

at spectra 18 and 24 for two undescribed trihydro derivatives ( $m/e$  403 to 413). The identity of the material for the peak at spectrum 38 ( $m/e$  487 to 497) is unknown, but the major peak at spectrum 63 is Kepone ( $m/e$  487 to 497), as was shown by the full mass spectrum.

Confirmation of Kepone in hexane extracts of soil was by electron impact GCMS set to monitor an ion characteristic of Kepone ( $C_{10}^{35}Cl_7^{37}Cl_2O^+$ ),  $m/e$  454.7 (13). Nanogram quantities well above the 500-pg limit of detection were observed. The presence of up to 3  $\mu g$  of mirex in the same injection gave no interferences at the retention time of Kepone, and its identification was unequivocal.

It appears that these dechlorinated products are formed when mirex bait or mirex deposited on soil particles after leaching from bait are exposed to sunlight, other forms of weathering, and microorganisms over a period of years. As the products are adsorbed onto or covered by soil, they would become less available for transport in the food chain and would be shielded from direct sunlight. The actual quantities remaining after some years is thus open to speculation. Since mirex is normally distributed in treatments at much lower quantities than in the two locations studied, the concentration of residues would also be much reduced and would not be observed in the course of a normal mirex monitoring program.

We feel that this decomposition sequence is likely to occur at any location where mirex or mirex bait is deposited on the soil. Although Kepone is the second most abundant product observed (up to 10 percent compared to recovered mirex), it is just one of a succession of products formed by exposure of mirex to light. This demonstrates a pathway by which mirex can disappear from the environment.

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- Mirex monitoring studies were conducted on samples from the Sebring pond in 1969 and 1970, and the possibility of breakdown of mirex by muck soil microorganisms from this pond was investigated. There were no reports that any mirex degrading microbes were found or that any mirex metabolites were detected. G. P. Markin, personal communication (1972).
- Fresh samples of 4X bait were exposed to ultraviolet light as a thin layer of particles in a Rayonet-type RS reactor for 19.5 hours and subsequently treated as bait from the pond. Gas chromatography analysis showed conversion of mirex to Kepone (0.2 percent), monohydro derivative (4) (19.9 percent), and other minor products.
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- Chemical ionization gas chromatography-mass spectrometry spectra were obtained with a Finnigan 1015 C mass spectrometer, interfaced to a Systems Industries 150 data system. A Varian 1400 GC, equipped with a stainless steel column (1.8 m by 2 mm, inside diameter) packed with 5 percent SE-30, was used as the inlet. Methane, used as the carrier and ionizing gas, was passed directly into the ion source where the pressure was maintained at 1.0 torr, and the heater was programmed from 150° to 240°C at 10°/min. The computer data system provided mass spectra, reconstructed gas chromatograms (RGC) representing normalized total ion current plotted as a function of spectrum number and limited mass range searches (LMS) representing ion clusters of specific masses plotted as a function of spectrum number.
- Confirmation of Kepone was by single-ion monitoring on an electron impact mass spectrometer (Varian CH5) in the low-resolution mode set to observe a characteristic ion in the Kepone spectrum,  $C_{10}^{36}Cl_7^{37}Cl_2O^+$  ( $454.7 \pm 0.1$ ), formed by loss of chlorine from the parent ion at  $m/e$  486 to 495. A Varian gas chromatography instrument equipped with glass columns (3 m by 2 mm, inside diameter) packed with 3 percent OV-101 and 3 percent OV-17 held at 275°C was used as the inlet. Injection of 0.5 ng of Kepone gave 6 percent pen deflection, which was considered the lower limit of detection.
- Mention of a pesticide or a commercial proprietary product in this report does not constitute a recommendation or endorsement of this product by the U.S. Department of Agriculture or by the University of Florida. This study reflects the results of research only. Supported in part by USDA Cooperative Agreement No. 12-14-100-10,953(33). We thank P. Cavalluzzo and P. S. L. Andrade for technical assistance; Drs. E. G. Alley and B. R. Layton for providing the authentic mirex derivatives; and personnel at the USDA-ARS Fire Ant Laboratory, Gulfport, Mississippi, for kindly providing the soil samples.

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## Ultrajiant Urban Aerosol Particles

**Abstract.** Measurements taken 300 meters above ground level show surprisingly high concentrations of ultrajiant aerosol particles both upwind and downwind of the St. Louis, Missouri, urban area. Assuming an average particle density of 2.0 grams per cubic centimeter, concentrations of particles with diameters between 5 and 55 micrometers sampled on 11 different days averaged 31 micrograms per cubic meter upwind and 55 micrograms per cubic meter downwind of the city.

As part of the University of Chicago's participation in Project METROMEX (1), extensive measurements of the airborne concentration of giant (diameter  $> 1 \mu m$ ) and ultrajiant (diameter  $> 10 \mu m$ ) aerosol particles were obtained in the vicinity of St. Louis, Missouri, during July 1975. All measurements were made during midafternoon from an instrumented aircraft flying 300 m above ground level. The speed and mo-

bility of the aircraft allowed collection of aerosol particles from relatively large areas upwind and downwind of the city on each flight.

Even though their low number concentrations make them difficult to measure, ultrajiant particles can compose a significant portion of the total aerosol mass. The high background levels of these particles found upwind of St. Louis and the difficulty in controlling many types of ur-

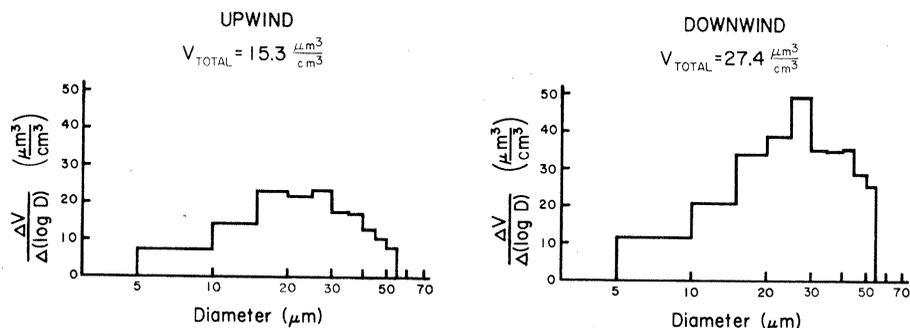


Fig. 1. Average daily volume distributions upwind and downwind of St. Louis.

ban sources (such as the disruption of surface dust by urban automobile traffic) may make clean air standards ( $75 \mu\text{g}/\text{m}^3$ ) difficult to attain. In addition, the increased concentrations of ultragiant particles over and immediately downwind of large cities may partially explain the rainfall enhancement associated with urban areas (2).

Particles were collected by exposing a small (1.0 by 7.5 cm) glass slide covered with a thin layer of high-viscosity silicone oil to the free airstream outside the skin of the aircraft. Each slide was exposed for 3 minutes. At normal aircraft speeds this corresponds to a sampling path length of 13.5 km. Particles captured on the slides were counted and sized manually from photographs taken of each slide. Only particles with diameters larger than  $5 \mu\text{m}$  were analyzed in order to minimize corrections for nonunity collection efficiencies for small particles. To ensure accurate counting statistics, an upper size limit of  $55 \mu\text{m}$  was imposed. The resulting diameter range between  $5$  and  $55 \mu\text{m}$  was evenly divided into ten size categories.

Measurements of the concentrations of aerosol particles upwind and downwind of the St. Louis urban area were obtained on each of 11 days in July 1975. Upwind and downwind locations were chosen from reported surface winds, confirmed by visual observations of smoke plumes and by on-board measurements of the concentration of Aitken particles at each location. Upwind data were typically taken in rural areas 20 to 30 km upwind of the center of the city. Downwind samples were usually taken immediately downwind of the industrial areas along the Mississippi River. A total of 15 upwind and 19 downwind slides were analyzed. If more than one upwind or downwind slide was exposed on a particular day, the results were averaged to get a single upwind and a single downwind particle size distribution for that day. The volume concentrations corresponding to each particle distribution are shown in Table 1. Although there is considerable day-to-day variation in the volume loading of the air, the city air is consistently dirtier than upwind air. Assuming an average particle density of  $2.0 \text{ g}/\text{cm}^3$ , these measurements indicate that the concentrations of particles between  $5$  and  $55 \mu\text{m}$  in diameter average  $31 \mu\text{g}/\text{m}^3$  upwind and  $55 \mu\text{g}/\text{m}^3$  downwind of St. Louis.

In recent studies of suspended particulate matter in air it has generally been concluded that the volume (or mass) distribution of these particles is bimodal (3). The average upwind and downwind volume distributions (Fig. 1) show good res-

Table 1. Daily volume concentrations of particles with diameters between  $5$  and  $55 \mu\text{m}$  upwind and downwind of the St. Louis urban area.

Date (July 1975)	Volume concentration ( $\mu\text{m}^3/\text{cm}^3$ )	
	Upwind	Downwind
1	13.6	20.9
2	17.1	29.3
3	20.4	23.4
7	4.4	8.4
8	14.6	26.7
9	15.6	30.8
10	23.3	41.8
11	16.2	42.3
12	6.6	28.8
16	23.6	27.6
18	12.5	20.5

olution of the upper volume mode and clearly illustrate the increased particulate loading over the city. The location and shape of the upper mode in Fig. 1 are in general agreement with the surface measurements of Okita (4) and Jaenicke and Junge (5), and with Hindman's aircraft measurements in a paper mill plume (6). These results indicate typical number concentrations of airborne particles larger than  $10 \mu\text{m}$  in diameter of  $7,500 \text{ m}^{-3}$  upwind and  $11,000 \text{ m}^{-3}$  downwind of the city. Particles larger than  $30 \mu\text{m}$  in di-

ameter were found in concentrations of  $200 \text{ m}^{-3}$  upwind and  $425 \text{ m}^{-3}$  downwind of the city. Such large concentrations show that sedimentation is relatively ineffective in removing these ultragiant particles from the air during periods of active mixing in the boundary layer. Unless scavenged by rain or ingested into clouds, giant and ultragiant urban aerosol particles will affect the quality not only of city air but also of air for many tens of kilometers downwind.

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## Short-Period Climatic Fluctuations: Effects on Diatom Biomass

**Abstract.** *An analysis of the weekly averages of diatom biomass measured near the coast of Southern California ( $32^{\circ}50'N$ ,  $117^{\circ}10'W$ ) during the period from 1928 through 1939 indicates that three major blooms account for 85 percent of each year's diatom biomass. The average duration of a single bloom is 5.5 weeks. The diatom blooms coincide with upwelling, but their individual characteristics depend on the detailed features of the circulation patterns of the water masses. That is, if upwelling takes place after a large influx of subtropical or even tropical water because of the slackening California Current, the resulting diatom blooms are smaller by several orders of magnitude than those observed when the flow of the current is strong. This influx of subtropical water into the region is reflected in positive anomalies of temperature, salinity, and sea level.*

Short-period climatic fluctuations often result in major changes in the chemical and physical parameters of the oceans (1). Most studies of the effects of such variations on the biological populations in the oceans have dealt with fishes (2). I describe here the effects of short-period climatological changes on the abundance of diatoms, at lower trophic levels than fishes, near the coast of Southern California during the period from 1928 through 1939. The phytoplankton ecology of this region has been extensively studied over periods ranging from hours to several months (3). I attempt to show here that, in addition to short-

term variations in diatom biomass as noted by these investigators, there are also year-to-year changes caused by climatological fluctuations.

The response of the diatom growth rate to environmental changes can be rapid (a few days or weeks). A data set based on daily or weekly samples acquired over a period of several years is therefore needed in order that a thorough analysis of the relationship between fluctuations in environmental factors and in diatom abundance can be carried out. Recently I gained access to the original data records of the net tow phytoplankton collections of W. E. Allen (4). Gathered