

TRICHLOROETHENE SORPTION TO WETLAND SOILS AND LIGNITIC SEDIMENTS FROM THE NORTHERN GULF COASTAL PLAIN A. E. Fryar¹, C. J. Sweat¹, and J. R. Sachleben² ¹Dept. of Geological Sciences, Univ. of Kentucky, Lexington, KY 40506-0053, afryar1@pop.uky.edu, ²Campus Chemical Instrument Center, Ohio State Univ., Columbus, OH 43210, jsachleb@chemistry.ohio-state.edu

Sorption of non-polar organic solutes to geologic media depends in part on the amount and structure of solid organic carbon (SOC). Various studies [1, 2, 3] have found that values of K_{oc} ($= K_p/f_{oc}$, where K_p is the sorption coefficient and f_{oc} is the fraction of SOC) are greater for sediments and sedimentary rocks than for modern soils. These differences have been ascribed to condensation of SOC during diagenesis, which results in increased aromaticity and decreased polarity. More recent studies using solid-state ¹³C nuclear magnetic resonance (NMR) spectroscopy have concluded that both aliphatic and aromatic groups contribute to sorption and that K_{oc} increases as SOC polarity decreases [4, 5].

We measured SOC compositions and trichloroethene (TCE) sorption for geologic media from the vicinity of the Paducah Gaseous Diffusion Plant (PGDP), a Superfund site in western Kentucky. TCE may sorb within a lignitic aquitard (the Levings Member of the McNairy Formation [Cretaceous]) beneath PGDP or in wetlands in the Ohio River flood plain where ground water discharges. We determined f_{oc} by combustion and CO₂ detection; soil and sediment samples were treated with 5% H₂SO₃ to remove inorganic C prior to analysis. Maximum f_{oc} values were 0.015 to 0.0376 for two wetland soil borings, 0.0171 to 0.0307 for two Levings sediment borings, and 0.222 to 0.394 for three Levings lignite samples. We extracted humic acids and humin from soil, sediment, and lignite samples with methyl isobutyl ketone (MIBK) [6]. Sample splits not reacted with MIBK were treated with HF to remove paramagnetic minerals. Using cross-polar magic-angle spinning, we obtained solid-state ¹³C NMR spectra. Treated soils showed carbohydrate (72 ppm) and carboxylic (172 to 173 ppm) peaks. Treated sediments, lignite, and lignite humic substances exhibited aromatic (127 to 144 ppm) peaks. All spectra showed aliphatic peaks (25 to 35 ppm). Total aromaticity (defined by [4]) was lower, and the fraction of polar SOC (defined by [5]) was higher, for soil and soil humin than for sediment and sediment humin.

For sorption experiments, TCE was dissolved in synthetic ground water and reacted with sorbent slurries in dialysis-tubing "bags" (to eliminate non-settling particles [7]) within amber glass vials. TCE was extracted with pentane containing 1,2-dibromoethane as an internal standard and analyzed on a gas chromatograph with an electron capture detector. Sorbed concentrations (q_e) were calculated as the

difference between average aqueous concentrations in triplicate reactive vials and in control vials without slurries. Time-series experiments indicated that dissolved TCE concentrations (initially 0.05 mg/L) approached steady state after 7 to 12 days, depending upon the sorbent. These results dictated the duration of isotherm experiments, in which we measured sorption using initial TCE concentrations of ~ 0.05, 0.5, 5, 50, and 500 mg/L. Isotherms were fit with the Freundlich equation $q_e = K_p C_e^n$, where C_e is the quasi-equilibrium aqueous concentration and n is the linearity factor (after [3]). Single-point K_p values, calculated by taking $C_e = 1$ μg/L (following [1]), were 13.4 to 30.5 (μg/kg)/(μg/L)ⁿ for soils, 34.1 to 47.7 (μg/kg)/(μg/L)ⁿ for sediments, and 371 (μg/kg)/(μg/L)ⁿ for lignite. Values of n ranged from 0.857 to 0.890 for four of five samples (n was 0.953 for one soil). K_{oc} values, which ranged from 358 to 2040 (μg/kg)/(μg/L)ⁿ, were similar to those reported for shales and low-rank coals [1], but less than those for kerogen-rich till [3]. Soils represented both our highest and lowest K_{oc} values; the sorbent with the longest reaction time (12 days) had the highest value. K_{oc} was more closely correlated to the fraction of polar SOC than to total aromaticity, consistent with the findings of [4] and [5].

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