0.00
95.75	9.42	0.23	4.37	3.07					
120.75	8.51	0.55	2.32	1.92					
% Sorbed:	80.25	(±1.37)	MSE	0.017	% Sorbed:	81.29	(±0.42)	MSE	0.026

Table A.3 Toluene desorption data from HDPE in methanogenic leachate after various aging times

| | 1 Week | | | | | 6 Months | | | |
| | Data | | Model | | | Data | | Model | |
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.5					0.5				
1.25	96.31	0.70	83.63	1.74	2	82.03	2.18	76.01	3.17
3	76.54	1.53	75.20	2.59	3.5	70.02	0.88	68.94	4.00
5.25	62.90	2.21	67.96	3.27	10.25	45.42	5.30	50.51	5.80
23	33.80	1.90	40.40	5.22	23	28.67	5.99	32.59	6.78
47	20.24	3.45	23.69	5.54	47.25	17.32	2.26	16.02	6.15
71	12.22	0.45	14.53	5.02	70.75	13.87	0.36	8.42	4.63
96.75	9.18	0.85	8.77	4.13	94.75	11.15	0.15	4.48	3.13
121.25	7.45	0.91	5.51	3.24	118.75	8.06	0.02	2.44	2.00
% Sorbed:	79.26	(±0.65)	MSE	0.019	% Sorbed:	80.61	(±0.91)	MSE	0.018

Table A.4 *o*-Xylene desorption data from HDPE in DI water after various aging times

| | 1 Week | | | | | 6 Months | | | |
| | Data | | Model | | | Data | | Model | |
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.25					0.5	97.27	0.66	91.82	0.43
0.5	99.06	1.29	92.41	1.13	1	92.35	0.79	88.41	0.62
0.75	95.84	3.38	90.74	1.40	2	86.43	1.20	83.93	0.85
1	94.60	3.62	89.27	1.64	3	81.74	1.71	80.51	1.03
3.75	81.43	3.43	79.95	3.05	7.25	70.84	2.99	70.64	1.50
6	75.94	1.66	75.03	3.75	11.25	63.00	2.80	64.24	1.77
11	66.50	4.92	67.11	4.79	23	50.73	3.53	51.43	2.25
24	53.79	7.10	53.90	6.29	30.25	44.40	3.42	45.72	2.41
31.25	46.10	7.16	48.63	6.78	48.25	33.73	2.76	35.19	2.62
47.75	38.53	7.39	39.43	7.45	72	24.69	1.89	25.70	2.64
72.75	30.29	8.63	29.68	7.77	95.75	19.48	1.77	19.06	2.50
96	21.82	6.10	23.22	7.65	120.25	16.11	1.62	14.10	2.27
121	16.26	5.95	18.03	7.26					
% Sorbed:	92.20	(±0.28)	MSE	0.010	% Sorbed:	93.01	(±0.31)	MSE	0.007

Table A.5 Toluene desorption data from PVC in DI water after various aging times

1 Day			1 Week				
Data			Data			Model	
Time (hrs)	Average	S	Time (hrs)	Average	S	Average	S
0.25	99.91	0.10	0.25	99.94	0.02	97.43	0.02
0.5	99.25	0.21	0.5	98.01	0.99	97.33	0.03
0.75	99.04	0.25	0.75	97.13	0.89	97.22	0.04
1	98.78	0.28	1	96.40	0.93	97.10	0.06
1.5	98.46	0.28	2.75	95.46	0.89	96.41	0.14
2	98.22	0.23	4	94.68	0.84	95.97	0.19
3	97.62	0.25	5.75	93.85	0.83	95.41	0.25
4	97.13	0.31	11.5	92.67	0.76	93.89	0.38
17.5	93.51	0.52	22.75	91.17	0.79	91.69	0.54
40.75	89.80	0.79	26.75	89.62	0.78	91.04	0.59
64	87.73	1.00	45.75	87.84	0.88	88.48	0.77
89.5	85.85	0.99	70.5	86.00	0.84	85.87	0.95
112.75	84.54	1.23	99.75	84.40	0.40	83.36	1.11
			123.5	83.04	0.20	81.60	1.22
% Sorbed:	90.84	(±0.18)	% Sorbed:	96.68	(±0.07)	MSE	0.003

1 Month					6 Months				
Data			Model		Data			Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.5	99.57	0.50	97.36	0.08	0.5	98.98	0.17	97.27	0.03
1.75	99.03	1.00	96.94	0.19	1	98.50	0.13	96.99	0.06
3	98.38	1.07	96.55	0.30	2	97.97	0.13	96.50	0.11
4.75	97.80	1.07	96.05	0.43	3	97.47	0.17	96.05	0.15
6.75	97.09	1.16	95.54	0.55	5.5	96.05	0.14	95.05	0.22
10.5	96.24	0.96	94.69	0.73	23.75	91.80	0.18	90.55	0.50
23	94.24	0.41	92.52	1.14	31	90.37	0.31	89.29	0.57
28.25	93.14	0.86	91.79	1.26	48.25	87.75	0.16	86.81	0.71
47.25	90.30	1.18	89.56	1.63	71	84.57	0.19	84.17	0.85
71.25	87.02	2.21	87.34	1.99	95.5	81.40	0.74	81.80	0.97
94.75	83.12	2.55	85.51	2.28	119.5	78.36	1.37	79.78	1.08
120	80.82	2.95	83.81	2.54					
% Sorbed:	98.32	(±0.61)	MSE	0.005	% Sorbed:	99.33	(±0.11)	MSE	0.004

Table A.5 (continued)

9 Months				
Data			Model	
Time (hrs)	Average	S	Average	S
1	98.12	0.56	96.94	0.04
2.25	95.71	0.56	96.27	0.08
6	93.30	0.52	94.66	0.15
22.5	90.02	0.69	90.32	0.31
43.75	87.22	0.71	86.76	0.43
68.5	84.32	0.72	83.64	0.53
92.75	81.59	0.68	81.14	0.61
116.75	78.66	0.44	79.00	0.67
% Sorbed:	98.88	(±0.89)	MSE	0.003

Table A.6 Toluene desorption data from PVC in acidogenic leachate after various aging times

1 Week					6 Months				
Data			Model		Data			Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.25					0.5	98.97	0.04	96.71	0.06
0.5					1	96.57	0.25	95.92	0.11
1	99.20	0.40	95.39	0.00	2.5	95.54	0.24	94.15	0.21
2	97.55	0.50	93.87	0.00	5.75	94.16	0.22	91.49	0.33
4.25	94.20	1.22	91.35	0.00	9.25	91.37	0.43	89.35	0.42
10.75	87.44	2.86	86.58	0.00	24.75	83.17	1.27	83.07	0.66
23	82.36	0.68	80.80	0.00	47.5	76.99	2.34	77.03	0.89
31.25	77.62	0.30	77.85	0.00	71.5	71.99	2.33	72.27	1.05
48.25	68.96	1.59	72.93	0.00	95.5	67.06	2.26	68.40	1.18
72.5	62.54	1.21	67.46	0.00	122.25	63.04	2.24	64.72	1.30
95.75	56.19	0.12	63.19	0.00					
120.75	50.30	0.76	59.28	0.00					
% Sorbed:	94.12	(±0.15)	MSE	0.011	% Sorbed:	98.56	(±1.26)	MSE	0.005

Table A.7 Toluene desorption data from PVC in methanogenic leachate after various aging times

	1 Week					6 Months				
	Data		Model				Data		Model	
Time (hrs)	Average	S	Average	S		Time (hrs)	Average	S	Average	S
0.5	99.46	0.40	97.31	0.20		0.5	99.84		97.31	
1.25	98.45	0.92	96.98	0.47		1.5	98.51	0.04	96.88	0.05
3	96.81	1.62	96.30	1.00		3.5	96.85	0.06	96.10	0.10
5.25	95.59	2.33	95.57	1.52		6	95.21	0.19	95.26	0.15
23	90.64	4.99	91.91	3.78		10.5	93.57	0.42	94.03	0.22
47	87.80	6.04	88.78	5.46		23	91.07	0.91	91.49	0.33
71	86.16	6.45	86.41	6.68		47.5	88.60	0.72	88.05	0.47
96.75	84.70	6.84	84.30	7.73		71	85.93	0.67	85.55	0.57
121.25	83.34	7.69	82.57	8.58		95.5	83.32	0.66	83.38	0.65
						120.75	80.76	0.66	81.45	0.72
% Sorbed:	98.50	(±0.59)	MSE	0.004		% Sorbed:	98.02	(±0.19)	MSE	0.003

Table A.8 *o*-Xylene desorption data from PVC in DI water after various aging times

	1 Week					6 Months				
	Data		Model				Data		Model	
Time (hrs)	Average	S	Average	S		Time (hrs)	Average	S	Average	S
0.25	99.99		97.42			0.5	99.80	0.01	97.52	0.02
0.5	99.25	0.57	97.34	0.04		1	99.65	0.13	97.49	0.04
0.75	94.56	1.28	97.12	0.20		2	99.28	0.17	97.43	0.06
1	94.11	1.14	96.97	0.27		3	98.72	0.37	97.38	0.08
3.75	92.88	0.61	95.69	0.77		7.25	98.48	0.30	97.16	0.20
6	92.44	0.55	94.84	1.05		11.25	98.34	0.35	96.96	0.29
11	91.04	0.50	93.32	1.49		23	97.57	0.50	96.42	0.54
24	87.90	2.36	90.46	2.23		30.25	96.78	0.96	96.12	0.66
31.25	86.42	3.71	89.20	2.54		48.25	95.92	1.35	95.44	0.93
47.75	85.41	3.57	86.82	3.11		72	94.45	1.48	94.68	1.20
72.75	84.13	3.56	83.93	3.78		95.75	93.69	1.20	94.00	1.43
96	83.40	3.56	81.70	4.28		120.25	92.49	1.34	93.38	1.63
121	81.50	3.81	79.61	4.74						
% Sorbed:	97.28	(±0.13)	MSE	0.007		% Sorbed:	99.19	(±0.34)	MSE	0.004

Table A.9 Toluene desorption data from fresh newsprint in DI water after various aging times

1 Day			1 Week				
Data			Data			Model	
Time (hrs)	Average	S	Time (hrs)	Average	S	Average	S
0.25			0.25				
0.5	129.80	19.17	0.5	72.71	4.93		
0.75	72.76	8.01	0.75	40.01	8.31	48.61	1.00
1	58.41	4.26	1	28.12	4.69	42.15	1.13
2	25.69	0.57	1.75	17.93	1.42	30.11	1.37
3.5	18.06	1.95	3.5	16.54	1.23	17.33	1.62
5.5	16.10	1.85	7	15.56	1.56	11.10	1.73
8.75	14.93	2.05	10.5	15.31	1.25	10.24	1.73
19.5	12.98	2.61	23.25	13.94	0.82	9.86	1.68
24.5	12.63	2.79	31.25	13.35	0.37	9.73	1.66
33.75	11.80	2.95	48	12.31	0.39	9.51	1.62
44.75	11.14	3.07	71.5	11.36	0.53	9.25	1.58
69.75	10.00	3.20	95.75	10.77	0.70	9.03	1.54
95	9.23	3.14	119.5	10.52	0.80	8.84	1.51
118	8.75	3.30					
% Sorbed:	23.49	(±1.46)	% Sorbed:	22.60	(±4.64)	MSE	0.055

1 Month					6 Months				
Data			Model		Data			Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.5	87.41				0.5				
1	38.76	14.18	42.96	3.05	1	55.59	13.38	48.28	9.48
1.5	21.61	5.71	34.59	3.51	2	32.80	10.28	35.35	9.23
2.5	17.10	5.19	24.01	4.08	3	23.01	4.52	28.50	7.57
5	15.01	3.73	14.39	4.58	7	20.26	0.93	19.64	1.62
10.5	14.27	2.89	11.49	4.66	9.75	18.80	0.24	18.27	0.16
22.75	14.03	2.76	11.09	4.54	23	17.88	0.30	17.16	0.43
30	13.99	2.81	10.96	4.49	31	17.77	0.24	16.95	0.30
47.5	13.88	2.79	10.69	4.38	48	17.19	0.11	16.57	0.06
72.25	13.81	2.80	10.39	4.25	71.75	16.26	0.98	16.16	0.21
100.75	13.79	2.83	10.10	4.13	96.25	15.58	0.27	15.79	0.43
					120.5	14.67	0.39	15.48	0.61
% Sorbed:	28.55	(±3.63)	MSE	0.037	% Sorbed:	25.85	(±1.92)	MSE	0.011

Table A.9 (continued)

9 Months				
	Data		Model	
Time (hrs)	Average	S	Average	S
0.5				
1.75	37.42	1.95	35.59	1.70
3	29.18	2.45	26.05	1.95
6.75	18.89	1.61	18.15	2.14
23.75	15.91	0.44	16.58	2.08
47	15.75	0.49	16.01	2.01
71.5	15.66	0.47	15.56	1.96
95	15.57	0.44	15.20	1.91
120	15.53	0.46	14.86	1.87
% Sorbed:	26.14	(±0.49)	MSE	0.004

Table A.10 Toluene desorption data from fresh newsprint in acidogenic leachate after various aging times

1 Week					6 Months				
	Data		Model			Data		Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.25					0.5				
0.5	56.25	21.53	52.55	1.24	1	53.30	2.15	44.94	9.33
1	38.71	13.56	37.56	1.65	2	34.08	5.62	32.89	7.71
1.75	28.06	5.84	25.99	1.96	3.75	25.45	5.66	24.58	4.52
3.25	21.63	2.86	16.33	2.23	6.75	21.58	4.82	20.66	3.50
5.75	15.70	1.20	12.58	2.32	10.75	19.23	4.69	19.74	3.52
11.25	11.55	1.52	11.90	2.33	23.5	19.10	4.62	19.48	3.47
23.25	10.34	1.70	11.81	2.32	28.75	18.99	4.66	19.43	3.45
29.75	9.91	1.99	11.77	2.31	47.5	18.90	4.61	19.27	3.40
48.25	9.02	1.93	11.67	2.29	71.75	18.82	4.63	19.10	3.35
71.5	8.45	1.97	11.56	2.27	95	18.74	4.64	18.96	3.31
94.5	7.93	2.31	11.46	2.25	121.25	18.63	4.78	18.82	3.27
% Sorbed:	21.94	(±0.39)	MSE	0.053	% Sorbed:	28.93	(±0.95)	MSE	0.002

Table A.11 Toluene desorption data from fresh newsprint in methanogenic leachate after various aging times

	1 Week					6 Months			
	Data		Model			Data		Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.75	83.99	19.68	48.89	1.89	0.5				
2.5	18.50	1.79	23.44	2.88	1.5	36.70	3.77	35.84	2.47
4.25	11.32	4.80	15.47	3.19	3.5	18.98	1.37	20.17	3.76
7	10.06	5.73	11.91	3.32	6	14.54	5.48	14.97	4.53
23	9.21	5.58	10.99	3.33	10.5	14.15	5.24	13.52	4.87
46.75	8.81	5.35	10.90	3.31	23	13.69	4.90	13.35	4.89
75.5	8.72	5.34	10.81	3.28	47.5	13.33	4.83	13.24	4.84
96.25	8.71	5.32	10.75	3.26	71	13.11	4.80	13.15	4.81
120.25	8.71	5.32	10.69	3.24	95.5	12.98	4.71	13.06	4.78
					120.75	12.91	4.77	12.98	4.75
% Sorbed:	24.36	(±2.02)	MSE	0.169	% Sorbed:	24.34	(±3.37)	MSE	0.001

Table A.12 *o*-Xylene desorption data from fresh newsprint in DI water after various aging times

	1 Week					6 Months			
	Data		Model			Data		Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.25					0.5				
0.5	78.30	8.77	65.53	0.99	1	73.79	5.04	61.86	3.51
1	42.87	11.46	53.40	1.37	2	45.34	5.21	51.29	4.49
2	30.41	5.09	40.32	1.77	3	39.71	2.94	45.04	5.03
3.25	25.12	3.64	31.05	2.05	5.75	36.64	5.52	37.21	5.63
5.25	22.94	1.52	23.93	2.27	10.75	35.17	5.52	34.08	5.84
9.5	22.09	1.86	19.44	2.40	23	34.38	6.09	33.41	6.06
21.5	21.51	0.90	18.41	2.40	28.25	33.86	6.82	33.31	6.13
26	20.72	1.24	18.35	2.39	46.75	33.38	6.73	32.99	6.35
48.75	20.36	0.81	18.09	2.36	71.25	33.09	6.33	32.65	6.57
69.5	19.43	0.63	17.89	2.33	94.5	32.53	6.69	32.36	6.74
					121.5	31.02	6.87	32.07	6.90
% Sorbed:	44.06	(±1.20)	MSE	0.062	% Sorbed:	45.89	(±0.19)	MSE	0.021

Table A.13 Toluene desorption data from degraded newsprint in DI water after various aging times

1 Day			1 Week				
Data			Data			Model	
Time (hrs)	Average	S	Time (hrs)	Average	S	Average	S
0.25			0.25	92.61	1.92	65.25	0.43
0.5	79.76	0.86	0.5	71.36	16.45	54.35	0.84
0.75	52.13	2.98	0.75	44.18	10.51	46.42	0.99
1	44.57	3.46	1	32.30	6.25	40.31	1.09
2	31.59	12.29	1.75	28.22	5.99	29.82	1.27
3.5	28.00	9.80	3.5	21.73	2.39	21.00	1.37
5.5	24.55	5.97	7	19.29	4.67	18.22	1.36
8.75	20.20	1.06	10.5	18.09	5.74	17.77	1.34
19.5	17.90	0.08	23.25	16.50	5.31	16.87	1.27
24.5	17.34	0.04	31.25	15.55	5.47	16.44	1.24
33.75	15.77	1.16	48	14.43	5.12	15.71	1.18
44.75	14.99	1.60	71.5	13.69	4.81	14.89	1.12
69.75	12.52	3.77	95.75	13.18	4.73	14.20	1.07
95	10.86	5.35	119.5	12.52	4.79	13.62	1.02
118	10.19	5.71					
% Sorbed:	33.39	(±1.77)	% Sorbed:	33.79	(±0.85)	MSE	0.101

1 Month					6 Months				
Data			Model		Data			Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.5	82.56	18.05	55.43	1.74	0.5	88.76	12.46		
1	42.20	11.69	41.75	2.29	1	54.39	22.20	46.68	12.87
1.5	28.75	7.07	34.36	2.57	2	30.94	6.84	35.72	10.84
2.5	22.93	3.74	26.26	2.87	3	27.22	3.04	30.63	7.66
5	19.87	1.18	20.95	3.02	7	24.84	0.96	24.36	1.12
10.5	17.63	3.09	19.67	2.95	9.75	24.14	0.83	23.29	0.08
22.75	16.88	3.73	18.70	2.81	23	22.25	0.31	21.76	0.42
30	16.64	3.95	18.27	2.74	31	21.80	0.11	21.20	0.46
47.5	16.16	3.73	17.41	2.61	48	20.53	0.83	20.25	0.51
72.25	15.78	3.70	16.45	2.47	71.75	18.93	1.09	19.18	0.56
100.75	15.36	3.52	15.57	2.33	96.25	18.10	0.43	18.28	0.61
					120.5	17.31	0.48	17.52	0.65
% Sorbed:	38.20	(±3.69)	MSE	0.115	% Sorbed:	36.51	(±2.47)	MSE	0.016

Table A.13 (continued)

9 Months				
Data			Model	
Time (hrs)	Average	S	Average	S
0.5				
1.75	30.74	2.61	32.87	0.90
3	25.88	3.23	25.76	0.99
6.75	20.87	2.44	21.74	1.01
23.75	18.86	0.37	20.06	0.94
47	18.77	0.40	18.76	0.88
71.5	18.66	0.40	17.74	0.83
95	18.56	0.40	16.93	0.80
120	18.49	0.38	16.20	0.76
% Sorbed:	36.68	(±0.33)	MSE	0.002

Table A.14 Toluene desorption data from degraded newsprint in acidogenic leachate after various aging times

1 Week					6 Months				
Data			Model		Data			Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.25					0.5	86.86	1.43		
0.5	71.61	0.14	67.81	0.00	1	65.27	5.67	58.28	0.50
1	43.48	0.08	56.01	0.00	2	45.69	1.89	47.17	2.15
1.75	36.12	0.06	45.29	0.00	3.75	33.84	4.94	35.36	2.21
3.25	29.80	0.05	32.67	0.00	6.75	26.87	3.90	26.25	2.67
5.75	25.26	0.04	22.41	0.00	10.75	22.87	3.16	22.03	3.55
11.25	20.53	0.03	15.54	0.00	23.5	20.52	3.74	19.81	4.36
23.25	15.09	0.02	13.81	0.00	28.75	18.73	4.23	19.57	4.43
29.75	14.56	0.02	13.57	0.00	47.5	18.20	4.73	18.92	4.60
48.25	14.01	0.02	13.08	0.00	71.75	18.00	4.85	18.28	4.75
71.5	13.93	0.02	12.59	0.00	95	17.88	4.94	17.76	4.87
94.5	13.93	0.02	12.19	0.00	121.25	17.79	4.96	17.26	4.99
% Sorbed:	30.86	(±0.06)	MSE	0.030	% Sorbed:	31.36	(±2.45)	MSE	0.003

Table A.15 Toluene desorption data from degraded newsprint in methanogenic leachate after various aging times

	1 Week					6 Months			
	Data		Model			Data		Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.75	53.41	19.02	54.87	0.26	0.5				
2.5	17.45	5.79	31.51	0.39	2	38.72	6.83	37.25	6.90
4.25	15.72	5.45	23.56	0.43	3.5	25.53	5.54	27.93	5.59
7	15.27	5.41	19.46	0.44	10.25	21.69	2.55	19.75	0.97
23	14.70	5.48	17.08	0.42	23	17.83	2.84	18.52	1.21
46.75	14.42	5.63	15.85	0.39	47.25	17.02	2.85	17.50	2.12
75.5	14.21	5.62	14.78	0.36	70.75	16.53	2.96	16.78	2.80
96.25	14.09	5.63	14.15	0.34	94.75	16.24	3.06	16.18	3.35
120.25	14.04	5.62	13.51	0.33	118.75	16.13	3.09	15.68	3.80
% Sorbed:	35.60	(±1.03)	MSE	0.027	% Sorbed:	40.56	(±4.72)	MSE	0.002

Table A.16 o-Xylene desorption data from degraded newsprint in DI water after various aging times

	1 Week					6 Months			
	Data		Model			Data		Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.25					0.5	90.72	2.43	70.17	2.59
0.5	90.38		68.51		1	50.54	4.03	60.05	3.05
1	65.83	15.05	56.05	2.57	2	45.19	3.18	49.45	3.00
2	44.49	12.23	44.29	3.30	3	40.41	3.54	43.43	2.46
3.25	35.30	8.79	36.36	3.79	5.75	35.75	0.50	36.47	0.62
5.25	30.95	5.90	30.77	4.13	10.75	35.20	1.08	33.99	0.84
9.5	27.46	5.69	27.78	4.30	23	34.98	1.38	33.56	1.05
21.5	26.61	5.14	27.26	4.31	28.25	34.57	1.25	33.51	1.01
26	25.96	4.51	27.22	4.31	46.75	33.98	1.15	33.34	0.89
48.75	24.45	4.19	27.05	4.28	71.25	33.20	0.88	33.14	0.75
69.5	23.28	4.64	26.90	4.26	94.5	32.53	0.05	32.98	0.64
					121.5	32.15	0.50	32.80	0.53
% Sorbed:	56.69	(±1.49)	MSE	0.061	% Sorbed:	57.79	(±1.26)	MSE	0.055

Table A.17 Toluene desorption data from fresh office paper in DI water after various aging times

| 1 Day | | | 1 Week | | | | |
| Data | | | Data | | | Model | |
Time (hrs)	Average	S	Time (hrs)	Average	S	Average	S
0.25			0.25				
0.5			0.5	80.84	16.98	76.89	0.76
0.75			0.75	74.21	10.50	73.44	2.06
1			1	61.83	5.18	69.77	2.36
1.5			2	53.43	3.77	60.54	3.11
2	96.24		3.75	47.87	3.17	51.25	3.82
3	83.19		7.25	44.17	3.31	42.76	4.41
4	87.85	17.38	12.25	41.97	4.29	38.70	4.59
21.5	41.55	2.71	23.75	39.88	5.01	36.38	4.49
45	33.41	4.85	29	37.34	4.53	35.83	4.43
68.25	30.15	5.82	48.25	35.00	3.59	34.25	4.23
92.25	28.52	5.99	72.25	32.68	3.57	32.71	4.04
116.75	27.68	6.03	96.25	31.43	3.79	31.44	3.89
			120.5	30.61	3.90	30.33	3.75
% Sorbed:	17.69	(±0.25)	% Sorbed:	17.43	(±1.07)	MSE	0.033

| 1 Month | | | | | 6 Months | | | | |
| Data | | | Model | | Data | | | Model | |
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.5					0.5				
1	76.03	8.81	71.03	1.18	1	66.43		66.95	
2	56.73	1.06	62.19	1.55	2	63.30	9.83	63.19	7.94
3	50.49	1.48	56.44	1.79	3	57.48	7.32	57.67	8.17
5.5	45.29	2.12	48.17	2.10	5.5	50.06	4.45	49.76	7.06
22.75	40.91	3.14	38.89	2.25	10	44.55	4.65	43.82	4.08
46.5	37.91	3.27	36.64	2.13	23.5	39.63	1.51	39.07	0.83
72.25	36.62	3.51	34.86	2.02	30.25	36.95	1.26	38.17	0.61
95	36.21	3.70	33.58	1.95	56	35.35	1.03	35.97	0.62
118.75	36.06	3.67	32.41	1.88	71	34.43	0.45	34.98	0.67
					94.75	33.70	0.49	33.63	0.74
					117.25	33.47	0.52	32.52	0.79
% Sorbed:	17.23	(±3.17)	MSE	0.018	% Sorbed:	18.38	(±0.92)	MSE	0.001

Table A.17 (continued)

9 Months				
	Data		Model	
Time (hrs)	Average	S	Average	S
0.5				
1.5				
3	68.34	19.84	60.00	7.04
6.25	56.48	13.83	50.95	8.49
22.5	44.81	10.07	43.42	8.89
47.25	37.16	3.88	40.81	8.37
71	35.17	2.99	38.98	7.99
94.75	33.81	2.02	37.47	7.68
120.25	33.49	2.11	36.08	7.39
% Sorbed:	19.12	(±1.17)	MSE	0.031

Table A.18 Toluene desorption data from fresh office paper in acidogenic leachate after various aging times

1 Week					6 Months				
	Data		Model			Data		Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.25					0.5				
0.5	87.50		73.50		1.5	75.17	1.40	62.52	7.44
1	48.23	6.09	64.67	1.37	2.75	56.56	21.10	57.79	10.84
3	35.19	8.61	44.82	2.09	4.5	44.86	11.78	49.64	11.49
4.75	27.56	3.81	35.11	2.42	11.5	33.63	7.11	34.86	9.38
9.75	20.35	1.19	21.24	2.79	27.5	26.30	5.06	25.28	5.39
34.25	14.84	1.14	10.67	2.47	48.75	21.57	2.95	20.76	2.79
38.5	13.88	1.14	10.28	2.39	71.25	18.26	1.51	17.77	1.20
58	12.42	0.85	8.91	2.08	98.75	15.02	1.12	15.07	1.14
84.5	12.00	1.45	7.53	1.75	119	12.58	2.19	13.48	1.75
107.25	9.76	0.53	6.60	1.53					
% Sorbed:	17.85	(±1.15)	MSE	0.044	% Sorbed:	20.91	(±1.75)	MSE	0.022

Table A.19 Toluene desorption data from fresh office paper in methanogenic leachate after various aging times

| | 1 Week | | | | | 6 Months | | | |
| | Data | | Model | | | Data | | Model | |
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.5					0.5				
1	72.73	0.93	69.23	3.05	1	75.86	10.21	70.89	4.00
1.75	58.77	5.42	61.87	3.77	2	59.84	3.32	62.28	4.77
3	53.37	7.69	54.37	4.43	3	54.97	2.57	56.84	4.98
5	49.92	7.93	47.67	4.93	4.5	51.39	2.97	51.67	4.80
9	44.16	7.09	42.30	5.14	10	46.06	3.09	44.49	3.36
23.25	39.73	5.98	38.62	4.91	22.75	40.79	3.92	41.23	2.78
31	37.52	4.78	37.70	4.79	46.75	37.80	4.40	38.57	3.13
50.75	35.99	4.63	35.82	4.55	71	36.30	3.44	36.61	3.39
72	32.29	2.12	34.22	4.35	94.5	35.12	2.63	35.04	3.60
95.75	31.76	1.88	32.73	4.16	120	34.30	3.79	33.59	3.78
120	29.49	1.34	31.41	3.99					
% Sorbed:	17.43	(±1.73)	MSE	0.009	% Sorbed:	17.89	(±0.74)	MSE	0.006

Table A.20 *o*-Xylene desorption data from fresh office paper in DI water after various aging times

| | 1 Week | | | | | 6 Months | | | |
| | Data | | Model | | | Data | | Model | |
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.25					0.5				
0.5					1	89.72		85.25	
1	87.23		73.83		2	82.26	11.10	77.08	7.30
2	68.81	21.76	68.32	4.51	3.75	74.12	11.30	71.02	8.32
4.25	54.18	9.37	57.78	6.05	6.5	67.86	9.41	65.35	8.34
6.5	49.93	7.47	51.45	6.95	11	62.60	6.62	60.20	7.03
10.75	43.93	7.62	44.50	7.87	23	56.11	3.39	54.24	3.97
23.5	39.45	7.62	37.87	8.53	29	54.47	2.90	52.78	3.27
29.5	38.29	6.96	36.97	8.52	47	51.24	2.08	50.37	2.71
47.5	36.48	6.56	35.72	8.35	71.5	48.34	2.75	48.67	2.83
74	33.75	5.02	34.60	8.09	95.5	47.93	2.87	47.47	3.00
95.75	32.36	6.99	33.85	7.91	118.75	46.60	3.09	46.49	3.14
% Sorbed:	25.86	(±2.59)	MSE	0.028	% Sorbed:	36.17	(±1.83)	MSE	0.002

Table A.21 Toluene desorption data from degraded office paper in DI water after various aging times

1 Day			1 Week				
Data			Data			Model	
Time (hrs)	Average	S	Time (hrs)	Average	S	Average	S
0.25			0.5				
0.5	78.37		1	60.76	3.04	61.61	1.13
0.75	76.98	11.73	2.5	46.13	4.25	47.21	1.45
1	68.15	5.23	5.75	39.20	2.20	36.52	1.53
1.5	57.57	2.11	9.25	34.42	1.31	33.16	1.46
2	52.01	4.45	24.75	27.29	2.02	28.66	1.26
3	45.98	5.95	47.5	22.77	2.29	24.90	1.10
4	42.12	6.09	71.5	22.11	0.83	21.92	1.34
21.5	22.66	6.34	95.5	20.84		20.53	
45	15.45	5.46	122.25	19.69		18.38	
68.25	12.09	4.77					
92.25	10.16	4.07					
116.75	8.92	3.65					
% Sorbed:	22.67	(±1.63)	% Sorbed:	29.57	(±0.90)	MSE	0.004

1 Month					6 Months				
Data			Model		Data			Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.5	89.61	7.99	73.43	1.15	0.5	92.26		79.70	
1	56.23	3.88	64.11	1.55	1	68.39	1.90	70.06	3.15
2	48.37	5.23	54.05	1.96	2	58.52	1.87	61.59	3.20
3	44.62	5.33	48.09	2.18	3	55.63	1.87	56.49	2.74
5.5	40.98	2.51	40.87	2.37	5.5	51.04	1.29	49.95	1.19
22.75	34.42	1.51	32.67	2.12	10	46.58	0.27	45.48	0.30
46.5	29.03	0.87	28.13	1.82	23.5	41.05	0.50	40.15	0.72
72.25	26.18	0.61	24.67	1.60	30.25	36.82	0.95	38.31	0.70
95	23.78	0.63	22.27	1.44	56	32.75	0.21	33.03	0.64
118.75	21.79	0.60	20.17	1.31	71	28.93	0.23	30.66	0.61
					94.75	27.60	0.74	27.54	0.57
					117.25	26.85	0.91	25.06	0.54
% Sorbed:	27.47	(±0.86)	MSE	0.044	% Sorbed:	26.04	(±0.83)	MSE	0.012

9 Months				
Data			Model	
Time (hrs)	Average	S	Average	S
0.5				
1.5	68.71	7.87	65.59	0.74
3	62.71	7.23	56.85	0.90
6.25	56.10	6.31	49.35	0.98
22.5	43.73	6.85	41.27	0.87
47.25	33.06	0.89	35.32	0.75
71	29.84	0.29	31.29	0.66
94.75	27.80	0.23	28.10	0.59
120.25	26.18	0.78	25.27	0.53
% Sorbed:	26.64	(±0.43)	MSE	0.003

Table A.22 Toluene desorption data from degraded office paper in acidogenic leachate after various aging times

1 Week					6 Months				
Data			Model		Data			Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.25					0.5				
0.5					1.5	76.65	15.51	71.32	5.88
1	69.99		70.07		2.75	61.16	4.30	63.93	6.65
3	53.31	6.42	55.13	1.92	4.5	56.16	1.98	57.64	6.75
4.75	48.61	5.17	47.56	2.22	11.5	48.62	2.66	47.75	4.42
9.75	41.55	4.50	37.21	2.58	27.5	42.30	2.82	42.39	1.96
34.25	30.47	3.11	29.42	2.53	48.75	38.83	2.22	39.36	2.30
38.5	28.91	4.11	28.99	2.49	71.25	35.84	3.61	37.06	2.98
58	25.15	3.74	27.37	2.35	98.75	34.92	4.09	34.79	3.73
84.5	24.26	2.91	25.63	2.20	119	34.48	4.25	33.37	4.22
107.25	22.40	1.65	24.38	2.10					
% Sorbed:	24.48	(±1.86)	MSE	0.006	% Sorbed:	27.30	(±2.62)	MSE	0.013

Table A.23 Toluene desorption data from degraded office paper in methanogenic leachate after various aging times

	1 Week					6 Months			
	Data		Model			Data		Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.5					0.5				
1	93.24				1	68.85	7.08	67.93	4.34
1.75	66.42	16.01	49.59		2	57.56	2.40	59.41	4.57
3	47.70	4.79	41.59		3	54.76	2.83	54.57	4.14
5	38.39	2.52	35.92		4.5	52.23	3.16	50.50	3.30
9	32.18	2.03	32.43		10	45.97	3.21	45.14	2.21
23.25	26.31	0.25	28.63		22.75	39.75	3.75	40.59	3.11
31	24.77	1.04	27.22		46.75	33.29	4.83	35.35	4.39
50.75	22.59	0.99	24.40		71	30.39	4.97	31.60	5.21
72	20.97	1.45	22.07		94.5	28.95	5.27	28.73	5.78
95.75	20.01	2.10	19.96		120	28.36	6.10	26.14	6.24
120	19.55	2.31	18.17						
% Sorbed:	25.04	(±1.82)	MSE	0.006	% Sorbed:	27.15	(±3.27)	MSE	0.003

Table A.24 *o*-Xylene desorption data from degraded office paper in DI water after various aging times

	1 Week					6 Months			
	Data		Model			Data		Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.5					0.5				
1	78.16	13.63	77.11	1.86	1				
1.5	65.08	8.48	72.92	2.23	2	90.28	8.21	76.31	2.63
2.75	55.83	7.50	65.28	2.87	3.75	71.48	12.56	71.66	3.75
4.5	49.68	5.21	58.24	3.45	6.5	59.53	3.00	65.68	3.91
9.25	46.33	4.88	47.64	4.26	11	58.26	2.75	60.08	3.61
21	41.82	5.63	39.01	4.74	23	54.40	3.54	53.86	3.18
27.75	39.57	5.39	37.43	4.74	29	53.13	3.08	52.42	3.17
67.75	34.65	7.22	34.09	4.41	47	50.40	2.67	49.89	3.08
					71.5	48.00	3.25	47.70	2.93
					95.5	46.24	2.48	45.99	2.86
					118.75	44.22	2.95	44.56	2.85
% Sorbed:	41.95	(±1.22)	MSE	0.031	% Sorbed:	42.65	(±6.45)	MSE	0.025

Table A.25 Toluene desorption data from degraded rabbit food in DI water after various
aging times

1 Day			1 Week				
Data			Data			Model	
Time (hrs)	Average	S	Time (hrs)	Average	S	Average	S
0.5	69.31	24.92	0.25	42.02	5.69	56.79	2.64
1	32.81	12.89	0.5	29.27	11.19	43.62	3.49
2.25	13.37	0.81	1	23.68	11.62	28.62	4.46
5	11.91	2.48	2.5	20.81	9.69	16.06	5.27
23.25	11.84	2.55	4.5	19.09	8.34	14.13	5.39
47.75	11.82	2.54	9.25	15.97	5.07	13.94	5.39
71.75	11.81	2.52	23	13.95	5.32	13.85	5.35
95.75	11.80	2.53	30.75	13.09	4.23	13.80	5.33
119.75	11.79	2.54	48	12.27	3.67	13.71	5.29
			70.75	11.82	3.40	13.60	5.25
			95.25	11.58	3.22	13.50	5.21
			118.75	11.46	3.13	13.41	5.18
% Sorbed:	62.54	(±0.65)	% Sorbed:	61.35	(±0.26)	MSE	0.043

1 Month					6 Months				
Data			Model		Data			Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.5	67.94	6.62			0.5	50.61	5.66	48.63	2.19
1	39.94	14.64	30.48	2.74	1	33.87	1.14	35.03	1.43
2	22.14	10.57	20.20	3.16	2	24.30	1.83	25.35	0.65
4.25	16.52	3.24	16.44	3.31	3	22.11	2.33	22.51	1.98
6.25	14.62	0.80	16.23	3.32	5.5	21.73	2.39	21.33	2.84
9.25	14.57	0.81	16.19	3.31	9.25	21.60	2.39	21.22	2.87
23.5	14.52	0.81	16.08	3.29	23.25	21.31	2.44	21.08	2.72
48	14.47	0.80	15.92	3.26	30.75	21.21	2.43	21.01	2.65
71.5	14.46	0.81	15.79	3.23	47.25	20.93	2.35	20.88	2.52
95.75	14.45	0.81	15.67	3.21	71.25	20.68	2.34	20.72	2.36
119.75	14.43	0.81	15.57	3.18	94.75	20.50	2.33	20.59	2.24
					119.75	20.39	2.31	20.46	2.12
% Sorbed:	62.32	(±0.39)	MSE	0.023	% Sorbed:	60.95	(±1.7)	MSE	0.002

Table A.25 (continued)

9 Months				
	Data		Model	
Time (hrs)	Average	S	Average	S
0.5	78.68	25.31		
1	41.31	1.34	35.77	4.31
2	28.50	10.74	26.29	4.97
4.25	24.86	9.21	22.82	5.20
6.25	21.04	4.12	22.61	5.21
9.25	21.02	4.10	22.56	5.20
23.5	20.90	4.09	22.41	5.17
48	20.89	4.08	22.19	5.12
71.5	20.87	4.09	22.01	5.07
95.75	20.87	4.09	21.85	5.04
119.75	20.87	4.09	21.70	5.00
% Sorbed:	61.26	(±1.57)	MSE	0.008

Table A.26 Toluene desorption data from degraded rabbit food in acidogenic leachate after various aging times

1 Week					6 Months				
	Data		Model			Data		Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.25	82.93				0.5	51.12	10.44	52.01	8.68
0.5	75.06	17.52	50.96	0.04	1.25	36.20	7.81	34.08	9.28
1	49.79	9.23	36.52	0.05	2.25	23.05	6.71	24.75	7.19
2	25.59	2.46	24.43	0.06	4	20.00	4.44	19.71	4.00
4.25	18.20	7.02	17.94	0.07	6	18.62	2.90	18.44	2.65
6.5	17.84	7.10	17.21	0.07	10.25	18.19	2.34	18.06	2.15
10.75	17.70	7.08	17.09	0.07	22.75	17.78	1.85	17.95	2.03
23.5	17.57	7.07	17.00	0.07	47	17.67	1.71	17.80	1.89
29.5	17.51	7.06	16.97	0.07	70.5	17.61	1.73	17.68	1.79
47.5	17.47	7.08	16.86	0.07	95.25	17.60	1.73	17.57	1.69
74	17.42	7.07	16.73	0.07	121.25	17.59	1.74	17.47	1.61
95.75	17.39	7.08	16.63	0.07					
% Sorbed:	62.59	(±0.90)	MSE	0.170	% Sorbed:	61.78	(±1.88)	MSE	0.001

Table A.27 Toluene desorption data from degraded rabbit food in methanogenic leachate after various aging times

1 Week					6 Months				
Data			Model		Data			Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.5	58.64		45.72		0.5	40.13	2.34	40.62	2.36
1	51.49	17.70	30.97	3.17	1.25	24.94	0.22	24.37	0.71
1.5	36.03	7.69	26.28	3.39	2.25	20.08	0.02	19.54	0.96
2.75	22.55	4.93	23.20	3.53	4	18.38	1.45	18.46	1.62
4.5	20.26	5.79	22.79	3.54	6	18.02	1.77	18.36	1.64
9.25	19.54	4.87	22.64	3.52	10.25	17.98	1.80	18.26	1.58
21	18.51	3.51	22.36	3.47	22.75	17.95	1.81	18.03	1.45
27.75	18.49	3.49	22.23	3.45	47	16.64		16.80	
67.75	18.17	3.60	21.61	3.35	70.5	16.61		16.63	
					95.25	16.59		16.48	
					121.25	16.55		16.34	
% Sorbed:	64.16	(±0.39)	MSE	0.075	% Sorbed:	61.58	(±2.97)	MSE	0.0002

Table A.28 *o*-Xylene desorption data from degraded rabbit food in DI water after various aging times

1 Week					6 Months				
Data			Model		Data			Model	
Time (hrs)	Average	S	Average	S	Time (hrs)	Average	S	Average	S
0.25	88.36	3.33	67.34	0.20	0.5	61.12	4.21	59.84	1.39
0.5	69.86	3.44	56.81	0.27	1	47.74	0.07	47.72	1.77
1	57.04	3.61	43.71	0.35	2	38.40	1.25	37.01	2.12
1.5	41.02	8.37	36.71	0.40	3	33.54	1.68	32.56	2.36
2.75	29.47	9.34	28.18	0.46	5.5	30.98	3.85	29.69	2.67
5	25.73	3.88	24.50	0.48	9.25	29.97	3.98	29.28	2.79
11.5	24.22	4.08	23.82	0.48	23.25	29.74	3.98	29.07	2.94
23	22.73	3.75	23.68	0.48	30.75	29.71	4.01	28.98	3.01
32.25	21.98	3.54	23.57	0.48	47.25	29.59	4.01	28.80	3.14
46	20.89	3.28	23.43	0.47	71.25	29.54	4.00	28.58	3.29
79.25	19.79	2.24	23.14	0.47	94.75	29.51	3.97	28.40	3.42
					119.75	29.47	3.97	28.22	3.54
% Sorbed:	79.50	(±0.81)	MSE	0.074	% Sorbed:	76.65	(±1.84)	MSE	0.001

B. Desorption Rate Data and Models
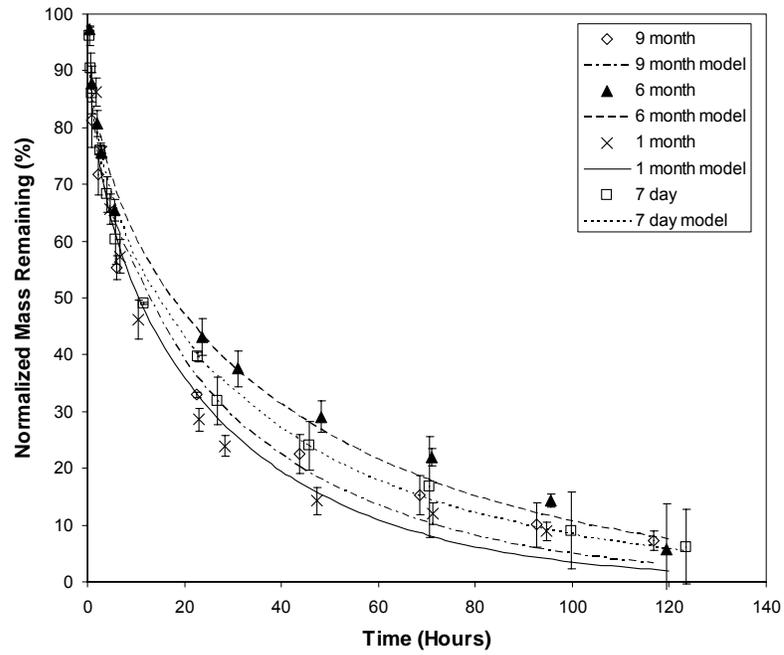
Figure B-1: Toluene desorption rate from HDPE in DI water over several aging times
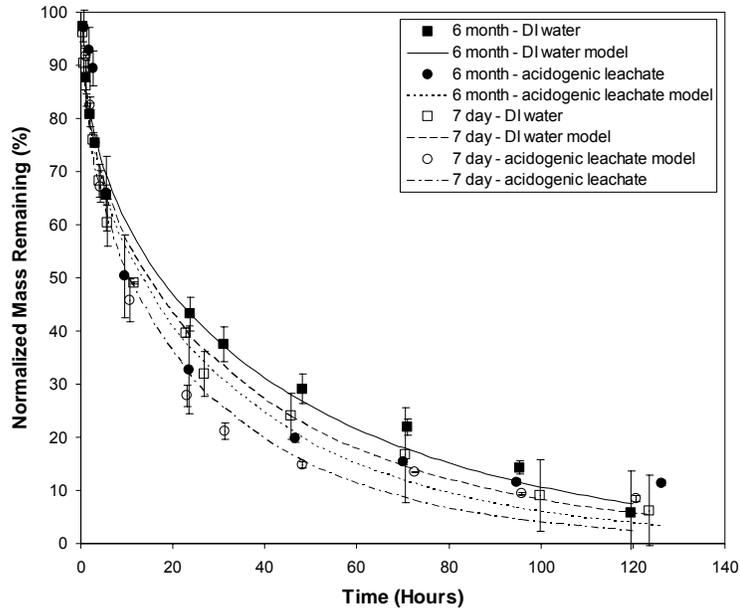
Figure B-2: Toluene desorption rate from HDPE in DI water and acidogenic leachate over several aging times
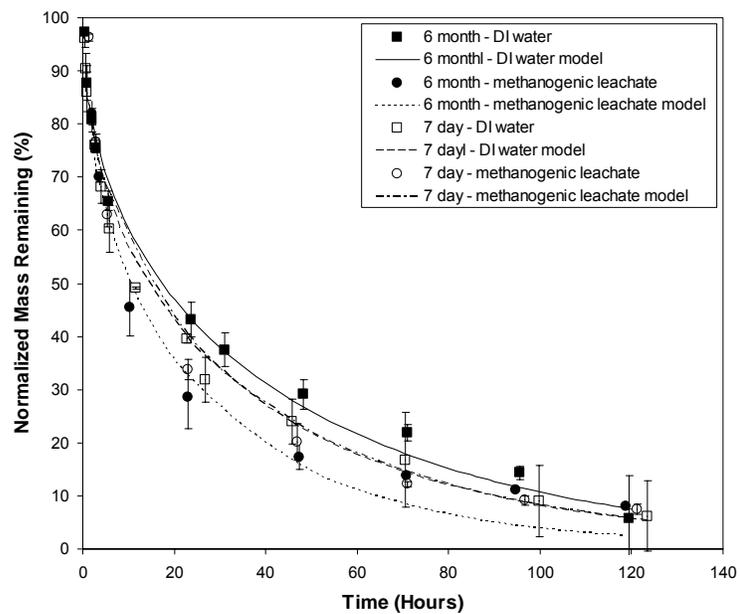
Figure B-3: Toluene desorption rate from HDPE in DI water and methanogenic leachate over several aging times
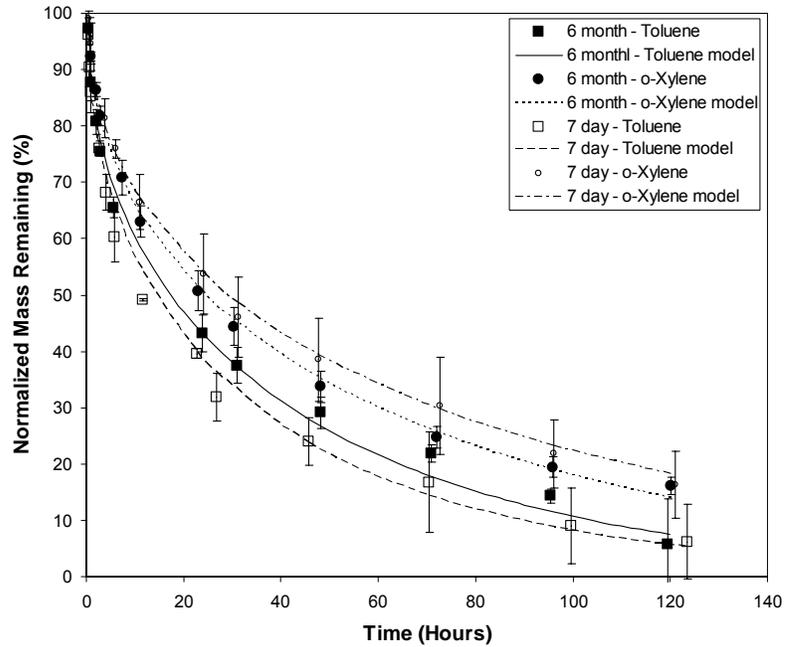
Figure B-4: Toluene and *o*-xylene desorption rate from HDPE in DI water over several aging times
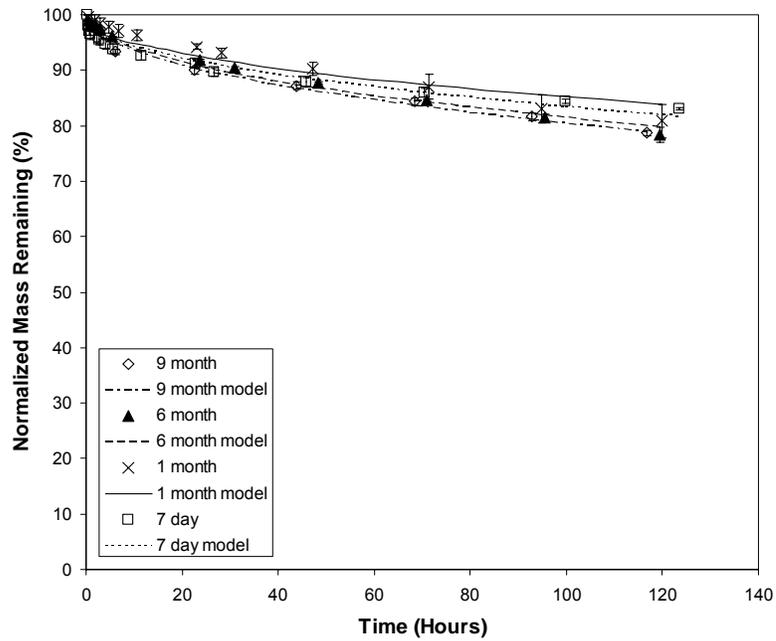
Figure B-5: Toluene desorption rate from PVC in DI water over several aging times
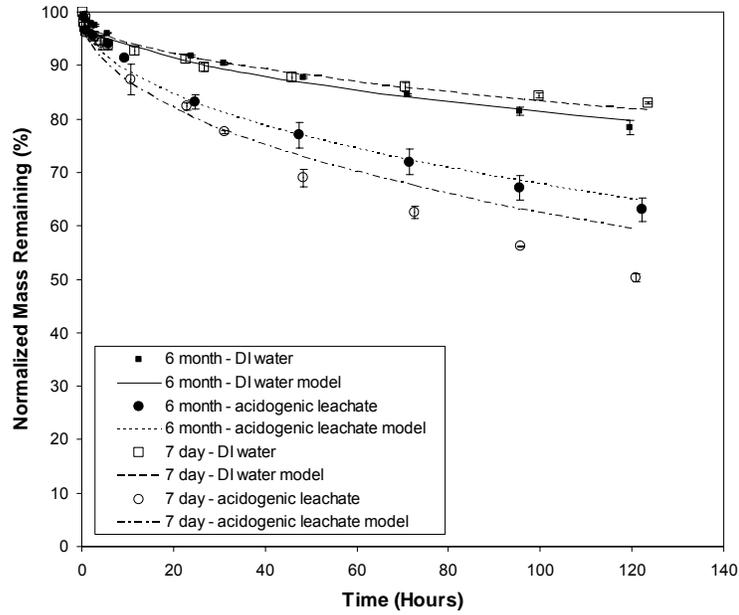
Figure B-6: Toluene desorption rate from PVC in DI water and acidogenic leachate over several aging times
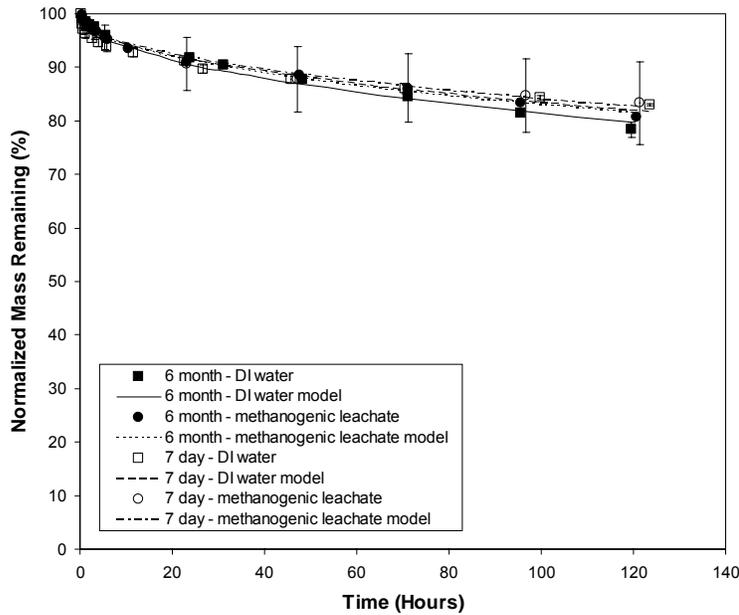
Figure B-7: Toluene desorption rate from PVC in DI water and methanogenic leachate over several aging times
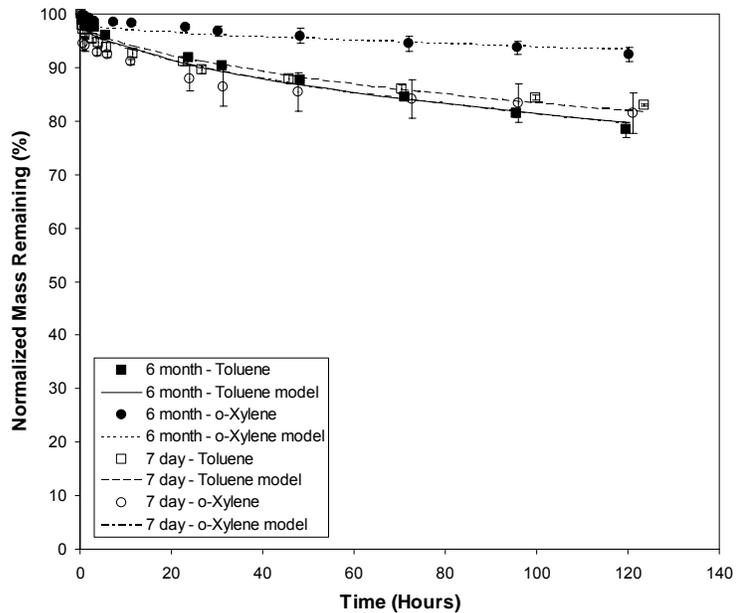
Figure B-8: Toluene and *o*-xylene desorption rate from PVC in DI water over several aging times
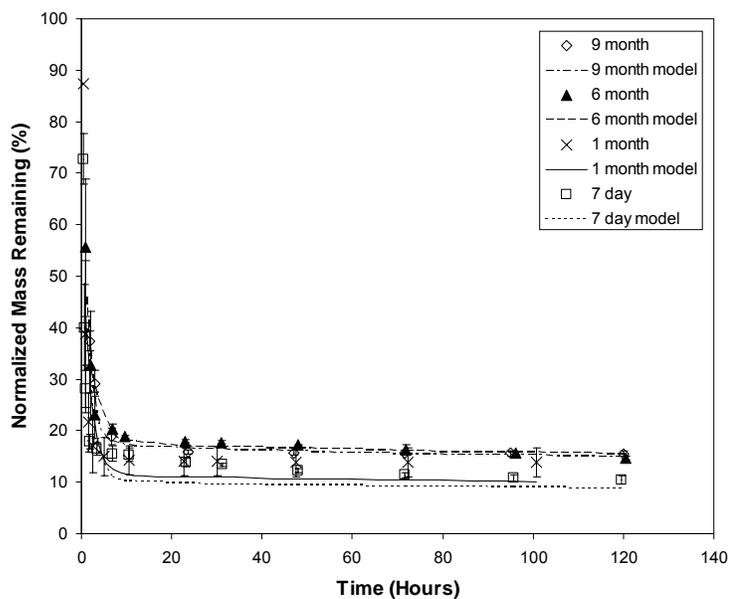
Figure B-9: Toluene desorption rate from fresh newsprint in DI water over several aging times
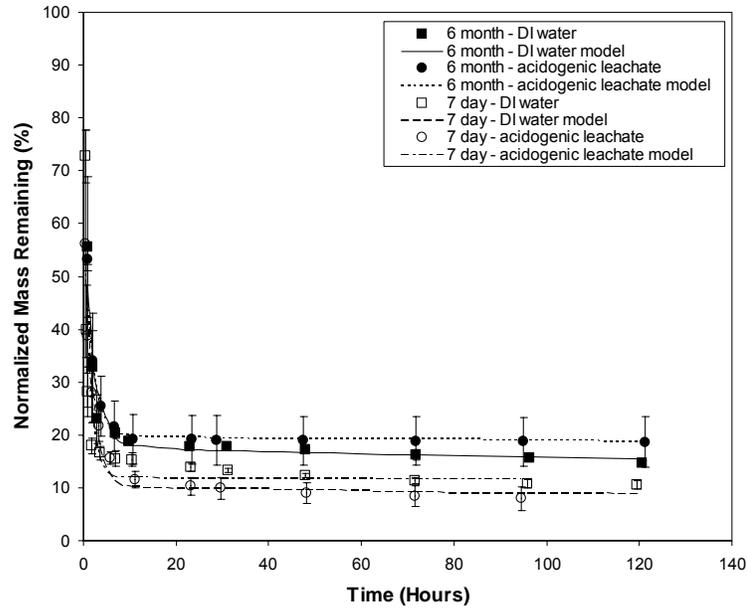
Figure B-10: Toluene desorption rate from fresh newsprint in DI water and acidogenic leachate over several aging times
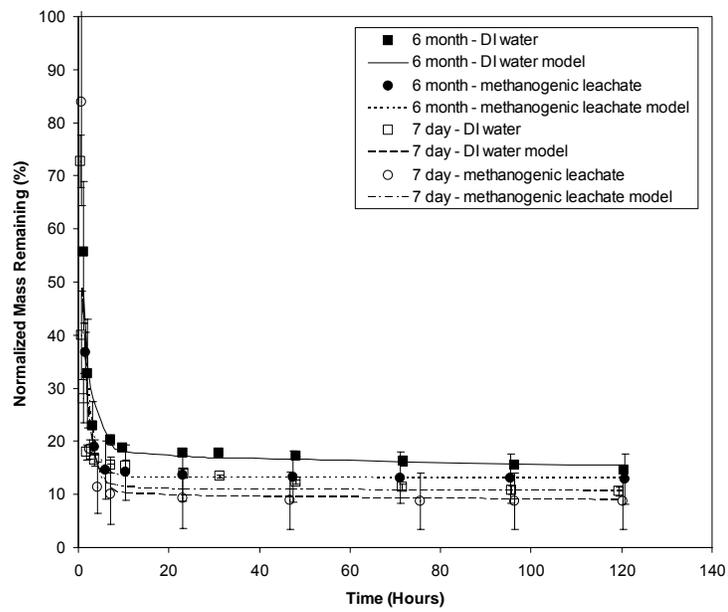
Figure B-11: Toluene desorption rate from fresh newsprint in DI water and methanogenic leachate over several aging times
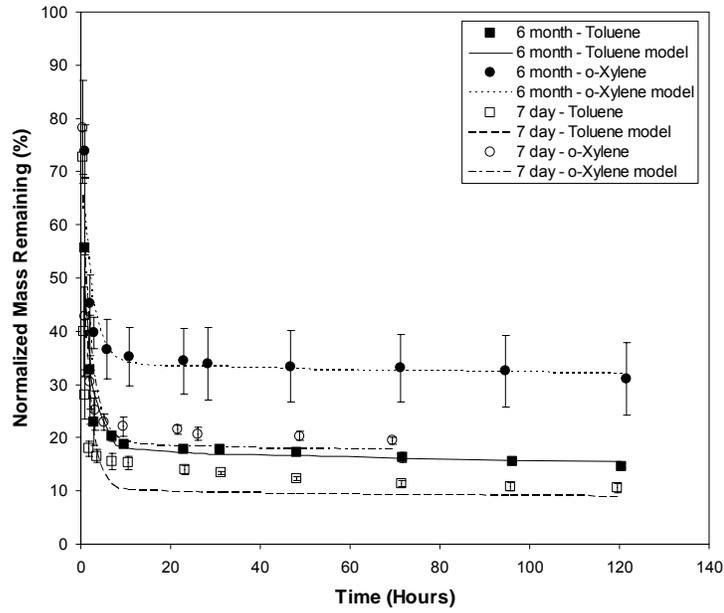
Figure B-12: Toluene and *o*-xylene desorption rate from fresh newsprint in DI water over several aging times
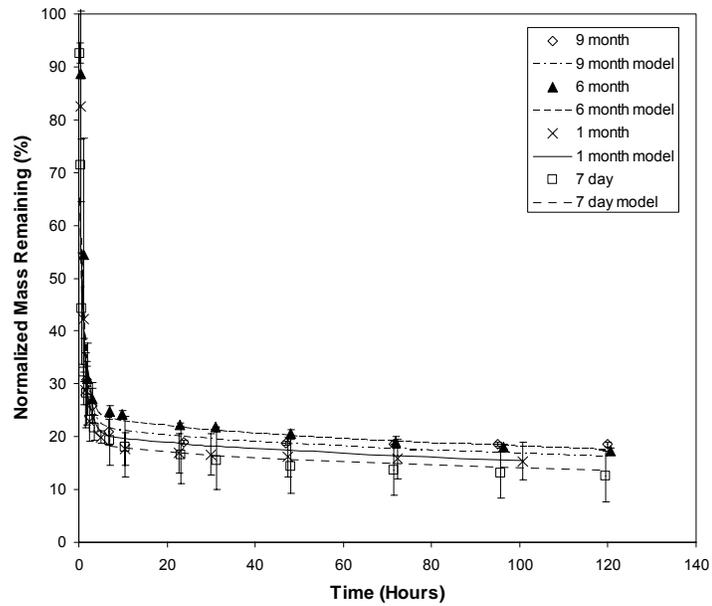
Figure B-13: Toluene desorption rate from degraded newsprint in DI water over several aging times
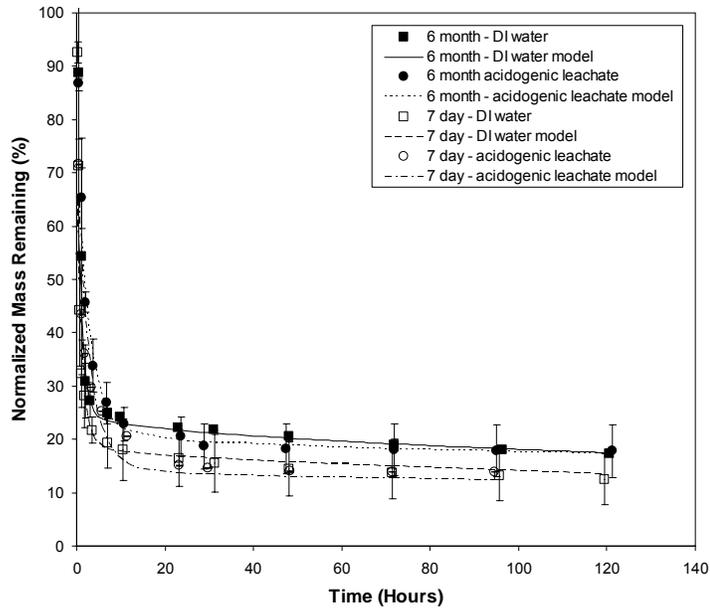
Figure B-14: Toluene desorption rate from degraded newsprint in DI water and acidogenic leachate over several aging times
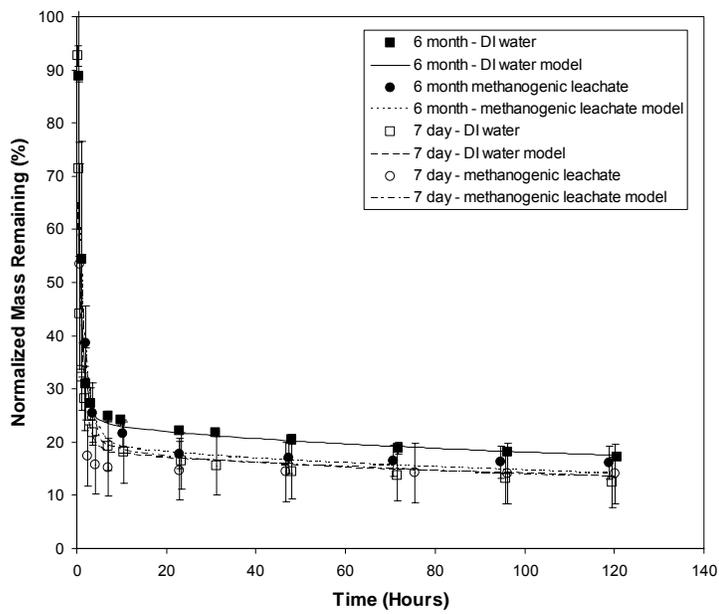

Figure B-15: Toluene desorption rate from degraded newsprint in DI water and methanogenic leachate over several aging times
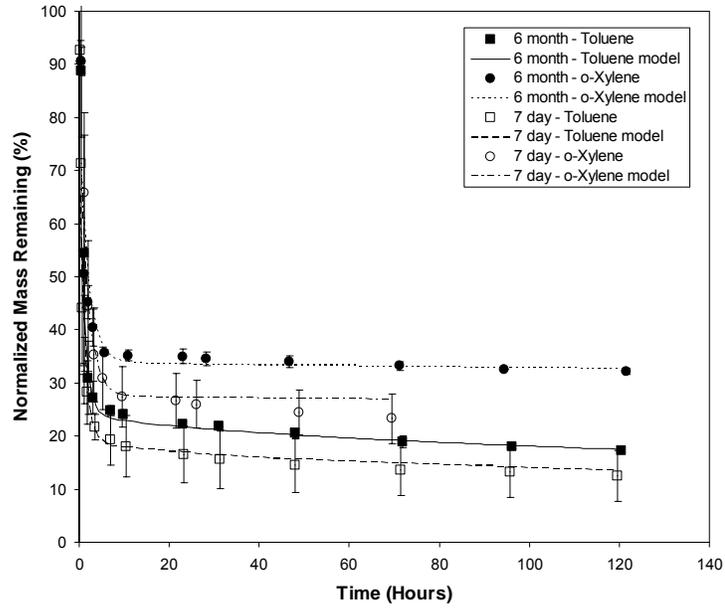
Figure B-16: Toluene and *o*-xylene desorption rate from degraded newsprint in DI water over several aging times
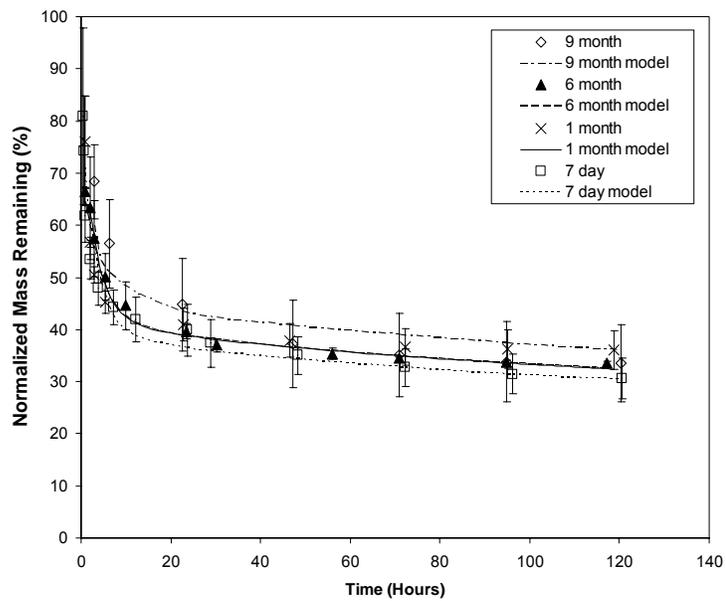
Figure B-17: Toluene desorption rate from fresh office paper in DI water over several aging times

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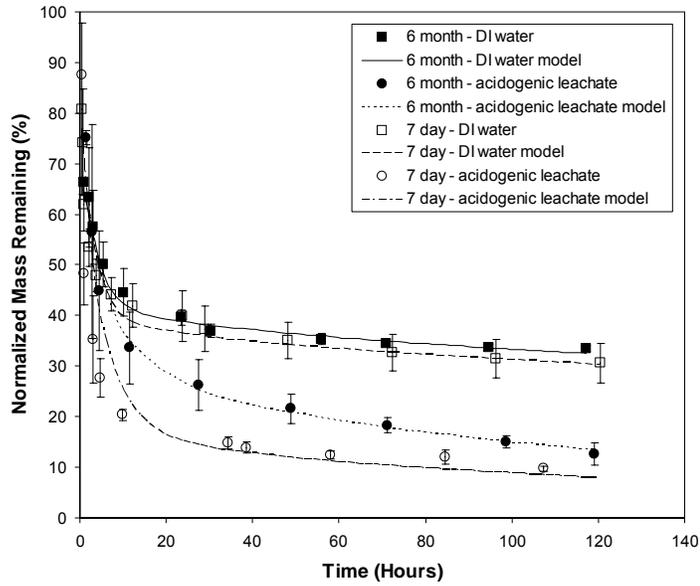
Figure B-18: Toluene desorption rate from fresh office paper in DI water and acidogenic leachate over several aging times
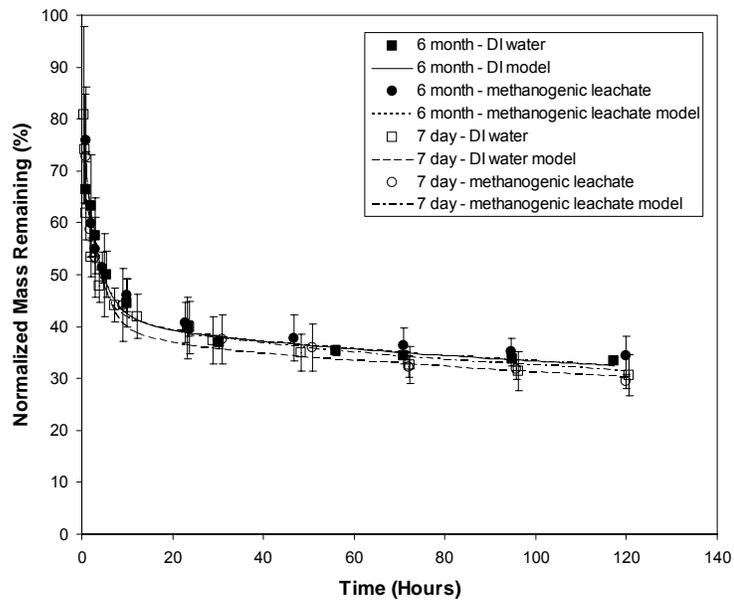
Figure B-19: Toluene desorption rate from fresh office paper in DI water and methanogenic leachate over several aging times
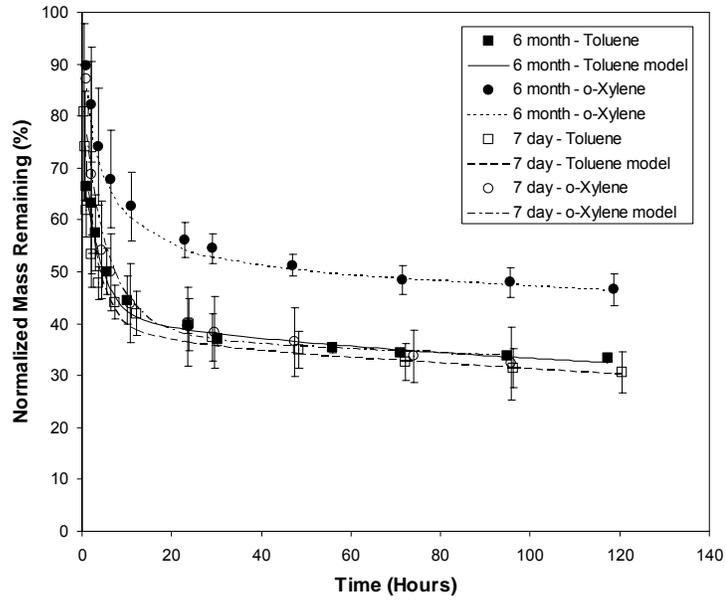
Figure B-20: Toluene and *o*-xylene desorption rate from fresh office paper in DI water over several aging times
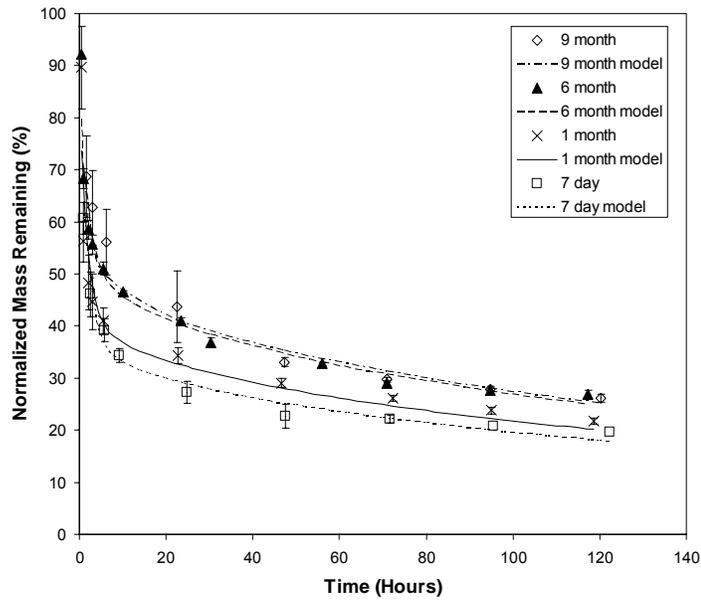
Figure B-21: Toluene desorption rate from degraded office paper in DI water over several aging times
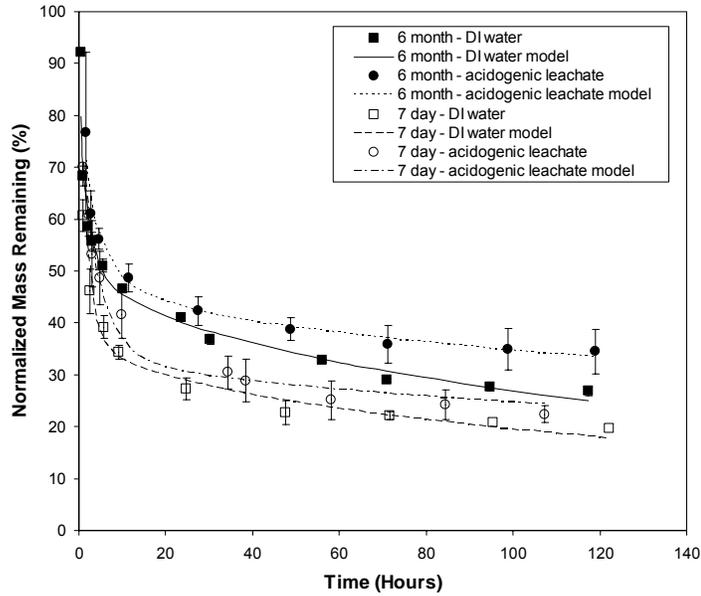
Figure B-22: Toluene desorption rate from degraded office paper in DI water and acidogenic leachate over several aging times
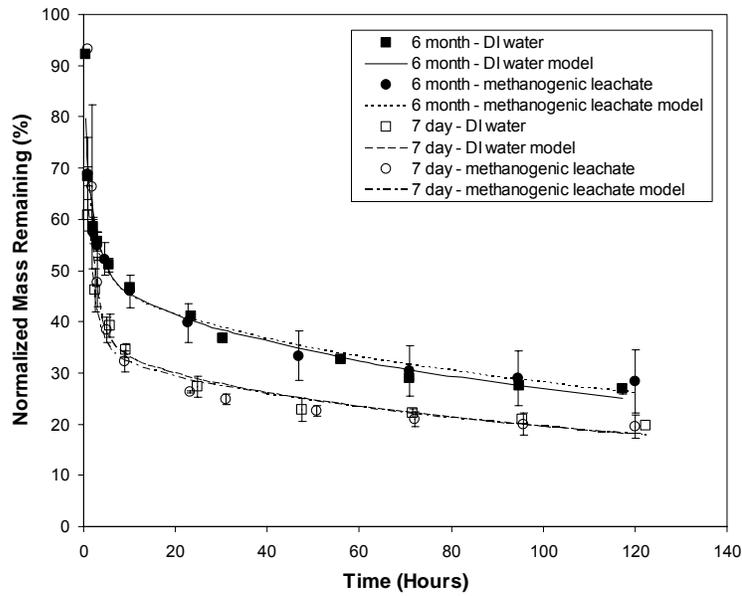

Figure B-23: Toluene desorption rate from degraded office paper in DI water and methanogenic leachate over several aging times
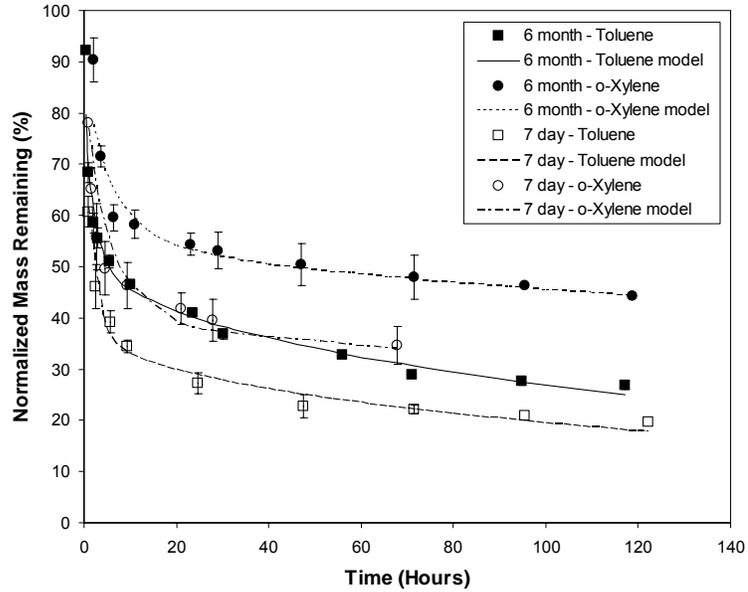
Figure B-24: Toluene and *o*-xylene desorption rate from degraded office paper in DI water over several aging times
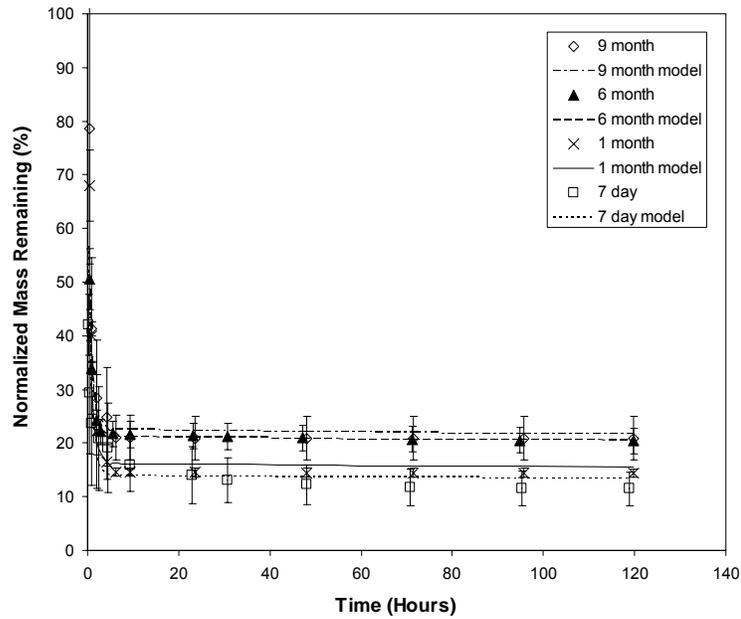
Figure B-25: Toluene desorption rate from degraded rabbit food in DI water over several aging times
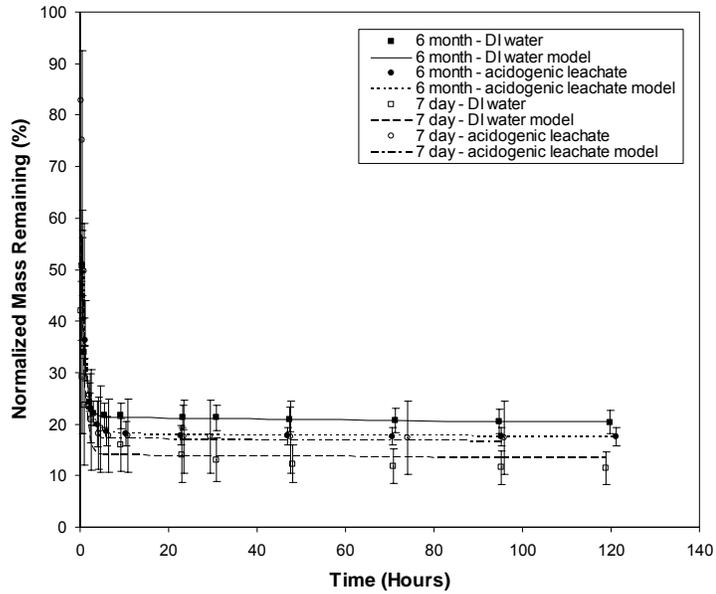
Figure B-26: Toluene desorption rate from degraded rabbit food in DI water and acidogenic leachate over several aging times
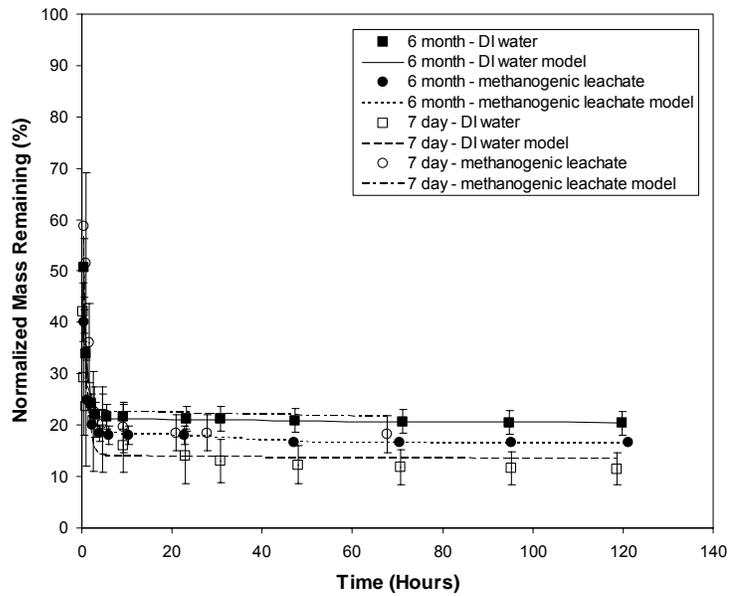
Figure B-27: Toluene desorption rate from degraded rabbit food in DI water and methanogenic leachate over several aging times

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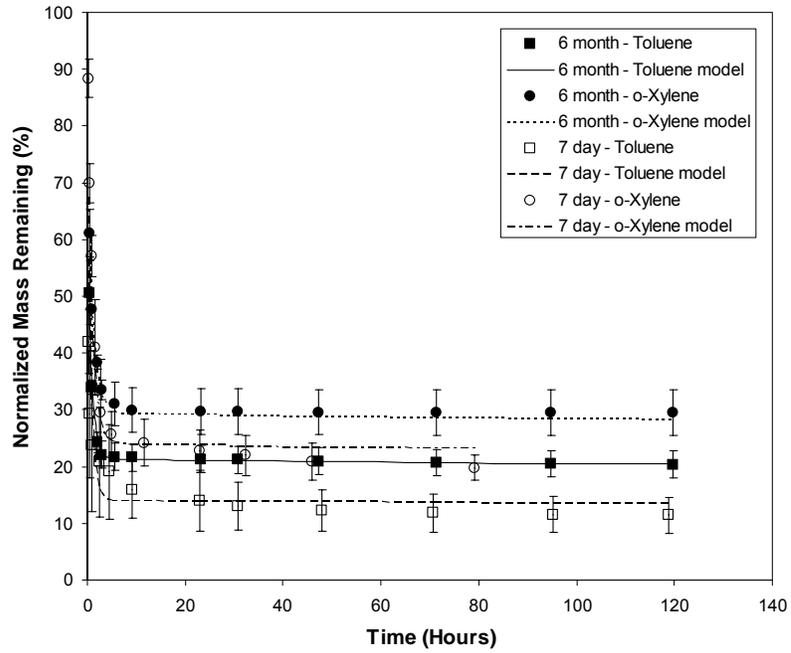
Figure B-28: Toluene and *o*-xylene desorption rate from degraded rabbit food in DI water over several aging times

C. Experimental Calculations

What follows is an example of how values were determined for this study. This particular examples is HDPE aged for 9 months in ultrapure water with toluene.

Discrepancies may appear in the following calculations due to rounding.

- Basic Parameters:

These values are known about the contaminant (for this example, contaminant = toluene):

Specific activity = 2.8 μCi/ μmol

Molecular weight = 92.14 g/mol

- How was the stock concentration assessed?

The concentration of the stock solution was calculated by spiking 20 μL of stock solution directly into scintillation cocktail. This produced an average value of 1,152,834 dpm with a standard deviation of 7,707 dpm after five replications. This average can then be converted into a concentration as follows:

$$\frac{1,152,834 dpm}{20 \mu L} * \frac{10^6 \mu L}{L} * \frac{\mu Ci}{2.22 * 10^6 dpm} * \frac{\mu mol}{2.8 \mu Ci} * \frac{92.14 \mu g}{\mu mol} = 854,425 \frac{\mu g}{L}$$

- How was impurity found?

20μL of stock solution was spiked into a solution containing 19.3 mL amended DI water and 0.6 mL of sodium azide and allowed to equilibrate after flame-sealing. When the solution was cracked open, an initial sample was withdrawn to check reproducibility of the spike. The sample was then sparged for 24 hours. After sparging, another measurement of the liquid phase was taken. This last sample represents the impurity. Five replications were performed. An example calculation is shown below:

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average final liquid phase measurement: 493 dpm/0.5mL ± 15.5 dpm/0.5mL

$$\frac{493dpm}{0.5mL}*20mL = 19{,}713dpm \qquad \%impurity = \frac{19{,}713dpm}{1{,}152{,}834dpm}*100\% = 1.71\%$$

- How was the percent lost due to cracking determined?

20μL of stock solution was spiked into a solution containing 19.3 mL amended DI water and 0.6 mL of sodium azide and allowed to equilibrate after flame-sealing. The sample was then cracked open and exposed to air for 30 seconds. Immediately after cracking, a liquid phase sample was taken. The samples were then capped and equilibrated for 30 minutes. A liquid phase sample was then taken after those 30 minutes had elapsed. Ten replications were performed.

Initial liquid phase average: 14,164 dpm/0.5mL ± 84 dpm/0.5mL
Final liquid phase average: 13,523 dpm/0.5mL ± 70 dpm/0.5mL

$$\%escaping = 100\% - \frac{13{,}523dpm/0.5mL}{14{,}164dpm/0.5mL}*100\% = 4.5\%$$

- How was % escaping into headspace (Henry's Law) determined?

20μL of stock solution was spiked into a solution containing 19.3 mL amended DI water and 0.6 mL of sodium azide and allowed to equilibrate after flame-sealing. The sample was cracked open and an initial liquid phase concentration was found. Using this information and the Henry's Law constant for toluene, the concentration in the headspace can be determined. Ten replications were performed.

Known Parameters:

Henry's Law constant = 0.66 kPa-m^3/mol @ 20°C (Solubility Data Series 1988)

Volume of headspace = 8mL

Volume of liquid = 20mL

$C_{liquid\ measured}$ = 28,328 dpm/0.5mL ± 1327 dpm/1.0mL

$$C_{sp\,arg\,able} = \frac{28,328\,\text{dpm}}{0.5\text{mL}} * \frac{\mu Ci}{2.22*10^6\,dpm} * \frac{\mu mol}{2.8\,\mu Ci} * = 0.00911 \mu mol\,/\,mL$$

$$moles_{(liquid)} = \frac{0.00911 \mu mol}{mL} * 20mL = 0.18 \mu mol$$

$$C_{(gas)} = \frac{\dfrac{0.66kPa - m^3}{mol} * \dfrac{0.00911 \mu mol}{mL} * \dfrac{1000\,Pa}{kPa}}{\dfrac{8.314m^3 - Pa}{mol - K} * 293K} = 0.0025 \mu mol\,/\,mL$$

$$moles_{(gas)} = \frac{0.0025 \mu mol}{mL} * 8mL = 0.02 \mu mol$$

$$\%\,in\,vapor = 0.02\,/\,0.18 * 100 = 10.83\%$$

	A	B	C	D	E	F	G	H	I	J	K
1	TEST PARAMETERS				**9 Monhts HDPE in DI Water**						
2											
3		Solid Sample Mass:			1 g		Volume Spiked:			20 µL	
4		Initial Sample Liquid Volume:			20 mL						
5		Amount of Sample Withdraw:			1 mL		Cocktail Trap Volume:			18 mL	
6		Final Sample Liquid Volume:			18 mL						
7		Initial Headspace Volume:			8 mL		Total Sample Bottle Volume:			28 mL	
8		Final headspace Volume:			10 mL		Cocktail Sample Withdraw:			0.5 mL	
9											
10	INHERIENT COMPOUND DATA										
11		Volatile Organic Compound Used:			Toluene 10X stock						
12											
13		Percent Impurity:			1.71 %						
14		Purity:			0.98						
15		Percent Henry's:			10.83 %						
16		Specific Activity:			2.8 µCi / µmol						
17		Molecular Weight:			92.14						
18		Concentration:			854,425 µg/L		Total Mass (µg):		17.09		
19		Percent Lost Due to Cracking:			4.5 %		Impurity (dpm):		19,713		
20								Impurity Mass (µg):	0.29		

	A	B	C	D	E	F	G	H	I
			dpm/1.0mL	dpm tot liquid	dpm tot liquid - impurity	dpm tot (spragable)	Tot Mass (µg) (l +g)	conc. (µg/L)	corrected conc. (µg/L)
21	BLANK								
22			52,578	1,051,560	1,031,847	1,143,596	17.24	779	766

INITIAL LIQUID PHASE DATA (row 24) — **INITIAL SOLID PHASE DATA**

		dpm/1.0mL	conc. (µg/L)	Total spargable liquid dpm	dpm in headspace	Total Spargable dpm		Tot dpm	% Sorbed
27	before samples:	13,297	197	246,232	26,667	260,618		882,978	77.21
28	after samples:	13,297		232,934	25,227	246,544			

SPARGING DATA (row 29)

		Sparged Counts (dpm/.5mL)			Sparged Counts (dpm)			Trap Sum @ time t (dpm)	Sum Over Time (dpm)	dpm in Solid	q/qo
Trap #		1	2	3	1	2	3				
Time (hrs)											
34	1	10,079.50	539.37	304.44	362,862	19,417	304	382,584	382,584	746,938	0.85
35	2.25	2,366.46	170.39	10.44	85,193	6,134	10	91,337	473,921	655,601	0.74
36	6	3,784.84	469.36	870.90	136,254	16,897	871	154,022	627,943	501,578	0.57
37	22.5	5,080.63	650.65	1,103.33	182,903	23,423	1,103	207,429	835,372	294,149	0.33
38	43.75	2,208.27	826.71	7,364.08	79,498	29,762	7,364	116,623	951,996	177,526	0.20
39	68.5	1,204.41	482.63	3,945.97	43,359	17,375	3,946	64,679	1,016,675	112,846	0.13
40	92.75	572.29	639.98	4,951.42	20,602	23,039	4,951	48,593	1,065,268	64,253	0.07
41	116.75	126.86	164.93	236.97	4,567	5,937	237	10,741	1,076,010	53,512	0.06

FINAL LIQUID PHASE DATA (row 43) — **EQUILIBRIUM PARAMETERS**

	dpm/.5	dpm remaining	q (µg Tol./ kg solid)	Kd (µg/kg*L/µg)
46	714.07	25,707	11,645	59.1

Figure C-1: Example Spreadsheet of Calculations

The following examples come from the spreadsheet (Figure C-1).

- How was Impurity (I 19) determined?

$$impurity = 20\mu L * \frac{L}{10^6\,\mu L} * \frac{854,425\mu g}{L} * \frac{\mu mol}{92.14\mu g} * \frac{2.8\mu Ci}{\mu mol} * \frac{2.22*10^6\,dpm}{\mu Ci} * \frac{\%impurity}{100}$$

$$impurity = 20\mu L * \frac{L}{10^6\,\mu L} * \frac{854,425\mu g}{L} * \frac{\mu mol}{92.14\mu g} * \frac{2.8\mu Ci}{\mu mol} * \frac{2.22*10^6\,dpm}{\mu Ci} * \frac{1.71\%}{100\%}$$

$$impurity = 19713\,dpm$$

- How was total mass (I 18) determined?

$$total\ mass = 20\mu L * \frac{L}{10^6\,\mu L} * \frac{854,425\mu g}{L}$$

$$total\ mass = 17.09\mu g$$

- How was impurity mass (I 20) determined?

$$impurity\ mass = 20\mu L * \frac{L}{10^6\,\mu L} * \frac{854,425\mu g}{L} * \frac{1.71\%}{100\%}$$

$$impurity\ mass = 0.29\mu g$$

The following examples concern the blank:

- dpm/0.5mL is a directly measured quantity obtained through sampling.
- dpm tot liquid (D 22): this measures both spargable and non-spargable counts

$$dpm\ tot\ liquid = \frac{dpm}{volume\ sampled} * total\ liquid\ volume$$

$$dpm\ tot\ liquid = \frac{52578\,dpm}{mL} * 20mL = 1,051,560\,dpm$$

- dpm tot liquid – impurity (E 22): this represents the spargable counts in the liquid

$dpm\ tot\ liquid - impurity = 1,051,560 - 19,713 = 1,031,847 dpm$

- dpm tot (F 22): this is the total spargable counts in the liquid and headspace.

$dpm\ tot = 1,031,847 * (1 + \%Henry's / 100)$

$dpm\ tot = 1,031,847 * (1 + 10.83 / 100)$

$dpm\ tot = 1,143,596 dpm$

- Total Mass (G 22): This will serve as a quality check. This value should be close to 17.09, as calculated from the known concentration of injected material.

$total\ mass = dpm\ tot\ liquid\ converted + (dpm\ tot\ liquid - impurity) * Henry's / 100\ converted$

$$total\ mass = 1,051,560 dpm * \frac{\mu Ci}{2.22 * 10^6 dpm} * \frac{\mu mol}{2.8 \mu Ci} * \frac{92.14 \mu g}{\mu mol} +$$

$$1,031,847 dpm * \frac{10.83\%}{100\%} * \frac{\mu Ci}{2.22 * 10^6 dpm} * \frac{\mu mol}{2.8 \mu Ci} * \frac{92.14 \mu g}{\mu mol}$$

$total\ mass = 17.24 \mu g$

This results in a 0.87% difference.

- Conc (H22):

$$conc. = \frac{dpm}{volume\ sampled}\ converted$$

$$conc. = \frac{52,578 dpm}{mL} * \frac{\mu Ci}{2.22 * 10^6 dpm} * \frac{\mu mol}{2.8 \mu Ci} * \frac{92.14 \mu g}{\mu mol} * \frac{1000 mL}{L} = 779 \mu g / L$$

- Corrected conc. (I 22):

$corrected\ conc. = conc. * purity$

$corrected\ conc. = 779 * (100 - 1.71) / 100 = 766 \mu g / L$

The following examples concern the initial liquid phase data:

- Conc. (D 27):

$$conc. = \frac{dpm\ measured}{volume\ sampled}\ converted$$

$$conc. = \frac{13,297dpm}{mL} * \frac{\mu Ci}{2.22 * 10^6\ dpm} * \frac{\mu mol}{2.8\mu Ci} * \frac{92.14\mu g}{\mu mol} * \frac{1000mL}{L}$$

$$conc. = 197\mu g / L$$

- Total spargable liquid count (E 27):

$$total\ sp\arg able\ liquid\ counts = \frac{dpm\ measured}{volume\ sampled} * total\ volume - nonsp\arg able\ counts$$

$$total\ sp\arg able\ liquid\ counts = \frac{13,297dpm}{mL} * 20mL - 19,713dpm$$

$$total\ sp\arg able\ liquid\ counts = 246,232dpm$$

- Dpm in headspace (F 27):

$$dpm\ in\ headspace = total\ sp\arg able\ liquid\ counts * Henry's$$

$$dpm\ in\ headspace = 246,232dpm * 10.83\% / 100\%$$

$$dpm\ in\ headspace = 26,667dpm$$

- Total spargable dpm (G 27):

$$total\ sp\arg able\ dpm = (total\ sp\arg eable\ liquid\ count + dpm\ in\ headspace) * (1 - \%loss\ cracking)$$

$$total\ sp\arg able\ dpm = (246,232dpm + 26,667dpm) * (1 - 4.5\% / 100\%) = 260618dpm$$

The after samples row is the sample equations as above. However, the sample volume is adjust 19 mL (in this case). This row represents the counts that are left in the system after all initial samples have been taken.

The following examples concern the initial solid phase data:

- Total dpm (I 27):

$$total\ dpm_{solid} = dpm\ tot\ sp\arg able_{blank} - total\ sp\arg able\ dpm_{initial}$$
$$total\ dpm_{solid} = 1,143,596 dpm - 260,618 dpm = 882,978 dpm$$

- % Sorbed (J 27):

$$\%sorbed = \frac{tot\ dpm_{solid}}{tot\ sp\arg able\ dpm_{blank}} * 100\% = \frac{882,978 dpm}{1,143,596 dpm} * 100\% = 77.2\%$$

The following examples concern the sparging data:

- dpm in solids (J 34-41):

$$dpm\ in\ solid = tot\ dpm_{solid} + total\ sp\arg able\ dpm_{after\ sample} - sum\ over\ time$$
$$dpm\ in\ solid = 882,978 dpm + 246,544 dpm - 382,584_{@t=1} dpm$$
$$dpm\ in\ solid = 746,938 dpm$$

This calculation is the same throughout the entire column. Data initially gets entered into the column when the value of the summation of sparged counts over time exceeds the counts in the total spargable dpm after sampling cell for the initial liquid phase data. In other words, whenever coumn I > G28.

- q/qo (K 34-41): for t=1

$$\frac{q}{q_o} = \frac{dpm\ in\ solid\ @t=1}{tot\ dpm_{solid}} = \frac{746,938 dpm}{882,978 dpm} = 0.85$$

The following examples concern the equilibrium data:

- $$\frac{q_t}{q_o} = \frac{q_o m_s - (M(t) - C_{eq} V_l)}{q_o m_s}$$

- $$q = \frac{corrected\ conc._{\cdot blank} - (conc._{\cdot sample} - \frac{impurity}{100} * conc._{\cdot blank})}{\frac{solid\ sample\ mass}{initial\ sample\ volume}}$$

$$q = \frac{766\,\mu g\,/\,L - (197\,\mu g\,/\,L - \frac{1.71\%}{100} * 779\,\mu g\,/\,L)}{\frac{1g\,/(kg\,/1000g)}{20mL/(L/1000mL)}}$$

$$q = 11{,}645\,\mu g\ Toluene\,/\,kg\ solid$$

- $$K_p = \frac{q}{conc._{\cdot sample}} = \frac{11{,}645\,\frac{\mu g}{kg\ solid}}{197\,\mu g\,/\,L} = 59.1\,\frac{\mu g\ Toluene}{kg\ solid} * \frac{L}{\mu g\ Toluene}$$

This value should be close to the values reported by Wu (2002) for HDPE aged in ultrapure water with toluene (Kp = 70.7 µg/kg*L/µg). There is a significant percent difference between these two values of 16.4%. However, one must remember that this is just one example of a triplicate calculation.