can keep up with a rising sea only if the sea level rise is no more than a few millimeters per year. Rapid oscillations of sea level occurred during much of the Quaternary (*20*), and these rapid oscillations probably occasioned interruptions in the stratigraphic records of extant reefs. Evidence for the interruption or termination of reef growth can indeed be found in drill holes (*21*) and seismic reflection profiles (*22*), although it is not certain that these interrupted records are entirely responses to rapidly rising sea level.

The same principle of reef growth limitation by a rising sea, and perhaps much the same absolute upper limit on reef growth rates, must have applied during much of geological time. Reef structures thus not only indicate rather precise paleobathymetric limits during the formation of these features but can also define a narrow range for long-term rates of sea level change.

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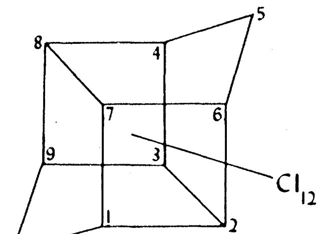
Mirex in the Environment: Its Degradation to Kepone and Related Compounds

Abstract. *The chlorocarbon mirex undergoes slow, successive loss of chlorine in the field to a series of related compounds that had lost one or more chlorine atoms. Soil samples were recovered 12 years after treatment at 1 part per million (ppm), and ant bait was recovered 5 years after an aircraft crash. As much as 50 percent of the original mirex was recovered at levels of about 0.5 and 640 ppm, respectively. Kepone was present at levels of 0.02 ppm in soil and 10 ppm in the bait or up to 10 percent of the recovered mirex, as determined by combined techniques of chromatography and mass spectrometry. This constitutes the first observation of the degradation of mirex in nature, and demonstrates a pathway for its eventual disappearance from the environment.*

We have recently detected degradation products of mirex (**1**) in samples from two locations in the field where unusually large amounts of mirex were deposited and left exposed to the elements for 12 and 5 years. The presence of Kepone (**2**) and several other dechlorinated derivatives of mirex was confirmed in extracts. Recent concern over environmental contamination involving Kepone prompts this report.

Mirex, which is the chlorocarbon insecticide dodecachloropentacyclo$[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]$decane (**1**), is the most effective bait toxicant known for use against imported fire ants, *Solenopsis invicta* and *Solenopsis richteri*. The bait is prepared by dissolving mirex in soybean oil which is then adsorbed onto corncob grits. A single application of this formulation, when applied by aircraft at the rate of 1.7 g/acre (4.2 g/ha) of actual mirex, provided 97 to 99 percent suppression of *S. invicta* (*1*). Mirex has been reported to be highly resistant to metabolic attack by soil microorganisms (*2*) and higher organisms including rats (*3*) and cattle (*4*), but was dechlorinated slowly to a monohydro derivative (**3**) by anaerobic microbes (*5*). Mirex, exposed to sunlight as a deposit on a silica gel thin-layer plate, was slowly converted to several products including two monohydro derivatives (**3 and 4**) of mirex, Kepone (**2**) and a monohydro derivative of Kepone (**6**). Mirex was shown to undergo photolytic dechlorination in solution (*6*) and on egg solids (*7*) with ultraviolet light to mono and dihydro derivatives **3** to **6**; Kepone was shown to undergo analogous loss of chlorine to a monohydro derivative (*6*).



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In 1962, mirex on attapulgite clay was applied as a residual treatment for fire ant control to experimental plots near Gulfport, Mississippi, at a dosage of 1 pound of mirex per acre (1120 g/ha) (*8*). Soil cores and samples of loose sandy soil were gathered from three plots in 1974 and held in sealed metal cans until extraction. Individual plugs or mixed soil samples (170 g) were stirred with hexane at room temperature for 24 hours. Also, 25-g samples were extracted with acetone in a Soxhlet extractor for four complete cycles in less than 2 hours. The samples were concentrated to 5 ml on a rotary evaporator, diluted with 250 ml of hexane, and again concentrated to 10 ml by evaporation. Portions of the soil samples were diluted for gas chromatographic (GC) analysis; the remainder was concentrated for gas chromatographic–mass spectral (GCMS) analysis.

In 1969, a plane carrying Mirex Granu-

Table 1. Compounds and concentrations, in parts per million (ppm), found in recovered soil and bait samples by electron capture gas chromatography.

Compounds	Tr*	Gulfport samples (ppm)†			Sebring samples (ppm)	
		Plot 27	Plot 42	Plot 70	Surface bait‡	Muck
Mirex (**1**)	1.00	0.497	0.310	0.192	633	0.206
Monohydro (**3**)	0.76	0.014	0.015	0.010	39	0.013
Monohydro (**4**)	0.67	0.110	0.092	0.054	65	0.020
Dihydro (**5**)	0.52	0.019	0.010	0.012	14	0.012
Kepone (**2**)	0.48	0.021	0.026	0.019	10	0.015
Dihydro (**6**)	0.42	0.021	0.018	0.008	17	0.005

*Tr, retention time relative to mirex (1.00) on a DC-200 column. †Soil extracted with acetone. ‡Bait mixed with soil in unknown proportion.

lated Bait 4X crashed at the edge of a small, shallow pond near Sebring, Florida, and dumped its entire load of bait into the pond. The resulting layer of bait, which contained 0.3 percent (by weight) of mirex (3000 ppm), covered an area of approximately 3 m in diameter and about 0.25 m deep in a location which is usually under about 0.2 to 0.5 m of water. The water has been observed to recede in the spring, which exposed the surface bait to direct sunlight. Samples of bait and underlying muck (70 g) were obtained during a dry period in March 1974 (*9*) and extracted with acetone in a Soxhlet extractor for four complete cycles in 2 hours. The extracts were concentrated to 5 ml with a Kuderna-Danish apparatus, diluted with 250 ml of hexane, and again reconcentrated to 5 ml. Portions of extracts were applied to thin-layer chromatographic (TLC) plates that had been coated with silica gel G (250 μm, Analtech). The plates were developed twice with *n*-heptane to a height of 10 cm, and three areas were scraped from the plates: the mirex area (R_F 0.8 to 0.9); an area immediately below the mirex (R_F 0.6 to 0.8); and the remainder of the plate (R_F 0.0 to 0.6). The silica gel from each area was extracted three times with 10-ml portions of hexane which was concentrated for GC and GCMS analysis.

The GC analyses were performed with Varian model 2100 instruments equipped with tritium electron capture detectors and glass columns (1.8 m by 2 mm, inside diameter) with helium or nitrogen carrier gas at flow rates of 20 to 23 ml/min. Columns were packed with 3 percent SE-30, 3 percent DC-200, 3 percent OV-101, or 1.5 percent OV-17 plus 1.95 percent QF-1 on Gas-Chrom Q.

Analysis by GC of crude extracts and TLC samples showed detectable quantities of mirex (**1**), dechlorination products (**3** to **6**), and Kepone (**2**, Table 1). The peaks coincident with those of authentic compounds **1** to **6** on all columns (*6, 7*) were quantitated. The distribution of degradation products obtained from soil and bait samples was remarkably similar to that obtained by photolysis of mirex (i) on silica gel TLC plates (*6*), (ii) in hexane solution (*6*), and (iii) in fire ant bait (*10*). The total masses of organochlorine compounds were determined by peak height, and calculations were made of their composition.

The concentrations of mirex plus mirex-related organochlorine compounds detected in the soil study (about 0.7, 0.5, and 0.3 ppm) represent about 50 percent of the mirex applied 12 years before. Mirex comprised 72.9, 65.9, and 65.1 percent of these residues, and Kepone comprised 3.1, 5.5, and 6.3 percent, respectively. In the Sebring bait and muck samples, mirex comprised 81.4 and 75.9 percent of the total organochlorine residues, respectively, while Kepone comprised 1.3 and 5.7 percent, respectively. Although the analyses varied slightly with polarity of the columns used, identities were confirmed on three columns. No interfering peaks were seen for compounds **1** to **6** in blanks of soil samples obtained locally. Several commercial samples of mirex from 1960, 1972, and 1975 had no other compounds present.

Methane chemical ionization mass spectrometry (CIMS) confirmed the existence of mirex and related compounds in the bait sample. The spectrum of mirex exhibited a simplified fragmentation pattern compared with the electron impact mass spectrum (*11*). The predominant ion seen for mirex was the molecular ion minus one chlorine atom (M − 35, *m/e* 505 to 515) and cleavage fragments of the pentacyclodecane nucleus, $C_5Cl_6^+$ (*m/e* 270 to 276) and $C_5Cl_5^+$ (*m/e* 235 to 241) (*12*). Authentic dechlorinated products exhibited similar fragmentation with major, unique clusters at *m/e* 471 to 481 for the monohydro derivatives (**3**, **4**); *m/e* 437 to 447 for the dihydro derivatives (**5**, **6**); and *m/e* 487 to 497 for Kepone. Cleavage of the pentacyclodecane nucleus gave characteristic fragments for $C_5Cl_6^+$ (*m/e* 270 to 276) and $C_5Cl_5^+$ (*m/e* 235 to 241), depending on the location of replaced chlorines.

In addition to mass spectra, the computer provided reconstructed gas chromatograms (RGC) (*12*) and limited mass searches (LMS) (see Fig. 1A) of the materials extracted from the TLC area immediately below mirex (R_F 0.8 to 0.6). The RGC indicated the presence of two peaks, and the LMS showed the presence of two monohydro derivatives. The RGC from extracts of the bottom of the TLC plate (R_F 0.0 to 0.6) showed the presence of seven compounds, while the LMS (Fig. 1B) showed two dihydro compounds at spectra 49 and 53. The earlier eluting materials gave an LMS peak at spectrum 6 for what is probably a previously undescribed tetrahydro derivative (*m/e* 369 to 379) and two LMS peaks

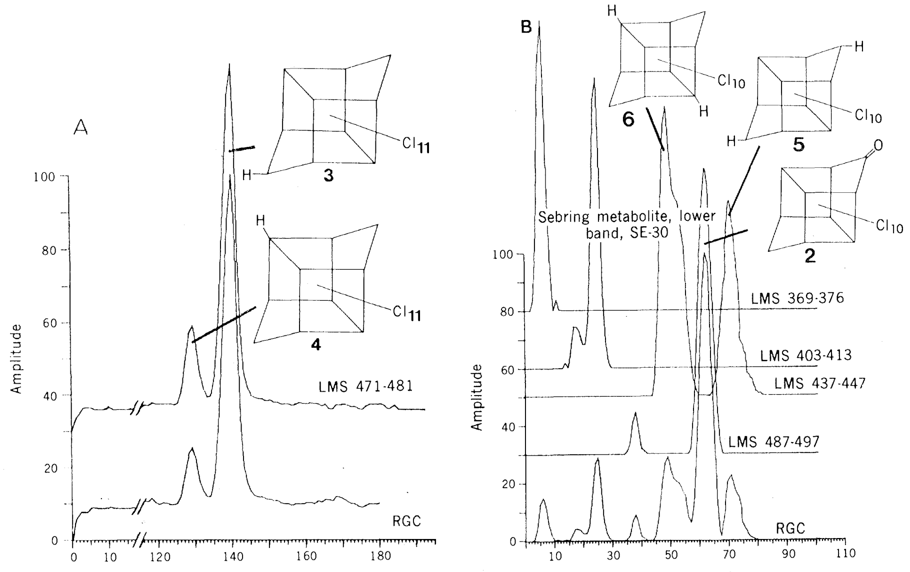

Fig. 1. (A) Computer-reconstructed gas chromatograms (*RGC*) and limited mass chromatograms (*LMS*) from stored chemical ionization mass spectra. Fragments from two monohydro derivatives (**3** and **4**) of mirex were observed. (B) Kepone (**2**) and two dihydro derivatives (**5** and **6**) were observed.

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 μg 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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10. 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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12. 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.
13. 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, $C_{10}{}^{35}Cl_7{}^{37}Cl_2O^+$ (454.7 ± 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.
14. 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.

1 June 1976

Ultragiant Urban Aerosol Particles

Abstract. *Measurements taken 300 meters above ground level show surprisingly high concentrations of ultragiant 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 μm) and ultragiant (diameter > 10 μm) 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 mobility 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, ultragiant 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-

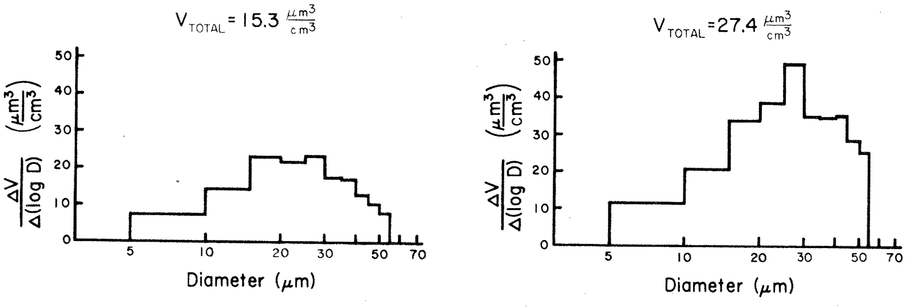

Fig. 1. Average daily volume distributions upwind and downwind of St. Louis.