sults are also consistent with data from searchlight probing of the lower atmosphere on clear nights in New Mexico (*12*).

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Humic Substances: Fulvic Acid–Dialkyl Phthalate Complexes and Their Role in Pollution

Abstract. *Fulvic acid is a water-soluble humic material with relatively low molecular weight that occurs widely in soils and waters. It can combine with lyophobic organic compounds such as alkanes, fatty acids, and dialkyl phthalates to form stable "complexes" that are soluble in water. Fulvic acid in an aquatic environment may act as a vehicle for the mobilization, transport, and immobilization of organic compounds, some of which may be toxic pollutants.*

Humic substances are among the most widely distributed natural products of plant decomposition on the earth's surface, occurring in soils, lakes (*1*), rivers (*2*), and the sea (*3*). In spite of their extensive distribution, little is known about their chemical structure and synthesis or mechanisms of their degradation and adsorptive properties. Of special interest are fulvic acids which are water-soluble, relatively low-molecular-weight humic materials that can form stable complexes with metal ions and hydrous oxides (*4*), can interact with clay minerals (*4*), and are physiologically active (*5*). Although interactions between fulvic acid and inorganic soil constituents have been investigated, very little is known about reactions of fulvic acid with organic compounds of concern to man, especially with those that are environmental pollutants.

We recently reported the isolation from a fulvic acid of small amounts of normal and branched cyclic alkanes and of fatty acids, ranging from C_{14} to C_{36}, that account for 0.25 percent of its dry, ash-free weight (*6*). Less than 10 percent of the alkanes and fatty acids could be extracted by organic solvents from untreated fulvic acids; the remainder was extractable only after methylation of the fulvic acid and adsorption on neutral aluminum oxide (*6*). Even though the nature of the molecular forces that hold the alkanes and fatty acids to the fulvic acid is still a matter for conjecture, results from infrared spectroscopy indicate that methylation reduces hydrogen bonding in the fulvic acid. This, in turn, may change the conformation of the fulvic acid polymer in such a manner as to make these compounds extractable by organic solvents. We report here the isolation and identification of small amounts of dialkyl phthalates in fulvic acid and suggest a possible role of fulvic acid in pollution.

The fulvic acid was extracted from the Bh horizon of a podzol soil in Prince Edward Island. Methods of extraction, purification, and drying as well as several physical and chemical characteristics of the fulvic acid have been described (*4*). Briefly, the fulvic acid is a chemically and biologically stable polyelectrolyte with a number-average molecular weight (measured by vapor-pressure osmometry) of 951 and contains 9.1 meq of COOH, 6.9 meq of total OH, and 3.1 meq of $C=O$ groups per gram (*4*). In the present investigation 100 g of air-dry fulvic acid (1.0 percent ash) was extracted for 24 hours in a Soxhlet apparatus first with 1 liter of *n*-hexane, then with 1 liter of benzene, and finally with 1 liter of ethyl acetate. The *n*-hexane extract contained small amounts of alkanes and fatty acids, but none of the extracts contained dialkyl phthalates. The remaining fulvic acid (98.5 g) was then methylated with silver oxide–methyl iodide (*7*). Four successive methylations increased the methoxyl content from 0.2 to 28.2 percent. The methylated fulvic acid (75.0 g) was refluxed with 1 liter of *n*-hexane. The *n*-hexane extract contained trace amounts of dialkyl phthalates. The methylated fulvic acid was then dissolved in benzene. The benzene-soluble material (41.3 g) was chromatographed over neutral aluminum oxide (2000 g) and eluted successively with 3000 ml of *n*-hexane, benzene, benzene–ethyl acetate (9:1 by volume), and benzene–ethyl acetate (1 : 1 by volume). Each extract was further fractionated by repeated thin-layer chromatography on Al_2O_3 and silica gel. Only the benzene–ethyl acetate (1 : 1) extract was found to contain dialkyl phthalates. The procedure employed for their isolation was as follows: The benzene–ethyl acetate (1:1) extract (0.51 g) was first separated by preparative thin-layer chromatography on Al_2O_3 with toluene–ethyl acetate (3:1 by volume) as solvent. The material near the solvent front was removed from the plates, extracted with ethyl acetate, and refractionated on Al_2O_3 plates with toluene–ethyl acetate (9 : 1); the yield was 0.04 g of extract. The location of phthalates on the plates was detected by examination under an ultraviolet lamp and by spraying a guide strip with hydroxylamine-ferric reagent (*8*). Four fractions were scraped off the thin-layer chromatographic plates; these fractions were eluted with ethyl acetate and further separated by preparative gas chromatography (Hewlett-Packard model 402 flame ionization detector, 122 × 3 mm glass column packed with 3 percent OV-17 on Chromosorb W HMDS, 60 to 80 mesh, programmed from 200° to 300°C at a rate of 7.5°C per minute). Materials representing the four major peaks, I, II, III, and IV, were eluted from the gas chromatographic column, collected in capillary tubes, and identified by ultraviolet spectroscopy, infrared spectroscopy (as micro KBr pellets on a Beckman IR 12 spectrophotometer equipped with a beam condenser), and mass spectrometric analysis (Consolidated Electrodynamics Corporation model 21-490 mass spectrometer, with the use of a heated direct-inlet probe).

Component I (5.4 mg) was identified as bis(2-ethylhexyl) phthalate, component II (3.5 mg) was dibutyl phthalate, component III (2.0 mg) was dicyclohexyl phthalate, and component IV (2.0 mg) was benzyl butyl phthalate. The ultraviolet, infrared, and mass spectra of each component were identical with those of the known ester to which the component corresponded and which was prepared by esterifying *o*-phthalic acid with the appropriate alcohol or alcohols and using concentrated H_2SO_4 as catalyst. The base peaks in all the mass spectra were at m/e 149, typical of dialkyl phthalates (*9*). The yield of each component was estimated from analytical gas chromatography and from the weight of each fraction. In total, about 13.0 mg of dialkyl phthalates was isolated from 100 g of fulvic acid. On the basis of preliminary experiments with known phthalates, at least 50 percent of the starting material was lost during the separation procedure. On the assumption that similar losses occurred in the case of the fulvic acid extracts, phthalates may account for up to 0.03 percent of the dry weight of the fulvic acid. It is noteworthy that, like alkanes and fatty acids, most of the dialkyl phthalates could be extracted from the fulvic acid only after methylation and adsorption on aluminum oxide; we found only traces of dialkyl phthalates in the original soil sample and in alkaline, extracted, nonpurified fulvic acid.

The origin of the dialkyl phthalates in the fulvic acid is uncertain. Phthalates are used in industry in the preparation of alkyd resins, as plasticizers and lubricants, and for dyes (*10*). We suspected that the phthalates were contaminants that had interacted with the fulvic acid during the extraction and purification procedure. All solvents were purified by distillation through high-efficiency columns and were found to be free of phthalates. Hot toluene washings of a polyethylene bottle used in the extraction procedure did not contain any alkyl phthalates. Prolonged extraction of 50 g of oven-dry Rexyn-101 exchange resin in the Na-form with 300 ml of hot toluene yielded 2.1 mg of solids in which we identified about 0.2 mg of component I and possibly traces of components II and IV. Cifrulak (*11*) reports the occurrence of unidentified phthalates in organic extracts of several soil samples that had been neither methylated nor in contact with exchange resins but that, in contrast to our fulvic acid, had been vacuum-distilled for several hours. The phthalates reported by Cifrulak may have originated from the oil in the vacuum pump or from polluted soils. One cannot, however, exclude the possibility that the dialkyl phthalates were produced biosynthetically. They have been reported to occur in plants (*12*), petroleum (*13*), and as fungal metabolites (*14*).

Administrations of components I and II are toxic to rats (*15*) and rabbits (*16*); component II has a severe effect on the hatching of chicks (*17*). How the interaction of alkyl phthalates with fulvic acid modifies their toxicity merits investigation.

Our results show that fulvic acid can interact with lyophobic organic compounds, some of which may be pollutants, and solubilize them in water by a yet unknown mechanism. Fulvic acid may thus mediate the mobilization, transport, and immobilization of such substances in an aquatic environment.

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Sulfur: Simulated Long-Range Transport in the Atmosphere

Abstract. *One way to examine the question of whether or not air pollutants are transported over distances on a continental scale is by numerical simulation. A simple atmospheric transport and accumulation model, together with mean wind data and an estimated source distribution in Western Europe, were used in this study. The results suggest that Great Britain and Central Europe contribute to the observed concentrations of sulfur in Northern Europe.*

From time to time recently, mention has been made of the possibility that some substantial part of the sulfur component in Scandinavian air and precipitation originates in other parts of Europe (*1, 2*). There is very little solid evidence, however, and few research papers on the subject have appeared. One reason is the obvious lack of pertinent data; compatible observations on a continental scale are difficult to obtain.

Blokker (*2*) has reviewed the mechanisms for removal of atmospheric sulfur compounds as well as the global circulation and the abundance of sulfur compounds in the atmosphere over Europe. He concludes that atmospheric sulfur pollution has increased substantially over Central and Northern Europe in the last several years. However, Eriksson (*3*) has recently reanalyzed the available data and concludes that, "The safest conclusion concerning trends seems to be that the series are too short yet for a firmer conclusion." A trend in either direction might be masked by transient phenomena, as Schmidt and Velds (*4*) have pointed out. They concluded that an observed decrease in SO_2 concentrations in Rotterdam during the winter seasons from 1962 to 1968 can almost completely be explained by meteorological circumstances. In particular, those winters were warmer than usual, so emissions were presumably reduced; and the local weather was characterized by relatively rapid dispersion and early removal of pollutants by precipitation.

The question of trends can be answered conclusively only when a sub-