Degradation of Malathion, Endosulfan, and Fenvalerate in Seawater and Seawater/Sediment Microcosms

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Two experiments were carried out to determine the persistence of malathion, endosulfan, and fenvalerate in seawater and seawater/sediment microcosms. The first experiment was carried out over 40 days using autoclaved and unsterile filtered seawater in half-liter flasks incubated under laboratory light at room temperature (20 °C). The second experiment utilized 7-cm sediment cores taken from a tidal creek at low tide with 130 mL of overlying seawater. Pesticide-fortified cores were incubated under laboratory light at 20 °C for 20 days. Half-lives of the pesticides in unsterile seawater at pH 8.0 were endosulfan I = 4.9 days, endosulfan II = 2.2 days, malathion = 2.6 days, and fenvalerate = 17 days. Half-lives of compounds in the seawater/sediment system at pH 7.3–7.7 were endosulfan I = 22 days, endosulfan II = 8.3 days, malathion = 2.0 days, and fenvalerate = 12 days. Endosulfandiol was identified as a degradation product of endosulfan.

Pesticides used for commercial agricultural purposes have the potential to greatly affect nontarget organisms due to the large amounts of chemicals used and manner of pesticide application. This is especially true for chemicals applied to croplands in coastal zones where fields are adjacent to ecologically delicate estuaries and salt marshes. Losses from aerial spraying, volatilization, and runoff are considered to be important in the transport of pesticides to the aquatic environment, so there is a compelling need to understand the behavior of pesticides in agricultural runoff and the impact of these pesticides on downstream water quality (Willis and McDowell, 1982).

According to the South Carolina Department of Wildlife and Marine Resources (1980), pesticide-related fish kills have been increasing in the estuaries of South Carolina since 1972. Throughout the 1970s and early 1980s, fish kills have been attributed to endosulfan, malathion, parathion, and toxaphene. In 1982, toxaphene was banned (*Fed. Reg.*, 1982) and was replaced in coastal South Carolina by fenvalerate, a pyrethroid. Recent fish kills have been caused by endosulfan, malathion, and fenvalerate (Scott et al., 1987). Fenvalerate and endosulfan are so toxic that the U.S. Fish and Wildlife Service (1984) has put them in their most lethal category, "supertoxic", reserved for chemicals having an LC_{50} below 0.01 mg/L to rainbow trout.

The accumulation of residues in aquatic organisms is a function of the pesticide concentration to which they are exposed and the exposure time. It is therefore important to know the persistence of these compounds in the estuarine environment. Numerous studies of the persistence of pesticides in freshwater have been carried out; however, far fewer seawater studies have been published. In this paper we report the persistence of malathion, endosulfan, and fenvalerate in seawater and seawater/sediment microcosms and the identification of an endosulfan degradation product.

MATERIALS AND METHODS

Chemicals. Malathion (99%), endosulfan I (99%), endosulfan II (97%), and fenvalerate (99%) were obtained from the EPA Repository for Pesticides and Industrial Organic Chemicals (Research Triangle Park, NC). Endosulfandiol, endosulfan ether, and endosulfan lactone were obtained from Crescent Chemical Co. (Hauppauge, NY) at ≥99% purity. Organic solvents used were pesticide residue analysis quality. Floridin Co. 60/100 PR grade Florisil (Berkeley Springs, WV) activated at 140 °C and ACS-grade anhydrous sodium sulfate baked at 400 °C in a muffle furnace were used for sediment cleanup.

Seawater Experiment. Seawater (salinity 34 ppt) obtained from North Inlet estuary, Georgetown County, SC, was filtered through 0.45-μm cellulose acetate filters (Millipore Corp.), and 450 mL was placed in each of 28 500-mL Erlenmeyer flasks. Fourteen of these flasks were autoclaved and cooled to room temperature. Each flask (unsterile and autoclaved) was then fortified with 122 ng of malathion, 28 ng of endosulfan I, 20 ng of endosulfan II, and 90 ng of fenvalerate in 0.5 mL of acetone. The flasks were plugged with two 1.5-cm-thick pieces of polyurethane foam (PUF) in order to maintain an aerobic environment. The first plug of PUF was used to adsorb any pesticides that may have volatilized, and the second plug was used to protect the first from atmospheric contamination. The flasks were incubated under laboratory light at 20 °C. Duplicate flasks from each of the two groups, unsterile and autoclaved, were sampled on days 0, 2, 4, 8, 16, 32, and 40.

Seawater/Sediment Microcosm Experiment. Sediment cores and about 130 mL of overlying seawater (salinity 30 ppt) were obtained from Leadenwah Creek located south of Charleston, SC, the site of repeated fish kills (Scott et al., 1987). The cores, averaging 7 cm in depth, were obtained in 22-cm-length, 5-cm-i.d. glass tubes. The sediment had a moisture content of 60% and contained 1.22% ± 0.30 total organic carbon (TOC) on a dry weight basis by oxidative combustion after leaching with 40% phosphoric acid solution to remove carbonate. pH and E_h determinations were made on an Orion Research Ionalyzer, Model 399A, with a combination pH electrode using a Ag/AgCl reference and a platinum wire electrode referenced against a saturated Ag/AgCl, KCl electrode, respectively. The performance of the platinum electrode was checked against Zobell's solution (Zobell, 1946). The pH of the overlying seawater averaged 7.7, and the pH of the interstitial water in the sediment layer at 1.5-cm depth averaged 7.3. E_h values for sediment at 1.5-cm depth and for the overlying seawater were 29 ± 36 and 394 ± 90 mV, respectively. pH and E_h measurements were made just before sampling. Cores were fortified with 3669 ng of malathion, 849 ng of endosulfan I, 591 ng of endosulfan II, and 2727 ng of fenvalerate by pipeting 0.5 mL of acetone solution into overlying water with gentle agitation. PUF plugs were utilized as above. Cores were incubated at 20 °C under laboratory light for the duration of the experiment. Duplicate cores were sampled on days 0, 1, 2, 4, 9, and 20. Water, sediment, and PUF were analyzed separately according to methods described below.

Analytical Procedure. *Water.* Water-borne pesticides were extracted on 6-mL SPE C_8 columns (J. T. Baker Chemical Co., Phillipsburg, NJ). Before use, C_8 cartridges were extracted in a Soxhlet apparatus for 3 h with 1:1 ethyl ether/*n*-hexane and dried in a heated vacuum desiccator at 40 °C. Immediately before sampling, the cartridges were activated by pulling 3 mL of

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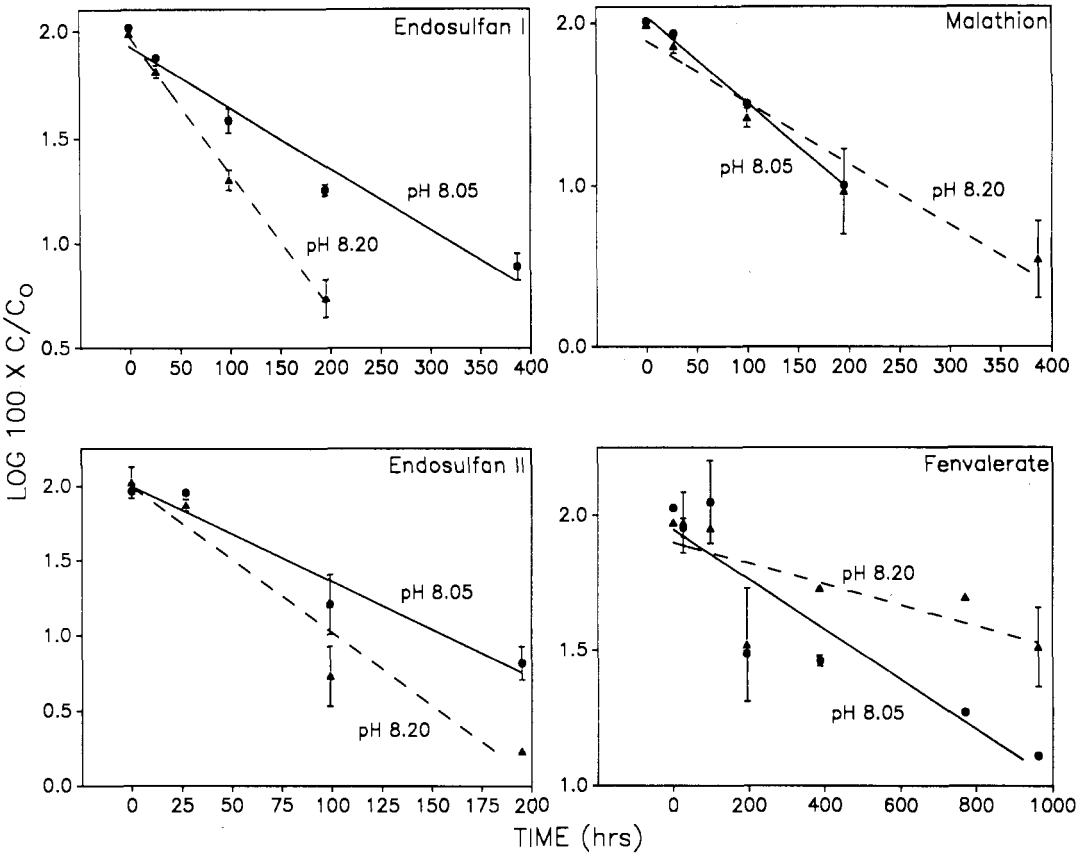


Figure 1. First-order degradation plots of pesticides in unsterile (·—·) and autoclaved (▲---▲) seawater.

methanol followed by 3 mL of distilled water through them. After the water was sampled (450 mL at 25–35 mL/min), the C_8 cartridges were eluted with 3 mL of 1:1 ethyl ether/isooctane. Ethyl ether was removed under a nitrogen stream, leaving the sample in 1 mL of isooctane (Hinckley and Bidleman, 1988).

Sediment. The top 1.5 cm of each sediment core was removed and freeze-dried in a Virtis Model 10-030 freeze-dryer. Samples were then transferred to solvent-cleaned cellulose Soxhlet thimbles and extracted for 14 h with a 60:40 acetone/hexane azeotrope. The extract was reduced to 5–7 mL on a rotary evaporator and transferred to a 10-mL centrifuge tube. Elemental sulfur was removed by treatment with tetrabutylammonium hydrogen sulfite (Jensen et al., 1977). Final cleanup utilized a modified Florisil column procedure originally designed for the analysis of fenvalerate in sediment (Schoor and McKenny, 1983). A 14.5-cm disposable Pasteur pipet was plugged with glass wool, 5 cm of activated Florisil (0.7 g) was placed in the pipet, and 0.5 cm of anhydrous sodium sulfate was placed on top of the Florisil. The column was washed with 5 mL of ethyl acetate, followed by 10 mL of isooctane. The sample, in 1 mL of isooctane, was then added to the column and eluted with 7 mL of 15% ethyl acetate in isooctane. The eluate was blown down with nitrogen to the final volume of 1 mL.

Polyurethane Foam. The inner PUF plugs were placed in a beaker and extracted by squeezing with three 20-mL volumes of petroleum ether. The combined extracts were reduced into 1 mL of isooctane via a nitrogen stream.

Chromatographic Analysis. Analysis was carried out on a Varian 3700 or a Carlo Erba 4160 gas chromatograph with ^{63}Ni electron capture detectors (GC-ECD). Both chromatographs contained a 25-m bonded-phase fused silica column (poly(dimethylsiloxane), 5% phenyl, Hewlett-Packard HP-5 or SGE Corp. BP-5). The sample (2 μL) was injected at 90 °C in the splitless mode with a 30-s Grob time. Following a 1-min hold, the oven was programmed at 7 °C/min to a final temperature of 285 °C and a final hold of 15 min. The carrier gas was hydrogen at 30 cm/s; the injector and detector temperatures were 240 and 320 °C, respectively. Chromatographic data were collected on a Hewlett-Packard 3390A or Shimadzu Chromatopac CR3A integrator.

GC–MS data were obtained with a Finnigan Model 4521 instrument equipped with the same type of column as used for GC-ECD work. Spectra were obtained at 70 eV in the electron-impact (EI) mode.

Endosulfan Metabolite Identification. Attempts were made to identify endosulfan transformation products (endosulfandiol, endosulfan ether, endosulfan lactone, endosulfan sulfate) in the seawater/sediment experiment. The latter three compounds chromatographed well on the HP-5 or BP-5 columns. Endosulfandiol, unstable toward gas chromatography, was analyzed as the trimethylsilane (TMS) derivative. Selected water sample extracts from the seawater/sediment system were reduced to 50 μL, treated with 50 μL of *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (Pierce Chemical Co., Rockford, IL), and heated to 70 °C in a water bath for 15 min. The mixture was diluted to 100 μL for GC–MS analysis and to 5 mL for GC-ECD analysis.

Data Treatment. Each set of experimental data was treated by a linear regression analysis routine provided by SAS software (SAS Institute, Cary, NC), assuming that compound degradation followed pseudo-first-order kinetics at constant pH.

RESULTS AND DISCUSSION

Persistence. *Seawater.* Figure 1 displays first-order plots of degradation for each pesticide. The half-lives are summarized in Table I. The pH values of autoclaved seawater were consistently higher by an average of 0.15 than those of unsterilized seawater. Half-lives were therefore adjusted to pH 8.0, with the equations below and assuming second-order kinetics, to facilitate comparisons between autoclaved and unsterile experiments and with literature values.

$$-dC/dt = k[C][OH^-] \quad (1)$$

$$\text{constant pH: } -dC/dt = k'[C] \quad k' = k[OH^-] \quad (2)$$

$$\log (C/C_0) = -k't/2.303 \quad (3)$$

Half-lives and their associated standard deviations were calculated from the slope and standard error of log (C/C_0)

Table I. Pesticide Half-Lives (Days (Standard Deviations)) in Seawater and Seawater/Sediment Systems

	seawater system						seawater/sediment system	
	unsterile		sterile		lit. values		this study;	
compound	pH 8.05	pH 8.0	pH 8.20	pH 8.0	unsterile	sterile	pH 7.3–7.7	lit. values
malathion	2.4 (0.1)	2.6 (0.1)	3.3 (1.5)	5.3 (2.4)		2.8; 4.9[a]	2.0 (0.3)	
endosulfan I	4.4 (0.4)	4.9 (0.4)	1.9 (0.1)	3.1 (0.2)			22 (9.5)	
endosulfan I + II					6.2–8.2[b]	2.8–4.4[b]		13.6–15.6[b]
endosulfan II	2.0 (0.3)	2.2 (0.3)	1.3 (0.2)	2.0 (0.3)	3.5[c]		8.3 (1.8)	
fenvalerate	14 (2.2)	17 (2.7)	33 (18)	41 (22)	>28[d]		12 (3.6)	34,[e] 3–9[f]

[a] 2.8-days value calculated using data reported for buffered, distilled water at pH 7.4, and 20 °C after adjustment to pH 8.0 assuming second-order kinetics (Freed et al., 1979); 4.9-days value at pH 8.0 calculated from temperature/rate constant data (Wolfe et al., 1977). [b] Isomers combined; pH not reported; estuarine water and water/sediment system at 25 °C (Walker, 1984). [c] Isomers combined; value reported for freshwater at pH 7.0; temperature not reported; adjusted to pH 8.0 assuming second-order kinetics (Goebel et al., 1982). [d] pH not reported; seawater system at 25 °C (Schimmel et al., 1983). [e] pH not reported; seawater/sediment system at 22–45 °C (Schimmel et al., 1983). [f] pH 7.82; temperature not reported; estuarine water/sediment system (Caplan et al., 1984).

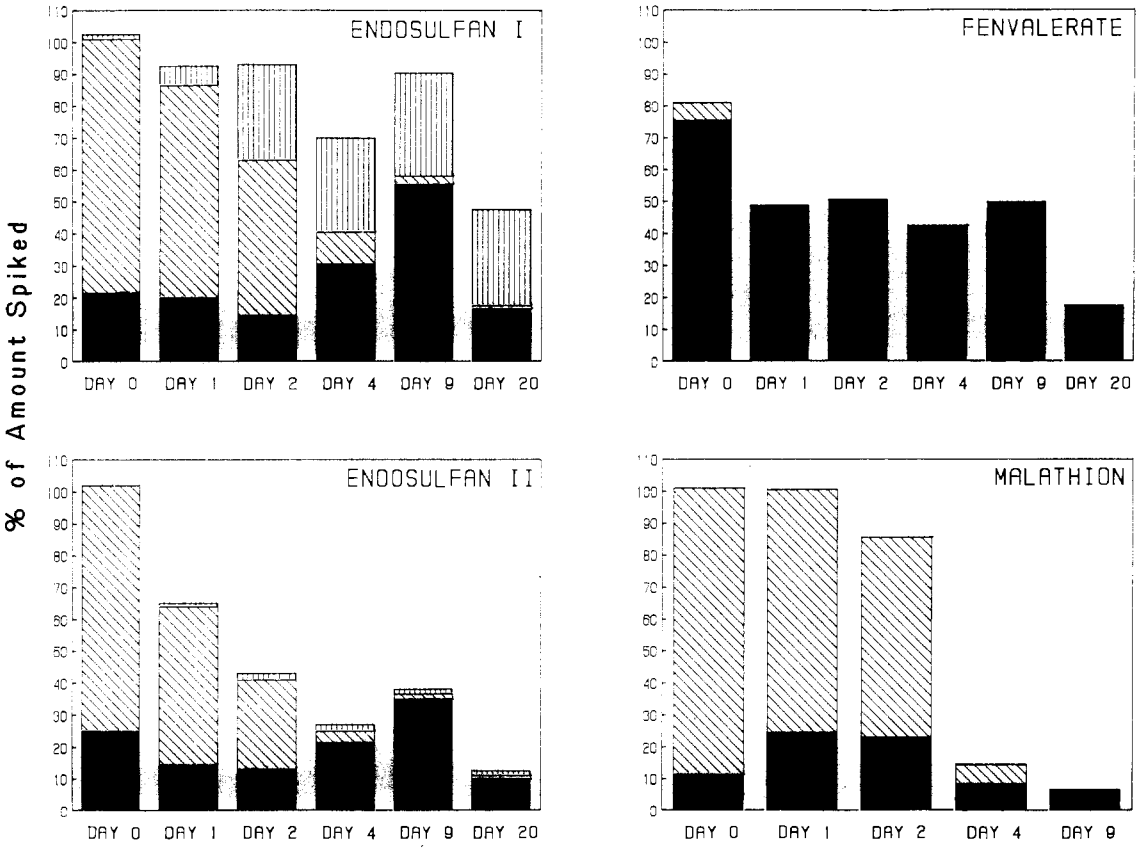


Figure 2. Pesticide distribution in seawater/sediment system: sediment, ■; water, ▨; PUF, ▥.

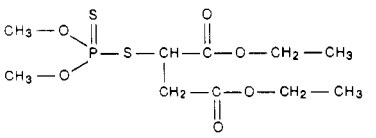
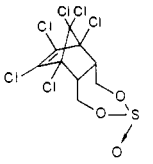
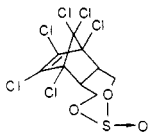
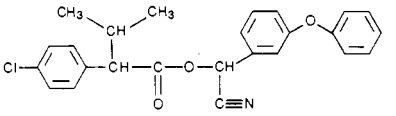
vs t. Differences in slopes among experiments were determined using a t-test with $\alpha = 0.05$.

The malathion $t_{1/2}$ value in autoclaved seawater was double the $t_{1/2}$ in unsterile seawater when values were normalized to pH 8.0. The markedly longer $t_{1/2}$ in the autoclaved seawater indicates that microbial degradation may play a role in malathion degradation in the estuarine environment. The hydrolysis of malathion in pH 7.4 buffer was reported by Freed et al. (1979). The malathion $t_{1/2}$ value at pH 8.0, calculated from its value at pH 7.4 assuming second-order kinetics, is about 2 times lower than our $t_{1/2}$ value for autoclaved seawater. Kinetics data for malathion produced by Wolfe et al. (1977) give a $t_{1/2}$ value of 4.9 days for pH 8.0 and 20 °C. This value agrees very well with our autoclaved half-life. Fenvalerate, the longest lived of the compounds studied, also displayed an increase in the half-life for the autoclaved system, again an indication that microbial degradation may be important.

Both isomers of endosulfan exhibited relatively short half-lives. This is probably due to the rather liable sulfite group that can either oxidize to endosulfan sulfate on soil or plant surfaces or, in water, hydrolyze to endosulfandiol (Goebel et al., 1982). It is interesting to note that the autoclaved sample showed a shorter half-life than the unsterile sample. Adjusting for the slight differences in pH brought these values into good agreement for endosulfan II but did not improve the agreement as well for endosulfan I (significant difference between the slopes at $\alpha = 0.05$). Walker (1984) found the same unexpected trend for endosulfan half-lives in both active and sterile estuarine water and water/sediment systems from Florida (Table I). Walker used both formalin and mercuric chloride as sterilizing agents, indicating that mode of sterilization did not cause this curious behavior. Freshwater half-life values for endosulfan reported by Goebel et al. agree well with half-live values determined in this study after adjusting for pH (Table I).

Seawater/Sediment. Figure 2 displays the results of the seawater/sediment persistence experiment. Half-life values were calculated from the total quantity of compound remaining in the sediment and water column with time. This method is valid for all compounds studied

Table II. Structures and Liquid-Phase Physical Properties (25 °C) of Pesticides Studied

compound	structure	water sol, mol/m^3	vapor pressure, atm	H, atm m^3/mol
malathion		4.4×10^{-1} [a]	1.7×10^{-8} [b]	3.9×10^{-8}
endosulfan I		9.1×10^{-3} [c]	6.1×10^{-8} [d]	6.7×10^{-6}
endosulfan II		5.2×10^{-2} [c]	3.2×10^{-8} [d]	6.2×10^{-7}
fenvalerate		5.7×10^{-5} [e]	8.0×10^{-12} [d]	1.4×10^{-7}

[a] Temperature not reported (Mulla and Mian, 1981). [b] Kim et al., 1984. [c] Calculated from 1.3×10^{-3} and 6.9×10^{-4} mol/m^3 for solid endosulfan I and endosulfan II, respectively (Weil et al., 1974), using $\ln (S_L/S_s) = 6.8(T_m - T)/T$ (Mackay et al., 1980). [d] Determined by capillary GC (Hinckley et al., 1988). [e] Seawater at 22 °C (Schimmel et al., 1983).

except endosulfan I, which exhibited substantial volatilization to the PUF (volatilization for the other compounds was less than 6% for both the seawater and seawater/sediment experiments). Obviously, including the amount of endosulfan I on the PUF in the calculation will make the half-life artifically long whereas not including it will make the half-life artificially short. However, by day 4, no more endosulfan I volatilized and the half-life calculation was made from the last four data points. It is interesting to note that although endosulfan I and endosulfan II are isomers, endosulfan I volatilized to the PUF to a much greater extent than endosulfan II. The Henry's law constant for endosulfan I, calculated by dividing its liquid-phase vapor pressure by its liquid-phase water solubility (Table II), is almost 1 order of magnitude greater than the Henry's law constant for endosulfan II, explaining the difference in the degree of volatilization. Both isomers of endosulfan had longer half-lives in the seawater/sediment system than in the seawater system, perhaps a consequence of lower pH in the seawater/sediment experiment.

Malathion is the most soluble of the compounds studied, and as expected a large portion remained in the water column as degradation took place. Hydrolysis of organophosphates proceeds at higher rates under alkaline conditions, indicating that hydroxide-catalyzed hydrolysis is more effective than hydronium- or water-catalyzed hydrolysis (Freed et al., 1979). Malathion had a half-life of 2.0 days in the seawater/sediment system (pH 7.3–7.7). If only the chemical hydrolysis were taking place, the half-life for malathion in the seawater/sediment experiment should be longer than that observed in the seawater at pH 8.0–8.2. The fact that malathion has such a short half-life at the lower pH indicates that microbial activity and/or interaction with the sediments may play a role in malathion degradation.

The 12-day half-life for fenvalerate in the seawater/sediment system falls between the two widely spaced literature values for seawater/sediment degradation, an indication that the type of sediment and its indigenous microflora are important to the rate of fenvalerate degradation. Fenvalerate, having the lowest solubility of the compounds studied (Table II), migrated immediately from the water column to the sediment. This property may affect fenvalerate bioavailability in the estuarine environment; however, the extremely low 96-h LC_{50} of fenvalerate to mysid shrimp, 0.008 μg/L (Schimmel et al., 1983), may outweigh any benefit derived from its low solubility.

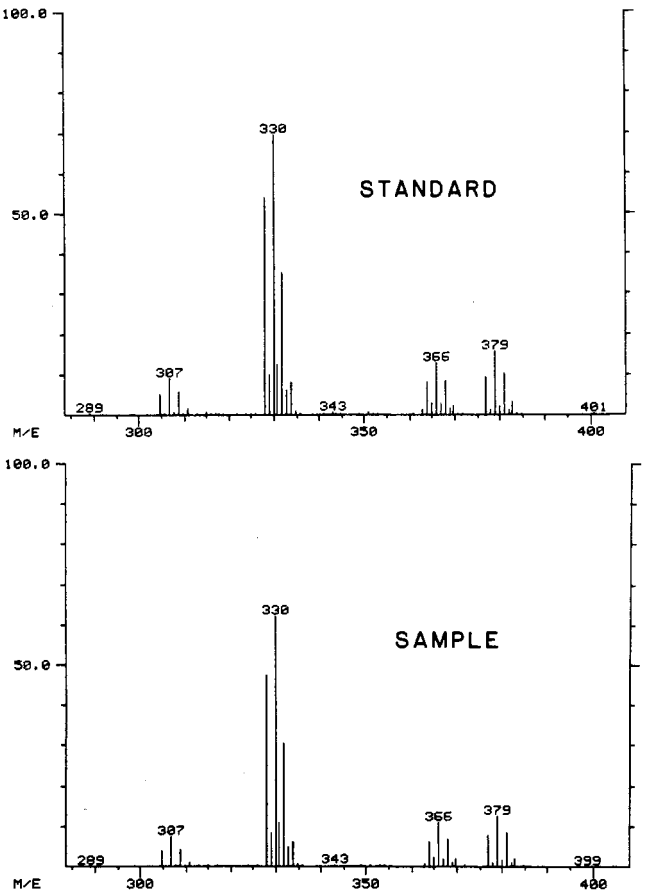


Figure 3. Mass spectra for TMS-derivatized endosulfandiol in standard and in seawater/sediment extract.

Metabolite Identification. Endosulfandiol was the only metabolite of endosulfan identified in the seawater/sediment experiment. Figure 3 displays a portion of the mass spectrum from both the standard and sample. Finding only the diol indicates that its formation is the dominant reaction in an aqueous environment or that other transformation products are more labile. Since only the seawater and not the sediments were analyzed for endosulfandiol, we cannot relate the amount of endosulfandiol found to the total endosulfan added to the system. However, it appears that once formed, endosulfandiol is then lost from the water column. Relative proportions of endosulfandiol in the water column of the seawater/sediment systems were as follows: day 1, 100; day 9, 85; day 20, 10. The disappearance of endosulfandiol indicates further degradation, probably to endosulfan hydroxy ether according to the reported degradation pathways for endosulfan (Goebel et al., 1982).

Although endosulfan sulfate was not found as a degradation product in these experiments, it has been found as a major endosulfan residue in tidal creek water adjacent to farms (Hinckley and Bidleman, 1988). This finding suggests that the source of endosulfan sulfate is runoff from fields, where endosulfan oxidizes to endosulfan sulfate on soil and plant surfaces (Goebel et al., 1982).

CONCLUSIONS

The compounds studied degrade faster in seawater than in freshwater. This is supported by freshwater hydrolysis half-life values for malathion of 11 days (pH 7.4, 20 °C) reported by Freed (1979) and 5 weeks for endosulfan (pH 7.0) reported by Goebel et al. (1982). It is interesting to note that when these half life values are converted to the shorter values representing pH 8.0, they agree quite well with the half-lives reported here (Table I). This indicates that, for malathion and endosulfan, hydroxide-catalyzed hydrolysis is a major pathway for their degradation in marine systems. Microbial action may also play a role in the degradation of malathion and fenvalerate.

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Registry No. Malathion, 121-75-5; endosulfan I, 959-98-8; endosulfan II, 33213-65-9; fenvalerate, 51630-58-1; endosulfandiol, 2157-19-9.

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