Transport And Persistence Of Chlorinated Organics In Varied Soil Environments

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INTRODUCTION

Chlorinated organics as a class are some of the most persistent organic contaminants in the environment. A large volume of scientific literature over the past twenty-five years has been devoted to environmental monitoring and the environmental behavior of these compounds. Monitoring studies have revealed that certain members of the class are ubiquitous, and they have been detected in some of the most remote regions of the world. Despite the large number of studies, a consensus on the adverse biological effects of these chemical continues to elude the scientific community. Part of the problem lies in the wide variation of the observed effects in different species, and another part relates to the uncertainties associated with the levels of exposure. The latter uncertainties can be alleviated by a better understanding of the environmental transport and persistence of these compounds. A major but often overlooked factor is the effect of other contaminants. The present studies were designed to provide a quantitative and qualitative measure of the transport and persistence of four types of organochlorine compounds under varied contamination scenarios. The organochlorines studied were polychlorinated dibenzo-p-dioxins (PCDDs), dibenzo-furans (PCDFs), polychlorinated biphenyls (PCBs), chlorinated phenols and chlordanes.

EXPERIMENTAL

A three-tiered experimental approach comprised of the following three elements was undertaken:

    A.   Laboratory studies on partition, leachability, volatilization and microbial degradation.

    B.   Laboratory and field column studies with uniformly contaminated soils.

    C.   Field plot studies.

The laboratory and field column studies were carried out with three types of uncontaminated and contaminated soils from sites with a history of contamination. The laboratory batch experiments were set up to differentiate acclimatized and non-acclimatized soil microbial populations which could degrade chlorinated phenols. Each type of acclimatized and non-acclimatized soil was homogenized separately. Aliquots from each batch were analyzed to

establish the initial concentration of the contaminant. Separate portions were taken and fortified with chlorinated phenols over a concentration range of 20-500 ppm. The fortified soil samples were transferred to shake flasks, and a known volume of sterilized water was added to each flask. Aliquots of soil and water were analyzed at time intervals ranging from 1 hr to 3 months. In a separate series of experiments, microbial cultures from each soil were isolated and tested for their ability to degrade chlorinated phenols.

The setup for laboratory column studies has been described earlier[1,2]. In these, the emphasis was placed on deciphering the role of co-contaminants on the transport of highly lipophilic molecules such as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). A uniformly contaminated 5 mm layer of soil was sandwiched between two 7 cm layers of uncontaminated soil. The conditions in the columns were varied to simulate vadose and saturated zones. The columns were allowed to equilibrate for periods of up to 15 months in a controlled environmental chamber. The columns were sectioned after set time intervals, and the concentration of contaminants was determined by standard validated analytical methodology.

The field experiments were carried out at the dioxin research facility at Times Beach, MO. A limited number of experiments were also carried at an old wood treatment facility in central California. These experiments took place in stainless steel bins capable of holding $0.16 \, m^3$ to $1 \, m^3$ of soil. Contaminated soils available at both sites were used. The mobility of PCDDs and co-contaminants such as pentachlorophenol and naphthalenes was monitored under unsaturated and saturated conditions.

RESULTS AND DISCUSSION

The batch partition experiments were carried out to monitor the effect of co-contaminants. Co-contaminants of interest were selected to reflect typical application or accident scenarios. Thus, surfactants were selected as co-contaminants in case of chlordane partition experiments. Technical chlordane formulations contain a mixture of variously chlorinated products of "chlordene", a Diels Alder condensate of cyclopentadiene. The commercial formulations also contain 5-10% of anionic/cationic surfactant. Results of partition experiments revealed that surfactants can significantly effect Koc values (soil/water partition coefficient) even at very low concentration levels. A 10-fold decrease in Koc values was observed for chlordane constituents with 0.01% lauryl sulfate in water. As expected, partitioning into the aqueous phase was found to be dependent on the number of chlorine substitutions, and decreased with an increase in the number of chlorines in the molecules. These results were supported by column leaching studies, which revealed that transport of chlordane constituents occurred during the initial period following application and was mediated by the presence of surfactants. Migration was dramatically reduced in the absence of surfactants. Studies also showed that the downward movement and transport rates are dependent on soil parameters, most noticeably the clay content. In vadose zones, development of cracks and pores, especially in clay soil (with large swelling and shrinking characteristics), can provide preferred paths for migration of all contaminants into deeper soil layers.

Since hydrocarbon carrier co-contaminants have been associated with many cases of accidental release of PCBs, PCDDs and PCDFs, batch partition experiments and column studies were carried out to measure the role of these and other co-contaminants such as

creosote compounds on the transport of chlorinated contaminants. The batch partition studies revealed that in hydrocarbon solvent/soil systems the distribution of chlorinated organics is largely in favor of the hydrocarbon solvent, thus permitting a ready transport of all PCDDs/PCDFs through the soil This conclusion was supported by data from column studies. An increase in the distribution coefficient was also observed in the presence of pentachlorophenol and creosote components such as naphthalene and methyl naphthalene through adsorptive displacement. These contaminants are associated with PCDD/PCDF contamination at wood treatment facilities. In the absence of carrier co-contaminants, little migration of PCDDs/PCDFs occurred, and was limited to the migration of mono and dichloro congeners. The results from column experiments extending over a 2 year period provided clear data on the stability of these compounds in soil environments. Only mono and dichloro congeners showed a measurable degree of loss through transformation or other processes. This apparent loss, however, was related to incomplete recovery of contaminants by traditional jar/sonification extraction procedures. However, later, more exhaustive extraction in Soxhlet with benzene showed that residue concentrations were nearly the same as the initial fortification levels (Table I). It is apparent that the binding of PCDDs/PCDFs to soil approaches irreversibility due to the encapsulation of these solutes in soil organic and

Table I: Comparison of extraction efficiencies of PCDD/PCDFs aged in weathered soil for 15 months.

Extraction Comparison of PCDD/Fs in Aged Soil (15 months)							
Extraction Method	28-F mcg	27-D mcg	124-D mcg	1234-D mcg	12378-D mcg	OCDD mcg	OCDF mcg
1. Soxhlet - 24 hrs Benzene	73	106	48	51	56	136	93
2. Soxhlet - 24 hrs MeCl₂	62	83	45	52	59	126	83
3. Ultrasound & Shaking - 24 hrs Benzene	74	109	50	55	56	103	70
4. Ultrasound & Shaking - 24 hrs 50/50 Cyclohexane and MeCl₂	56	83	42	49	51	96	66
5. NaOH Treatment #1 followed by 24 hr 50/50 Cyclohexane and MeCl₂	74	99	48	47	37	87	54
6. NaOH treatment-dup followed by 24 hr 50/50 Cyclohexane and MeCl₂	75	100	49	48	42	97	66

mineral matter. It is clear that, while these chemicals are very stable in the soil environment, their availability to the biosphere may be reduced over a period of time.

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