

red 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 H₂SO₄ 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. How-

ever, 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 SO₂ 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-

stantial monitoring program has been operating for several years. In the meantime, I have attempted to assess the likelihood that pollutants such as sulfur compounds could reasonably be transported from Great Britain and Central Europe to Scandinavia in sufficient quantity to account for a significant portion of the sulfur component observed there.

Even if all the appropriate data were available, conventional diffusion models of the atmosphere obviously could not be expected to provide reliable estimates of concentration patterns over such enormous distances. There is no gen-

erally realistic atmospheric model available for use in continental air pollution problems. The model used here was developed for application on a regional scale (5). In brief, it consists of an array of boxes within the region of interest. The material in question is assumed to be mixed uniformly within each box; various mechanisms operating on the micro- and mesoscales can be expected to contribute to that mixing. Net motion through the boxes can be determined if an appropriate wind field is available, and then, by simple consideration of mass continuity, it is possible to keep track of the transport and accumulation

of pollutants so as to calculate the concentration in each box.

As a first approximation, pollutants are assumed to be contained within the lowest 3 km of the atmosphere. It is further assumed that the transporting wind field can be approximated adequately by the wind at 850 mb (about 1.5 km). Crude estimates of fuel consumption were made from data published by the Organization for Economic Cooperation and Development (6), and sulfur emission rates were assigned to boxes 2° in latitude by 2° in longitude on the basis of a 2.5 percent sulfur content in all the fuel consumed. Each

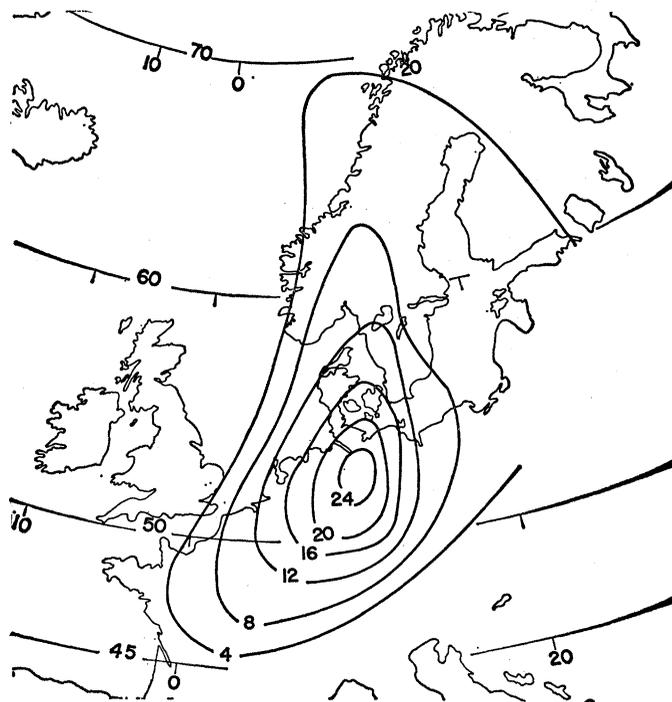
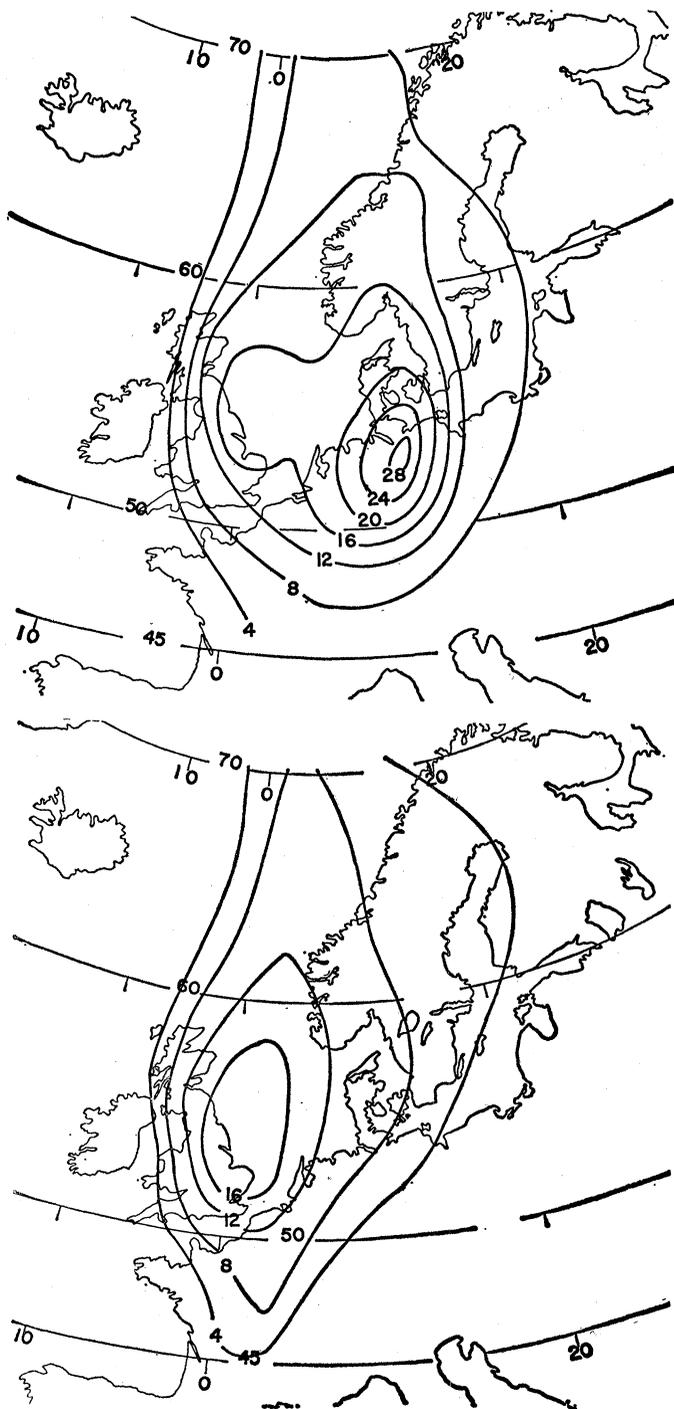


Fig. 1 (above left). Mean concentration of total sulfur (in micrograms per cubic meter) during a simulated air pollution episode in winter. Sulfur emitted in all Western European countries.

Fig. 2 (above right). Mean concentration of total sulfur during a simulated air pollution episode in winter, except that there were no sulfur emissions in the United Kingdom.

Fig. 3 (below left). Mean concentration of total sulfur during a simulated air pollution episode in winter, except that there were no sulfur emissions in Germany, Belgium, Netherlands, and Luxembourg.

box is treated as a uniform area source; emitted material and transported material are assumed to be distributed uniformly in time.

In this model the uniform concentration within a particular box at any time is a function of the box volume, the rate at which material is being imported, the emission rate, the concentration within the box in the preceding time increment, and residual fractions of the three mass terms that describe the amount of material remaining in the box. For box n , that functional relationship is

$$C_{n,t} = \frac{1}{V_{n,t}}(r_{n,t}q_{n,t} + R_{n,t}Q_{n,t}) + \rho_{n,t}C_{n,t-1}$$

where $C_{n,t}$ and $C_{n,t-1}$ are concentrations at time t and $t-1$; $V_{n,t}$ is the box volume, $q_{n,t}$ is the mass of material advected into box n , and $Q_{n,t}$ is the mass of material emitted within box n during time increment t ; and $r_{n,t}$, $R_{n,t}$, and $\rho_{n,t}$ are the residuals of $q_{n,t}$, $Q_{n,t}$, and $C_{n,t-1}$, respectively, which remain in box n at the end of time increment t .

The dimensionless residual fractions are simple geometrical relationships between the wind vector and the box dimensions (5). The computational time increment used here is 5 days in order to enhance the validity of the uniform distribution assumption within these large boxes. If better data were available, it would probably be preferable to use smaller boxes and shorter time intervals to allow for differences and changes that can easily occur on smaller scales.

Seasonal wind data are available in the form of mean vector components and standard deviations along meridional cross sections (7). From these, I constructed wind fields for the 850-mb surface over the area between 10°W and 30°E longitude and 44°N and 70°N latitude. On the basis of these mean wind fields, the seasonal concentration patterns very much resemble large plumes extending from Western Europe through Poland.

However, the vector components of the wind are essentially normally distributed about the means (7); thus numerical simulation is easy and should provide a realistic approximation of individual or sequential wind data. I simulated values of each component at an arbitrary point and constructed new vector fields in such a way that the patterns for each component were the same as in the original mean vector fields of the components. Because the

simulated components vary randomly and independently, the total field of vector sums also varies from one time interval to the next. The concentration pattern shown in Fig. 1 illustrates one simulated 10-day episode of light southwesterly wind, based on the winter season means. The pattern is similar, both quantitatively and qualitatively, to those found by de Bary and Junge (8) and by Odén (9). Two additional patterns, calculated with the wind field of the same simulated episode, show the effects of closing down all fuel sources of sulfur in the United Kingdom (Fig. 2) and all those in Germany, Belgium, Luxembourg, and the Netherlands (Fig. 3). Separate elimination of various major source areas in this way gives some indication of the relative contributions these source areas might be making to the overall pattern in Northern Europe.

In all cases, the concentration indicated is of total sulfur, uniformly distributed in a layer of air 3 km deep. No natural sources have been included, nor is any removal mechanism considered. The sulfur might therefore be in the form of sulfur dioxide, sulfate, or sulfuric acid. Robinson and Robbins (10) estimate that nearly twice as much sulfur enters the atmosphere in the form of hydrogen sulfide as is absorbed in the form of sulfur dioxide by the oceans and vegetation. They also esti-

mate that 80 percent of the remainder ultimately is removed in precipitation.

Concern over long-range transport of various pollutants appears to be growing, and the results shown here suggest that during periods of dry weather, when the major removal mechanism is not operating, sulfur in some form may be carried substantial distances. A cooperative international program to provide all the necessary data is the only way to confirm the extent of that transport.

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Chemically Induced Porphyria: Prevention by Prior Treatment with Phenobarbital

Abstract. *The excessive induction of hepatic δ -aminolevulinic acid synthetase in rats after the administration of porphyria-inducing compounds is prevented by prior treatment with phenobarbital. Studies in vivo and in vitro indicate that phenobarbital prevents the induction of chemical porphyria by increasing the rate of detoxification of inducers by way of drug-metabolizing enzymes of the hepatic endoplasmic reticulum.*

The basic defect in chemically induced and genetically transmitted porphyria is reflected by an increased activity of hepatic δ -aminolevulinic acid synthetase, the first and rate-controlling enzyme in porphyrin and heme biosynthesis (1). Although there are several hypotheses regarding the mechanism of induction of this enzyme (2), virtually nothing is known about the metabolic fate of porphyria-inducing compounds. This latter facet is of importance since the duration and intensity of action of many drugs are largely determined by the speed at which they are metabo-

lized in the liver. Moreover, the activities of drug-metabolizing enzymes in liver microsomes are increased when animals are treated with various hormones, drugs, insecticides, and carcinogens (3). Phenobarbital (PB) has been used as a prototype of the compounds known to stimulate drug metabolism. For example, PB stimulates bishydroxycoumarin [which is 3, 3'-methylene-bis-(4-hydroxycoumarin)] metabolism in vivo in the dog and man, resulting in a decrease of its anticoagulant activity (4). We now show that inducers of porphyria are metabolized by microsomal en-