## Interactions between Hydrophobic Organic Contaminants and Dissolved Organic Matter in Methanogenic Leachate

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Low-level contamination of groundwater by hydrophobic organic compounds (HOCs) such as tetrachloroethene (PCE) and toluene is frequently detected down gradient of unlined municipal landfills. Associations between HOCs and humic matter affect the persistence of HOCs in the subsurface and may thus determine remediation endpoints for HOCs. The objectives of this research are (1) to determine factors that affect HOC associations with dissolved leachate organic matter, (2) to determine whether the associations are covalent or noncovalent in nature, and (3) to evaluate the effects of these interactions on HOC bioavailability.

Initial results indicated that redox potential affects HOC-humic interactions. A protocol was therefore developed to examine HOC-humic interactions as a function of redox potential. Under abiotic conditions, <sup>14</sup>C-labeled toluene or PCE was spiked into 20-mL ampules containing laboratory-generated methanogenic leachate in reduced ( $\sim$  -330 mV) and oxidized ( $\sim$  +520 mV) states. After flame sealing and seven days of mixing, ampules were broken and sparged first with nitrogen and then hydrogen (as a reductant) to quantify the binding of toluene or PCE to leachate organic matter and to evaluate the reversibility of the binding process. The molecular size distribution of <sup>14</sup>C bound in macromolecules was assessed by high performance size exclusion chromatography (HPSEC).

At an initial concentration of 100 ppb, about 93% of toluene was bound to oxidized leachate organic matter, and  $12\% \sim 18\%$  toluene was bound to reduced leachate organic matter. Data showed that this binding process was irreversible under the tested experimental conditions. HPSEC results showed that bound toluene was primarily associated with molecules that have an apparent molecular weight of about 1800 daltons. Tests at an initial concentration of 500 ppb exhibited a similar trend. No apparent binding was observed for PCE with both oxidized and reduced leachates.

Future research will focus on the influence of pH and Fe on HOC-humic interactions. Spectroscopic techniques (<sup>2</sup>H-NMR, <sup>13</sup>C-CP/MAS NMR, TMAH-chemolysis GC/MS, and pyrolysis GC/MS) will be employed to determine whether covalent binding or noncovalent interactions control contaminant sequestration.

## References

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- 2. Schlautman, M. A., and Morgan, J. J. 1993. Effect of Aqueous Chemistry on the Binding of Polycyclic Aromatic Hydrocarbons by Dissolved Humic Materials. *Environ. Sci. Technol.* 27: 961-969.