Reactions Between Fulvic Acid, a Soil Humic Material, and Dialkyl Phthalates[1]

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In a recent communication from this laboratory the isolation of small amounts of dialkyl phthalates from fulvic acid (FA), a water-soluble, relatively low-molecular-weight soil humic fraction, was reported (1). It was suggested that FA could complex hydrophobic dialkyl phthalates, solubilize them in water and so mediate their mobilization, transport and immobilization in soils and waters. Dialkyl phthalates are widely used in industry as plasticizers and in the manufacture of lubricants, alkyd resins and dyes (1). In view of the ubiquitous occurrence on the earth's surface of FA and the reported toxicity (1) of some dialkyl phthalates, we were interested in obtaining more detailed information on the extent and nature of reactions of FA with some of the more prominent phthalates that we had found in the earlier investigation.

Materials and Methods

FA

The FA was extracted from the Bh horizon of an imperfectly drained Podzol soil from Prince Edward Island, Canada. Methods of extraction and purification as well as a number of physical and chemical characteristics of FA have been described (2). Briefly, FA is a chemically and biologically stable polyelectrolyte with a number-average molecular weight (measured by vapor pressure osmometry) of 951. Its elementary composition on a dry, ash-free basis, is: 50.92% C, 3.34% H, 0.74% N, 0.26% S and 44.74% O. One g of FA contains 9.1 meq COOH, 3.3 meq phenolic OH, 3.6 meq alcoholic OH and 3.1 meq C=O groups (2). The FA is completely soluble in water.

Dialkyl phthalates

The dibutyl phthalate (I) and the bis(2-ethylhexyl) phthalate (III) were purchased commercially. The dicyclohexyl phthalate (II)

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was prepared by esterifying o-phthalic acid with cyclohexanol in the presence of a few drops of conc. H_2SO_4. The identity and purity of each phthalate was checked by IR spectroscopy and mass spectrometry and by gas chromatography.

Reactions between FA and dialkyl phthalates

Increasing amounts of phthalates, ranging from 50 to 400 mg, were added to glass stoppered 50-ml Erlenmeyer flasks, containing 125 mg of FA dissolved in 25 ml of distilled water (final pH = 2.45). Each flask was tightly stoppered and shaken at room temperature for 24 hours. The solution was then transferred to a separatory funnel and extracted three successive times with 25 ml of redistilled toluene. The toluene extracts were filtered through dry filter paper to remove most of the water, the filter paper was washed with 50 ml of toluene, and the extract plus washings was dried in a rotary evaporator. The resulting material was dissolved in 2 ml of benzene; appropriate aliquots of the latter solution were injected into a gas chromatograph for quantitative analysis. We found that with all three dialkyl phthalates, gas chromatographic peak heights were directly proportional to concentrations over the range of 0.1 to 5.0 $\mu g/\mu \ell$. The gas chromatographic conditions were as follows: Hewlett-Packard Model 402, flame ionization detector, 1800 x 4 mm glass column packed with 5% SE-30 on Chromosorb W HMDS, 60 to 80 mesh, programmed from 150 to 300°C at a rate of 7.5°C per min. The retention times for the phthalates under these conditions were: I, 8.3 min., II, 14.0 min., III, 15.9 min. Blanks, consisting of 25 ml of distilled water and the same weights of phthalates as were used in the presence of FA were run concurrently. The recoveries of the phthalates in the blanks ranged between 98 and 100%. The FA contained only negligible amounts of I and II but 0.6% of III. All results involving III were corrected for amounts of III in the FA.

Results and Discussion

As shown in Figure 1, the maximum amounts of dialkyl phthalates solubilized by the FA depended on the nature of the phthalate. Thus, 125 mg of FA "complexed" a maximum of 203 mg of III, or one number-average molecular weight of FA reacted with 4 moles of III. By contrast, 125 mg of FA solubilized a maximum of only 65 mg of II and 35 mg of I. This is equivalent to reactions of two number-average molecular weights of FA with three moles of II and of one number-average molecular weight of FA with only one mole of I. Raising the pH of the FA solutions from 2.45 to 7.00 decreased the amounts of dialkyl phthalates "complexed" by approximately 25%. The ability of FA to "complex" III most efficiently is in accord with recent findings in our laboratory which showed that 1 g of FA contained 8.0 mg of dialkyl phthalates. The latter consisted of 6.0 mg of III and of only 0.5 mg of II and 0.03 mg of I.

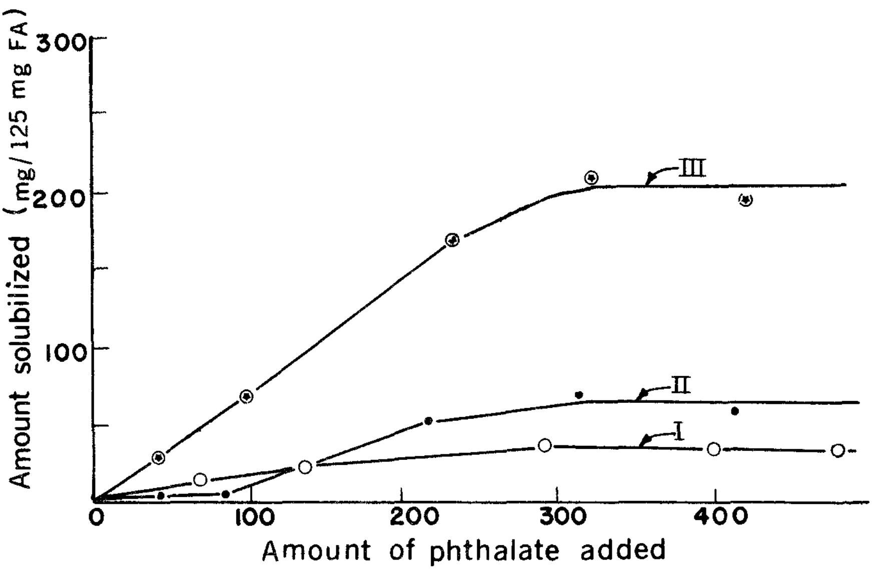

Figure 1. Reaction of fulvic acid with dialkyl phthalates. I, dibutyl phthalate; II, dicyclohexyl phthalate; III, bis(2-ethylhexyl) phthalate.

In order to obtain information on the mechanism of the reactions of FA with the dialkyl phthalates, IR spectra of untreated FA, the phthalates and of the "complexes" were run. This situation is illustrated in Figure 2, taking III as an example. The IR spectrum of FA (curve a) shows broad absorption bands in the 3,500 to 3,000 cm^{-1}, the 1,750 to 1,625 cm^{-1} and the 1,450 to 1,150 cm^{-1} regions, reflecting the preponderance of OH, COOH and C=O groups. The relatively poor definition of the spectrum is due to overlapping of individual absorptions. The spectrum of III (curve b), shows sharp bands in the 3,000 to 2,800 cm^{-1} region, at 1,735 cm^{-1}, near 1,600 and 1,450 cm^{-1} and between 1,400 and 950 cm^{-1}. There are several bands between 800 and 700 cm^{-1}. This spectrum is identical with spectrum 28 of the Sadtler Standard Spectra. The spectrum of the FA-III "complex" (curve c) shows the principal IR bands of III at the same frequencies at which they occur in the pure compound (curve b), superimposed on the FA-spectrum. There is no indication of a chemical reaction between the two components. The IR spectra of I and II and of their "complexes" with FA provided the same type of information as the data in Figure 2. It appears, therefore, that dialkyl phthalates are adsorbed on the surface of the FA to form stable water-soluble complexes by a mechanism that is as yet unknown.

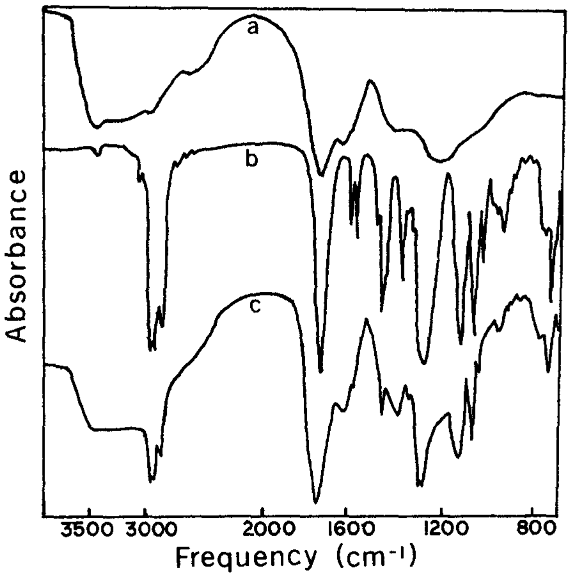

Figure 2. IR spectra of (a) fulvic acid; (b) bis(2-ethylhexyl) phthalate; (c) FA-bis(2-ethylhexyl) phthalate "complex".

Summary

Fulvic acid, a water-soluble soil humic material that occurs widely in soils and waters, can "complex" hydrophobic dialkyl phthalates and make them soluble in water. The extent of the reaction depends on the type of phthalate. Thus, one number-average molecular weight of FA can solubilize four moles of bis(2-ethylhexyl) phthalate but only one mole of dibutyl phthalate, while 2 number-average molecular weights of FA can interact with three moles of dicyclohexyl phthalate. IR spectroscopy failed to provide evidence for the occurrence of chemical reactions between FA and the phthalates. The latter appeared to be adsorbed on the surface of the FA molecule.

Our results show that FA can interact with substantial amounts of hydrophobic organic compounds - some of which may be toxic pollutants such as herbicides, pesticides and oils - solubilize them in water and so modify their mobility, and possibly also their activity, in aquatic environments.

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References

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