

## Effects of Anaerobic Sorbent Degradation on the Sorption of Toluene and *o*-xylene to Municipal Solid Waste Components

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**Abstract.** The overall objective of this research is to develop an understanding of factors controlling the bioavailability and fate of hydrophobic organic contaminants (HOCs) sorbed to components of municipal solid waste (MSW). Plastics (PVC, HDPE), paper (newsprint, office paper), and rabbit food, a model food and yard waste, were chosen to represent sorbent organic matter in landfills, and biodegradable components were tested in fresh and anaerobically decomposed form. To characterize biopolymer-containing sorbent organic matter, fresh and anaerobically decomposed materials were characterized by chemolytic and spectroscopic techniques. Results showed that biologically mediated changes in the sorbent organic matter decreased the polar character of the degraded materials relative to the starting materials. Sorption isotherm data showed that partition coefficients normalized by sorbent organic carbon content ( $K_{oc}$ ) increased with increasing sorbate hydrophobicity ( $K_{ow}$ ) and decreasing sorbent polarity. The normalized sorption parameter [ $\log (K_{oc}/K_{ow})$ ] decreased linearly with increasing O-alkyl to alkyl ratio of the sorbent organic matter as determined by  $^{13}\text{C}$  CP-MAS NMR spectroscopy. The O-alkyl to alkyl ratio recognizes that HOC sorption capacities decrease with increasing sorbent polarity and that small amounts of lipophilic extractives greatly increase HOC sorption capacities. Compared to previously employed parameters for the assessment of sorbent polarity, such as the polarity index [(O+N)/C] or percent polar organic carbon from  $^{13}\text{C}$  CP-MAS NMR spectroscopy, the O-alkyl to alkyl ratio represents an improved predictor for HOC sorption capacities on young organic matter because of its greater sensitivity to lipophilic extractives.

**Introduction.** Approximately 25% of the sites on the National Priority List (NPL) of Superfund are municipal landfills that accepted hazardous waste (1). Unlined landfills typically result in groundwater contamination, and priority pollutants such as alkylbenzenes are often present (2). Ultimately, strategies are needed to manage these landfills, as well as thousands of sites not on the NPL, in a manner that is both cost-effective and protective of the environment. To select cost-effective risk management alternatives, better information on factors controlling the fate of contaminants in landfills is required. A mechanistic understanding of the factors controlling sorptive processes in landfills is limited. Landfills differ from more extensively studied environments involving geosorbents such as soils and sediments because MSW has a large organic carbon content, a large fraction of sorbents in MSW consist of young organic matter that is readily biodegraded, and landfill leachates have a high dissolved organic carbon concentration. Consequently, the principal objective of this research was to elucidate factors that control the sorption of toluene and *o*-xylene in landfills. Specific objectives were to determine (1) the sorptive capacity of model MSW components, (2) the effects of sorbent decomposition on sorbent hydrophobicity and contaminant sorption, and (3) the effects of leachate composition on contaminant sorption.

**Results and Discussion.** Physical and chemical characteristics of the studied MSW components are summarized in Table 1. For biodegradable MSW components, the data indicate that biodegradation resulted in the preferential removal of cellulose and hemicellulose and the enrichment of lignin. Table 1 further shows that protein accumulated during degradation, suggesting that microbial cell components constituted a portion of the degraded materials. Relative to cellulose and hemicellulose, losses of lipophilic extractives were smaller, a result that can be explained by microbial resynthesis of lipids (cell walls, lipid bilayers of cell membranes) and the poor biodegradability of such lipids. Ash contents increased upon biodegradation, a result that can be explained in part by the conversion of organic matter to CO<sub>2</sub> and CH<sub>4</sub>, and in part by the addition of sodium carbonate for pH neutralization, especially during the preparation of degraded rabbit food. Anaerobic degradation decreased the organic carbon contents of office paper and rabbit food by about 9.5% while that of newsprint remained approximately constant.

Single-solute toluene and *o*-xylene isotherms were obtained with each model MSW component, and *o*-xylene isotherm data for non-degraded materials are depicted in Figure 1. The relatively high sorption capacity of PVC (Fig. 1) can be explained on the basis of solubility parameters ( $\delta$ ), where sorbate/sorbent systems with matching solubility parameters represent a compatible solute/solvent system (3). Thus, PVC [ $\delta = 7.8-11 \text{ (cal/cm}^3)^{1/2}$  (3)] represented a suitable sorbent for *o*-xylene [ $\delta = 8.9 \text{ (cal/cm}^3)^{1/2}$  (3)] because the solubility parameter range of PVC includes that of *o*-xylene. Furthermore, a nonlinear adsorption component on the surfaces of internal nanovoids contributed to *o*-xylene uptake by the glassy PVC polymer (4). HDPE exhibited a smaller *o*-xylene sorption capacity than PVC because the solubility parameter for *o*-xylene falls outside of the range for HDPE [ $\delta = 7.7-8.2 \text{ (cal/cm}^3)^{1/2}$  (3)] and because an adsorption component was absent on this rubbery polymer. The biopolymer-containing materials exhibited lower sorption capacities than plastics because (1) the differences in solubility parameters between *o*-xylene and lignin or cellulose were greater than those between *o*-xylene and PVC or HDPE, and (2) the content of highly compatible sorbent fractions, such as lipophilic extractives, was small in the biopolymer-containing materials. The order of sorbent affinity for toluene was the same as that shown in Figure 1 for *o*-xylene, a result that can be expected given that the solubility parameter of toluene [ $\delta = 8.8 \text{ (cal/cm}^3)^{1/2}$  (3)] is similar to that of *o*-xylene. As shown in Figure 2, the normalized sorption parameter [ $\log (K_{oc}/K_{ow})$ ] decreased linearly with increasing O-alkyl to alkyl ratio of the sorbent organic matter as determined by <sup>13</sup>C CP-MAS NMR spectroscopy. The correlation developed in Figure 2 substantiates that HOC sorption capacity decreases with increasing sorbent polarity. However, it also recognizes the importance of lipophilic extractives on HOC sorption.

The results of this study illustrate that toluene and *o*-xylene sorption in landfills will be strongly influenced by the presence of plastics and lipophilic compounds. The recalcitrance of these compounds in conjunction with the microbial synthesis of proteins and lipids will increase the sorbent organic matter affinity for HOCs as biologically mediated sorbent degradation proceeds in the landfill. Consequently, HOC leaching from landfills into groundwaters may decrease as sorbents degrade and HOCs are sequestered in glassy and/or paraffinic organic matter. To better address the environmental significance of sorptive processes, additional studies are needed to quantify mass transfer rates of aged alkylbenzenes from fresh and degraded sorbents suspended in acidogenic and methanogenic leachates, and these experiments are currently underway in our laboratory.

Table 1. Characteristics of solid materials<sup>a</sup>

Sorbent	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Lipophilic extractives (%)	Crude protein (%)	Ash (Wt %)	f <sub>oc</sub>
Poly(vinyl chloride)	N/A <sup>b</sup>	N/A	N/A	N/A	N/A	0.00	0.389
High density polyethylene	N/A	N/A	N/A	N/A	N/A	0.01	0.876
Fresh office paper	64.7	13.0	0.93	0.7	0.31	11.6	0.373
Degraded office paper	36.2	6.9	4.8	3.3	4.99	38.4	0.278
Fresh newsprint	48.3	18.1	22.1	1.6	0.44	2.0	0.451
Degraded newsprint	35.1	16.0	32.3	1.4	3.74	6.4	0.455
Fresh rabbit food	30.6	15.4	9.5	4.9	18.1	7.7	0.423
Degraded rabbit food	7.1	5.7	25.2	4.5	20.6	34.5	0.329

<sup>a</sup> values are averages of replicate analyses

<sup>b</sup> N/A: not analyzed

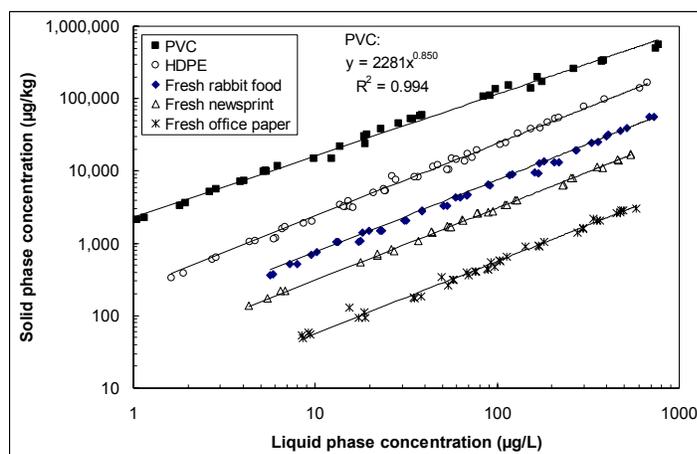


Figure 1. Single-solute *o*-xylene isotherms on model MSW components. Solid line through PVC data indicates the best fit of the Freundlich isotherm equation. Solid lines through all other data sets indicate best fits of the linear partition model.

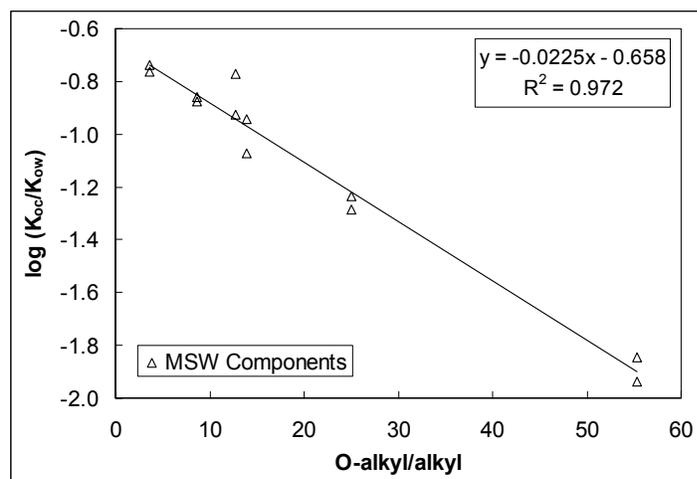


Figure 2. Dependence of normalized sorption parameter on sorbent polarity as expressed by the O-alkyl to alkyl ratio.

## References

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