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POLYCHLORINATED BIPHENYL DESORPTION FROM LOW ORGANIC CARBON SOILS: MEASUREMENT OF RATES IN SOIL-WATER SUSPENSIONS

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ABSTRACT

The desorption of 13 PCB congeners from four soils has been investigated using the gas purge technique. The soils from PCB spill sites had been in contact with Aroclor 1242/1254 mixtures for 3 or more years; thus, sorption equilibrium is presumed to have been obtained. Soils were "engineered" ground cover materials used at utility industry substations and consisted of fine rock chips and sand-silt-clay fractions with organic carbon < 0.2%. The congeners contained from three to five chlorine atoms. Agreement of measured Henry's Law constants for the ^{14}C-labeled congeners 24', 22'55' and 22'44'55' with literature values established the proper function of the gas purge technique for measurement of congener release rates from soil-water suspensions. For all 13 congeners and all soils: 1) the labile fraction was typically 80 to 90% of the total congener concentration, 2) the majority of the labile fraction was desorbed or released within 48 hours of contact with water, and 3) the release of the remaining nonlabile fraction persisted for over 6 months with complete release estimated to be 1 to 2 years. Release rate constants, k_d, decreased with increasing chlorine number with typical values for labile and nonlabile fractions ranging from 1.4 to 0.5 d^{-1} and 0.008 to 0.0006 d^{-1}, respectively.

INTRODUCTION

Polychlorinated biphenyls (PCBs) used in industrial applications since the early 1930s consist of mixtures of individual PCB congeners that differ in the number and position of the chlorine atoms substituted for hydrogen in the biphenyl ring. The widespread environmental contamination caused by PCBs led to discontinuation of their use in the early 1970s. However, because of the chemical and biological stability of PCBs, high levels currently persist in the environment. In soil-water systems PCB congeners are strongly sorbed by, or partitioned into, the organic fraction of suspended solids, soils and sediments because of their low water solubility and high octanol-water partition coefficients (K_{ow}). The soil-water partition coefficients (K_p) describing this hydrophobic sorption of PCB congeners increase with increasing chlorination and consequent increasing hydrophobicity of the congeners. In these soil-water systems sorption/desorption is a major process limiting the migration of PCBs into surface and groundwaters. Both the chemical stability and strong sorption contribute to the persistence of PCBs at historical spill sites. A key unresolved issue at these sites, however, is the rate of desorption or release of individual PCB congeners from the contaminated materials when in contact with surface and subsurface waters. Situations of this type occur at sites where soils and engineered ground cover materials, e.g., near capacitor and transformer installations, have been contaminated with PCBs and periodically flooded by surface runoff and/or snowmelt waters. To address this issue, a gas-purge technique was used in this study to simultaneously measure the desorption-release rates of individual PCB congeners from contaminated soils suspended in water.

Congener mixtures commonly used by the utility industry in the United States were designated by the tradename Aroclor. Given the wide range of physical characteristics [e.g., solubilities, vapor pressures, K_{ow}s (Shui and Mckay, 1986)] of individual congeners in Aroclor mixtures it is highly likely that the release of individual congeners from soils and the subsequent mobility in soil-water systems will be subject to a differentiation or chromatographic separation among congeners with distance from the source. Within the PCB sorption/desorption literature (see review, Sklarew and Girvin, 1987) most investigations reported on the sorption/desorption of Aroclor mixtures rather than individual congeners. A more accurate method of treating PCB sorption/desorption by soils, sediments and subsurface aquifer materials (sorbents) is to consider the individual congeners and to measure equilibrium K_ps and desorption-release rates for individual congeners. This is the approach taken here.

Previous studies designed to examine the sorption/desorption kinetics of hydrophobic, nonionizable organic compounds (HNOC) from soils and freshwater sediments found that the sorption/desorption process consists of an initial rapidly released (labile) component followed by a slowly released (nonlabile) component (Karickhoff, 1980, 1984; Karickhoff and Morris, 1985; Coates and Elzerman, 1986; Wu and Gschwend, 1986; Brusseau and Rao, 1989). The labile and nonlabile components of sorption kinetics can be described by a conceptual model that treats the sorbent as distinct regions. The labile sorption/desorption component arises from a rapid equilibration between the bulk solution sorbate and the accessible region of the sorbent surface. The nonlabile sorption/desorption component results from kinetic limitations of sorbate mass transfer to inaccessible regions of the aggregated soil or sediment assemblages that are not in direct contact with the bulk solution. HNOC sorption kinetics measured using the gas stripping technique (Karickhoff, 1980, 1984; Karickhoff and Morris, 1985; Oliver, 1985; Coates and Elzerman, 1986; Wu and Gschwend, 1986) are consistent with the hypothesis that nonlabile sorption/desorption is due to diffusional mass transfer between accessible and inaccessible regions of the sorbent (Karickhoff and Morris, 1985; Brusseau and Rao, 1989). The characteristic time scales for labile and nonlabile sorption/desorption are hours to days and weeks to months, respectively.

For individual PCB congeners the nonlabile component of desorption from sediments was found to increase as the 2:1 expandable clays and the resultant aggregation of the sediment assemblage increased (Coates and Elzerman, 1986). In view of the presumed contribution of both intrasorbent diffusion and sorption/desorption processes to the observed removal of congeners from the sorbent to the bulk aqueous solution, we will refer to the combined process as "release" rather than "desorption." No long-term observations of PCB congener release from contaminated soil materials have been made for Aroclor-soil mixtures that have been equilibrated under natural conditions for extended periods of time. In this study congener release from soils has been observed for up to 6.5 months for 13 of the most abundant congeners in Aroclor 1242 and 1254. The following experimental approach was taken. The Henry's Law constants, H_c, for ^{14}C-labeled dichloro, tetrachloro, and hexachloro PCB congeners (IUPAC numbers 8 (24'), 54 (22'55') and 153 (22'44'55'), respectively) were measured with the same purge gas apparatus used for the release rate experiments. These H_c data were compared with literature values to demonstrate that gas-solution equilibrium was achieved in the purge apparatus. This purge apparatus was then utilized to simultaneously measure the release rates for 13