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Feasibility of Toxaphene Transport through Sandy Soil

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Toxaphene, produced by the chlorination of camphene, is a chlorinated hydrocarbon insecticide that was widely used to control a variety of insects on crops and to control livestock skin parasites. It is known to be a toxic and a highly persistent chemical in soil where its half-life can be in excess of ten years, depending on the environmental conditions (Seiber et al. 1979; Nash and Woolson 1967; Mc Dowell et al. 1981). Therefore, this along with other factors, caused the cancellation of many uses of toxaphene in 1973 by the U.S. Environmental Protection Agency (EPA). This study was conducted in an attempt to explain a finding in this lab of high concentrations of toxaphene (2600 ppm) in soil sampled at a depth of 1 m (*W. Winterlin, personal communication*). The source of the sample was from a pesticide waste facility in northern California. This site was a disposal facility for many years where unused pesticides and rinsates collected from applicator planes were drained into an unlined bed of soil. The paradox of this discovery was that toxaphene, being hydrophobic, has been shown to be restricted in its movement from agricultural applications to a reported maximum of 30 cm, with the bulk of material concentrated in the upper 10 cm; although repeated occurrences of toxaphene below 30-45 cm in soils have been reported (LaFleur et al. 1973; Nash and Woolson 1968; Swoboda et al.1971).

Toxaphene is known to undergo anaerobic degradation that changes its gas chromatography "profile" (Williams and Bidleman 1978). The toxaphene analyzed in this sample had an "unweathered" profile similar to technical toxaphene, implying that no degradation had occurred. Since a waste disposal facility is faced with abnormally high concentrations of pesticides and formulation components, it was of interest to ascertain if movement in a soil profile was possible when such concentrations prevail in a waste facility.

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MATERIALS AND METHODS

Our concern was to investigate the leaching potential of toxaphene through a soil profile. Therefore, identifying the possibility of toxaphene movement was completed first through a relatively non-adsorbing (low carbon content) soil such as sand, and then a more organic sandy loam soil. Toxaphene was applied as either the technical material or as the emulsifiable concentrate formulation: 1064 g/L of technical toxaphene; 244 g/L of technical xylenes; 41 g/L of emulsifier mixture; (2.42% Atlox 4302; 0.63% Atlox 4303 (v/v)). Water was added to imitate the action of rain by potentially facilitating any movement. Also, a lab generated emulsifiable concentrate (EC) formulation mixture of xylenes and emulsifiers was added to see any possible effect on toxaphene's movement. This was completed to imitate the presence of other organic pesticides and their formulation components, as would be found in a waste disposal site. One final consideration was to determine the effect of drying and wetting the soil on the leachability of toxaphene, since various reports identify a relation between degree of compound adsorption to soil and this treatment. (Green and Obien 1969; Saha et al. 1969).

Technical toxaphene was obtained from Hercules, Inc. Solvents utilized were Baker Resi-Analyzed or of equivalent quality. The soils obtained were classified as West Sacramento sand and Davis sandy loam, and were dried, seived to less than 1.65 mm, and stored at room temperature until use. Characterization of the soils was completed and is shown in Table I. The moisture content of air-dried soils was determined by drying duplicate 50 g samples overnight at 105°C. The pH, organic carbon by the Walkley-Black method, and soil texture analysis by the hydrometer method were completed as described by Smith (1975). Classification of the soils is according to the USDA soil textural triangle chart. The organic matter was determined by muffle furnace as outlined in Hess (1971). Soil columns were prepared as follows: to fritted glass columns (15 cm x 6 cm id) was added 2 cm of glass wool, approximately 15 g sand prerinsed with ethylacetate and dried, 150 g of soil (100 g of the sandy loam), 15 g sand, and topped with 2 cm of glass wool. About 50 mLs of distilled water was added to each column until the soil was saturated.

To each soil column was added 100 ppm toxaphene as technical material or as the 90% emulsifiable concentrate formulation (personal communication with J Brandon, Helena Chemical Corp). Samples were run in duplicate, along with blanks. The columns were eluted with distilled water, 100 mLs at a time, for a total of 1000 mLs, which is equivalent to 36 cm of rain, the average annual precipitation for Sacramento Valley where the sample was taken (California Dept of Food and Agriculture 1978). Each 100 mLs of eluant was collected, extracted twice with an equal volume of ethyl acetate, dried with Na_2SO_4, reduced to 5 mLs on a rotary evaporator.

Table 1: Characterization of Soils

	West Sacramento Sand	Davis Sandy Loam
Moisture Content	1.6%	3.8%
pH	6.66	8.10
% organic carbon	0.33	1.51
% organic matter	0.94	3.33
% sand	96.	55.
% silt	0.	25.
% clay	3.	18.

The sandy loam column contents were then removed intact, separating the layers into the glass wool, sand, and soil constituents, and extracting for remaining toxaphene. Extraction of the toxaphene components was carried out by adding the components to 50 mLs of ethylacetate and blending for 30 sec with a Markson Tissumizer, filtering the extract through anhydrous Na_2SO_4, and concentrating.

The sand and sandy loam experiments were each run under two different conditions: 1) adding the water dropwise and avoiding soil drying, and 2) allowing the soil to completely dry before adding the next water 100 mL aliquot of water.

Variations in the experiment were the two soil types (sand or sandy loam), toxaphene application method (technical or EC formulation in 1.5 mLs solvent and in 15 mLs solvent), elution solvent (water and formulation material or water alone), and soil treatments (continuous wetting versus wetting and drying).

Two different gas chromatographs were used in the analysis of the samples. The samples of sand were analyzed using a packed column in a Varian 2100 gas chromatograph equipped with a ^3H electron capture detector. The glass column was 180 cm x 2 mm id packed with 3.5% SE-30 (gc grade) on 100/120 mesh Varaport #30. The nitrogen carrier gas had a flow rate of 30 mL/min. The oven temperature was maintained at 200°C. Analysis of the sandy loam samples was carried out using a Hewlett-Packard 5880A capillary gas chromatograph with a ^{63}Ni electron capture detector. The column was a 5 m x 0.25 cm id DB 1701 at 200°C. For both instruments, the limit of detection for toxaphene was

1 ng. Samples showing the presence of toxaphene were compared to standards prepared from technical toxaphene in ethyl acetate. Measurement of the peak size was accomplished following the method of Gallagher, et al. (1979), where the peak height of the five largest peaks was measured for quantification after background subtraction.

RESULTS AND DISCUSSION

The sand and sandy loam soil columns which were continuously wetted with water gave no evidence of toxaphene elution through the column. However, when the sandy loam soil was treated with extra formulation material and was allowed to completely dry out between water applications, crevices were observed forming, and toxaphene was detected in the eluant, ranging from 25%-68% of the material applied. See Table II for a summary of soil columns treatments and results. Each aliquot of water added after the formulation contained both toxaphene and the formulation materials. As each 100 mLs of water were added to the column, some of the formulation (xylenes and emulsifiers) was seen as a cloudy emulsion in the water prior to extraction and increased the overall baseline. Figure 1 shows an elution profile for the representative sandy loam soil column that had toxaphene applied as the emulsifiable concentrate formulation, had extra formulation material applied, and was allowed to dry out between water applications.

Table 2. Summary of experimental conditions and results

Sample	Conditions	Results
Sand		
technical toxaphene		
continuous wetting	no formulation	no leaching
formulated toxaphene		
continuous wetting	no formulation	no leaching
Sandy Loam		
formulated toxaphene		
continuous wetting	no formulation	no leaching
continuous wetting	extra formulation	no leaching
dry/wet cycling	no formulation	no leaching
dry/wet cycling	extra formulation	leaching

The sandy loam soil columns that were extracted and analyzed showed greater than 60% of the toxaphene present in the top 2 cm of soil. Less than 25% of the toxaphene was in the lower column components, and

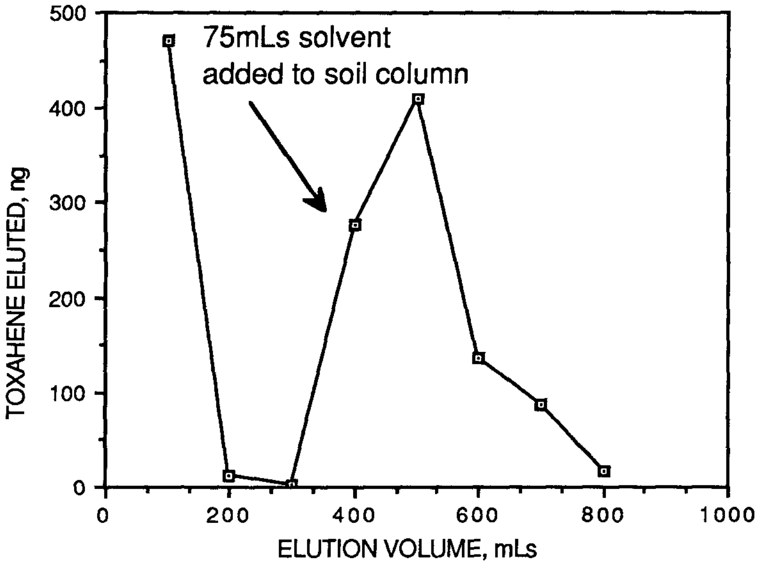

Figure 1. Toxaphene elution from a sandy loam soil column with water and solvent as eluants

the remaining 15% was in the top glass wool and sand components.

Toxaphene applied as an EC formulation leached through sandy loam under the extreme conditions of added formulation compounds (organic solvent and emulsifier) following soil drying and wetting. These soil conditions have been shown to have pronounced effects on sorption phenomena, providing a mechanism for movement through soil. The water that eluted through the soil after the formulation solvent and emulsifiers were added contained some of the formulation materials. Since no toxaphene movement was seen in soil without added formulation, the toxaphene was transported by means of dissolving in the formulation, and leached as the resulting water emulsion. The average total amount of toxaphene which leached through the soil samples was 1.5 mg, which is 15% of the total toxaphene added to the soil column. It should be noted that the amount of toxaphene leached was mostly concentrated in the formulation leachate and the few water leachates that followed.

Therefore if toxaphene is present in a sand or sandy loam waste bed, it normally would be expected to be immobilized by being tightly adsorbed to the sand. However, its ability to move through the sandy textured soil with water is related to the amount of organic solvating materials available. Therefore, if toxaphene is present in such a bed with high or repeated amounts of formulations (organic solvents and emulsifiers) it could foreseeably leach to greater depths. These results also indicate that other similarly persistent and water insoluble compounds in a highly utilized waste facility may leach to greater degrees than previously believed.

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