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Impact of Former Pesticide Application Facilities on Adjacent Surface Waters

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The presence of organochlorine (OC) insecticides (*i.e.* DDT, aldrin, dieldrin, endrin, toxaphene, chlordane, endosulfan, heptachlor and hexachlorocyclohexane (HCH)) in surface waters and sediments adjacent to, or nearby agricultural land and industrial facilities has been thoroughly documented (Kaminsky *et al.* 1983; Colombo *et al.* 1990). Off-site migration occurs primarily through adsorption onto particulate matter in both surface waters and stormwater runoff, and as drift during pesticide application. Atmospheric transport and subsequent deposition are important globally, but typically result in low level, local contamination. Due to their hydrophobic nature, OC insecticides that have entered the aqueous environment tend to accumulate in biota or associate with particulate matter, eventually settling to the bottom sediments. The latter is an important fate process for these pollutants, because most of the OC insecticides are more rapidly degraded by anaerobic biodegradation than by any other degradation process. For this reason, a survey of residues in sediment samples can provide useful information concerning the type and extent of contamination and degree of degradation of hydrophobic pollutants.

The data presented here are based on a larger study of contaminants in sediments from throughout the State of Florida (Delfino *et al.* 1991). The primary purpose of that study was to determine the types and concentrations of Section 307(a) Federal Clean Water Act organic priority pollutants (OPPs) in water and sediments adjacent to, nearby or downstream from potential pollutant sources. Sampling sites were chosen based on the suspected magnitude of contamination and the likelihood of that contamination migrating off-site. Thirty-one sites were chosen throughout the state of Florida.

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Samples were extracted and analyzed by gas chromatography/electron ionization mass spectrometry (GC/EI) using an ion trap detector.

The purpose of the research reported here was to more thoroughly study some of the sediment extracts from selected sites for OC insecticides and their degradation products in order to establish the extent of contamination and degradation of these compounds adjacent to the sites. Four sites with the highest OPP pesticide contamination were selected from the larger study. Sample extracts were analyzed by both GC/EI and gas chromatography/ negative chemical ionization mass spectrometry (GC/NCI).

MATERIALS AND METHODS

The sampling locations chosen for investigation included two Palm Beach County sites, one Lee County site and one Polk County site. Selected samples (from a total of 10 collected at each site) were chosen for further evaluation. The type of facility adjacent to each sampling site, the dates of operation of the facilities and previously reported off-site sediment contamination are listed in Table 1. A site map and detailed site descriptions are included in Delfino *et al.* (1991).

Table 1. Sampling locations, adjacent facilities and previously reported sediment contamination

LOCATION	TYPE OF OPERATION	DATES	CONTAMINATION REPORTED
Palm Beach County	Pesticide application	1972-1984	DDE (0.89-3.22 mg/kg)
			DDD (0.21-7.78 mg/kg)
Palm Beach County	Pesticide application	1969-1980	DDE (0.57-2.40 mg/kg)
			DDD (0.18-1.07 mg/kg)
Lee County	Pesticide application	1973-1985	DDT (0.32-1.93 mg/kg)
			DDE (1.78-6.17 mg/kg)
			DDD (0.13-72.1 mg/kg)
Polk County	Pesticide blending/ manufacture/storage	1940-1987	DDE (0.18-0.71 mg/kg)
			DDD (0.49-0.98 mg/kg)
			Chlordane (2.15 mg/kg)

A description of the sediment collection and extraction procedure has been reported by Delfino *et al.* (1991) and Davis *et al.* (*submitted to J Chromat 1992*). Briefly, sediment samples were collected using a petite ponar dredge. The samples were stored on ice during transport to the laboratory, where they were then stored at -20°C.

Approximately 30 g wet sediment were extracted by sonication in acetonitrile. The acetonitrile extract was concentrated to 6 ml and was termed the "crude" extract.

Two milliliters of the "crude" extract were passed through a C18 solid-phase extraction cartridge and analyzed by GC/NCI. The remaining 4 ml were used in the liquid-liquid extraction described below.

The "crude" extract (after the addition of 50 ml deionized water) was extracted with methylene chloride. This extract was concentrated to a final volume of 0.5 ml. The final extract was centrifuged for 15 min to settle out any particulates, and analyzed by GC/EI.

GC/EI: A Perkin-Elmer model 8500 GC interfaced with a Perkin Elmer model 6210 ion trap detector was used for GC/EI. The column was a 30 m DB5 column (0.25 μm film thickness, 0.25 mm i.d., J&W Scientific). The injector temperature was 250°C. The oven temperature program was 50°C (for 1.5 min) to 130°C (for 3.0 min) at 20°C/min, 130°C to 180°C at 12.0°C/min and 180°C to 300°C (for 32.0 min) at 7°C/min. GC/NCI: A Finnigan MAT 4500 GC/MS system was used for GC/NCI. A 30 m DB5 column (0.25 μm film thickness, 0.25 mm i.d., J&W Scientific) was used. The injector temperature was 265°C. The oven temperature program was 50°C (for 1 min) to 280°C (for 10 min) at 8°C/min. The source temperature was 100°C, and methane was used as the buffer gas.

Recovery data for 12 OCs spiked onto sediment samples (2 - 5 mg/kg dry sediment) and into "crude" extracts (3 - 6 ug/ml) were used as indicators of overall extraction recovery for the OC insecticides and their degradation products. The OCs chosen for the recovery tests included alpha-HCH, beta-HCH, delta-HCH, gamma-HCH (lindane), heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, DDT, DDD and DDE. Recovery results ranged from 27 ± 18% for endrin to 100 ± 51% for DDE.

RESULTS AND DISCUSSION

Nine compounds were positively identified, while four compounds were tentatively identified. Positive identifications, based on both mass spectrum and retention time (retention window 10 sec.), were confirmed with authentic standards. Tentative identifications were assumed when the mass spectrum of the sample closely matched a spectrum found in the literature or Wiley/NIST mass spectral library. The compounds detected included formerly or currently used pesticides, contaminants present in pesticide formulations, pesticide degradation products and a number of presently unidentified halogenated compounds

DBP, 4,4'-dichlorobenzophenone, was positively identified by GC/EI in one sample from Lee County. The base peak (m/z 139) represents a *p*-chlorophenyl carbonyl ion resulting from alpha-cleavage of the molecular ion (m/z 250). Other minor fragments result from losses of CO, HCl and Cl· (McKinney *et al.* 1974). DBP is an anaerobic biodegradation and photodegradation product of DDT (Fries 1972; van Middelem 1966).

DDMU, 1-chloro-2,2-bis(*p*-chlorophenyl)ethylene, was tentatively identified by GC/EI in six samples from Lee County and both Palm Beach County sites. Identification was based on comparison of the sample spectra with a standard spectrum found in the Wiley/NIST mass spectral library. The molecular ion is relatively stable (relative intensity about 60%) and occurs at m/z 282. A loss of Cl_2 from the molecular ion yields a base peak at m/z 212. Other fragments result from losses of HCl and Cl (McKinney *et al.* 1974). DDMU is a degradation product of DDT under both aerobic and anaerobic conditions (Fries 1972).

The *o,p'*-isomers of DDT, DDD and DDE were positively identified by GC/EI in at least one sample from each site. *o,p'*-DDT was detected in two samples from Lee County and Polk County. *o,p'*-DDD was found in every sample analyzed, and *o,p'*-DDE was found in two samples from Lee County. The EI mass spectra of the *o,p'*-isomers are identical to those of the *p,p'*-isomers. DDT and DDD have similar spectra. The base peak of both compounds is m/z 235, representing the $C_{13}H_9Cl_2^+$ ion. The parent ions are very weak (relative intensity <1%). Other characteristic fragments, representing losses of Cl atoms, occur at m/z 200 and 165. The base peak of DDE is m/z 246, representing a loss of two Cl atoms from the molecular ion. A moderately stable (relative intensity about 50%) molecular ion exists at m/z 318. Other fragments correspond to losses of HCl and Cl (McKinney *et al.* 1974). The *o,p'*-isomers of both DDT and DDD are present, as impurities, in technical grade DDT. The *o,p'*-isomers of DDD and DDE may be formed during DDT degradation (Melnikov 1971). Although DDT is no longer used in U.S., residues of *p,p'*-DDT, *p,p'*-DDD and *p,p'*-DDE were found at all of the sites examined (Delfino *et al.* 1991).

Chlorothalonil, 2,4,5,6-tetrachloro-1,3-benzendicarbonitrile, was positively identified by GC/EI in one sample from Lee County. An isomer of chlorothalonil, 3,4,5,6-tetrachloro-1,2-benzendicarbonitrile, was tentatively identified by GC/EI in this sample. Identification of the isomer was based on comparison of the sample spectrum with one present in the Wiley/NIST mass spectral library. The molecular ions and base peaks of both isomers occur at m/z 266. Minor fragments result from losses of CN and Cl. Chlorothalonil is a fungicide which is registered in the U.S. for use on a variety of fruits and vegetables (CPCR 1990).

Nonachlor, 1,2,3,4,5,6,7,8,8-nonachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene, was tentatively identified by GC/EI in two samples from Polk County. Identification was based on comparison of the sample spectra to those present in the Wiley/NIST mass spectral library and reported by Damico *et al.* (1968). A loss of Cl from the molecular ion yields a very strong base peak at m/z 409. Nonachlor is a contaminant found in both technical grade chlordane and heptachlor (Melnikov 1971). Heptachlor is still used in the U.S. for termite control (CPCR 1990). Chlordane is no longer used, but it was previously detected in one sample from this site (Delfino *et al.* 1991).

Several other compounds were detected by GC/EI, but not identified. One group, containing the m/z 235 and 165 ions characteristic of DDT and DDD, most likely includes various DDT degradation products and isomers (Sundstrom and Jansson 1985). These compounds were detected in seven samples from Lee County and both Palm Beach County sites. Four other unidentified halogenated compounds were found at the Lee County site (Figure 1). The apparent molecular weights of these are 187, 220, 232, 332 daltons. The lack of fragmentation of these compounds hindered structural elucidation and suggested that they contain aromatic or cyclic groups.

Endosulfan I, endosulfan II and endosulfan sulfate were positively identified by GC/NCI in six Lee County samples. The GC/NCI spectra of endosulfan I and endosulfan II are virtually identical. The molecular ions and base peaks of both compounds occur at m/z 406. A fragment at m/z 372 represents a $(M-Cl+H)^-$ ion (Stemmler and Hites 1988). Some minor fragments include losses of Cl and HCl. The base peak of endosulfan sulfate is m/z 386 and represents the loss of a HCl group from the molecular ion. The molecular ion, m/z 422, is relatively abundant (Stemmler and Hites 1988). A minor fragment at m/z 352 represents a loss of two Cl atoms from the molecular ion. Technical grade endosulfan is composed of two isomers, endosulfan I and endosulfan II. Endosulfan is still used in the U.S.; it is registered for use on tobacco, ornamentals and a variety of fruits and vegetables (CPCR 1990). Endosulfan sulfate is a major degradation product of endosulfan, and occurs from the oxidation or biotransformation of either isomer (Melnikov 1971).

Chlorbicyclen, 5,6-bis-(chloromethyl)-1,2,3,4,7,7-hexachlorobicyclo-(2,2,1)-2-heptene, was positively identified by GC/NCI in one sample from Lee County. The molecular ion, m/z 398, is the base peak. A loss of HCl

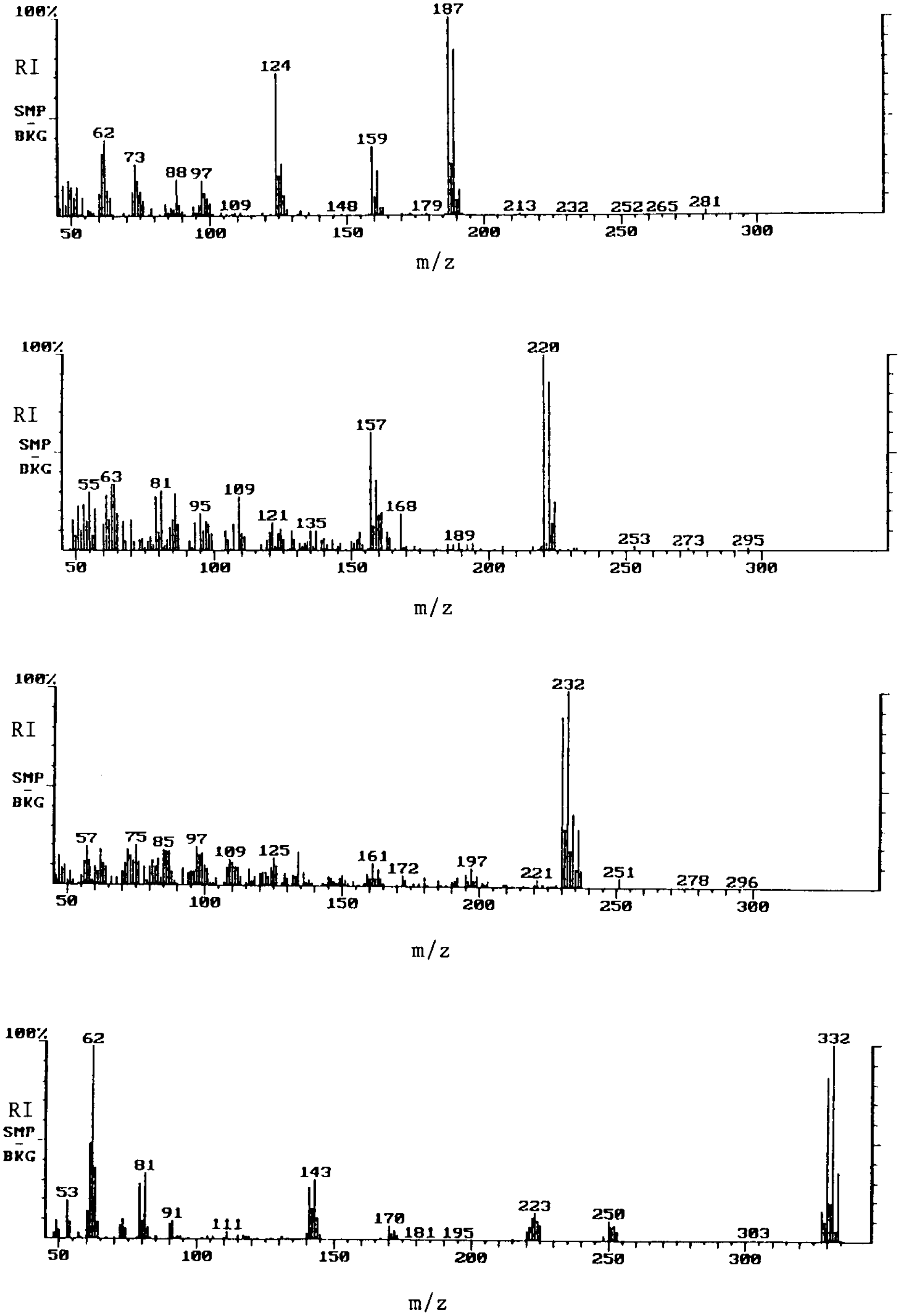

Figure 1. GC/EI mass spectra of unidentified halogenated compounds.

yields a fragment at m/z 362. The retro-Diels-Alder fragmentation of the molecule in combination with the loss of a Cl atom yields a $C_5Cl_5^-$ ion at m/z 235 (Dearth and Hites 1991). Chlorbicyclen is a minor component (about 5%) of technical grade chlordane (Dearth and Hites 1991).

Toxaphene was tentatively identified by GC/NCI in seven samples from Lee County and Palm Beach County. Identification was based on comparison of the sample spectra with those found in the literature. Two of the most abundant and toxic components of technical grade toxaphene are toxicant A and toxicant B. Toxicant A is a $C_{10}H_{10}Cl_8$ derivative. The base peak of toxicant A is m/z 377, representing a loss of HCl from the molecular ion. A weak molecular ion appears at m/z 412. Minor fragments result from subsequent losses of Cl and HCl. Toxicant B is a $C_{10}H_{11}Cl_7$ derivative. The base peak of toxicant B (m/z 343) represents the loss of Cl from the molecular ion. The molecular ion is not present in the spectrum and some minor fragments represent losses of Cl and HCl groups (Rosen 1987). Toxaphene is no longer used in the U.S. (CPCR 1990).

Fourteen other halogenated compounds were detected but not identified, by GC/NCI. Molecular weights ranged from 230 to 462 daltons. Since GC/NCI spectra typically contain few fragments, structure elucidation of these compounds is difficult.

The former pesticide application facilities examined in this study remain a source of OC insecticide contamination to adjacent surface waters. We developed our source hypotheses based on the types and concentrations of the residues found, current or past use of these insecticides and past management practices of the nearby facilities. It is likely that the following residues originated from these facilities: DDT, DDD, DDE, DBP, DDMU, endosulfan I and II, endosulfan sulfate and nonachlor. We are uncertain at present that the facilities were responsible for residues of toxaphene, chlorbicyclen, chlorothalonil, 3,4,5,6-tetrachloro-1,2-benzendicarbonitrile and the unidentified halogenated compounds.

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