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Degradation of N-methylcarbamate and Carbamoyl Oxime Pesticides in Chlorinated Water

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Pesticide contamination of groundwater has become a key environmental topic of the 1980's. Even though about half of the drinking water in the U.S. is from groundwater, most of this water is treated prior to human consumption. Therefore, if human exposure to pesticide residues is a major concern, then the fate of pesticides under typical water treatment conditions must be understood. Although the usual processing of municipal water supplies involves physical, biological, and chemical treatment of natural waters, many groundwaters and other pristine sources are sometimes not treated at all or are only chlorinated.

Considerable effort has been directed towards studying the formation of trihalomethanes (THMs) which occur in drinking water as a result of chlorination of natural organic matter (Rook, 1974). Recently, dichloroacetonitrile and chloral hydrate, as well as chloroform, have been shown to be chlorination products of amino acids in natural waters (Trehy et al., 1986). Also, chloropicrin, a pesticide, has been found in processed drinking waters and shown to be the product of chlorination of some naturally occurring organic materials (Merlet et al., 1985). These studies show that chlorination of relatively innocuous compounds can result in potentially toxic products.

Fate studies on pesticides in chlorinated water have shown that paraquat and diquat (Gomaa and Faust, 1971), phenylureas, phenylamides, and phenylcarbamates (El-Dib and Aly, 1977), thiobencarb (Au et al., 1984), diazinon (Dennis et al., 1979), and bentazon (Handy et al., 1985) degrade faster in the presence of chlorine, and that pH is an important factor in degradation rate. Although oxidation is a major effect of chlorination, other mechanisms such as hydrolysis and chlorination occur when organic compounds react with chlorine in water.

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In this study, degradation rates of the N-methylcarbamate pesticides carbaryl and propoxur and their major hydrolysis products 1-naphthol and 2-isopropoxyphenol were determined in the presence and absence of chlorinated water. Similar studies were performed with the carbamoyl oxime pesticides aldicarb and aldicarb sulfoxide and the hydrolysis product aldicarb sulfoxide oxime.

MATERIALS AND METHODS

Carbaryl, 1-naphthol, propoxur, aldicarb, and aldicarb sulfoxide were obtained from the U.S. Environmental Protection Agency's Chemical Repository (RTP, NC). Aldicarb sulfoxide oxime, aldicarb sulfoxide nitrile, and aldicarb sulfone were obtained from Union Carbide (RTP, NC) and 2-isopropoxyphenol was purchased from Aldrich Chemical Co. (Milwaukee, WI). Stock solutions of each chemical (1000 mg/L) were prepared in acetonitrile (Fisher, HPLC grade) and working standards were prepared daily in deionized water. A phosphate buffer was prepared by adding 1.36 g of KH_2PO_4 (Fisher) in one liter of deionized water (0.01 M) and the pH was adjusted by addition of HCl or KOH. Buffered solutions of each test chemical (1.0 mg/L) were prepared and split such that one served as a control while the other was chlorinated with 10 mg/L of hypochlorite solution (Chlorox$^{(R)}$). All experiments were performed in duplicate and samples were stored in darkness at room temperature between analyses. Residual free chlorine was measured by the orthotolidine test (Standard Methods, 1976).

The amount of pesticide remaining in each test solution was measured periodically by HPLC using a method described previously (Miles and Delfino, 1984). Chlorinated pesticide solutions were analyzed for volatile compounds after one half-life degradation using EPA Method 624 protocol with a Finnigan 4000 GC/MS and a Techmar LSC-2 purge and trap device.

RESULTS AND DISCUSSION

Carbamate and carbamoyl oxime pesticides degrade by acid- and base-catalyzed hydrolysis in water (Bank and Tyrrell, 1984). An increase in pH from 7 to 8 decreased the half-lives of the test pesticides from 6- to 162-fold with the exception of aldicarb whose half-life is very long at these conditions (Table I). Chlorinated water shortened the half-lives of all the pesticides (except aldicarb) from 3- to 62-fold. The effect of chlorination on half life was greater at pH 8 than pH 7, suggesting that chlorine speciation ($HOCl/OCL^-$ pK_a = 7.5) is important in degradation of these pesticides in chlorinated water. The effect of chlorinated water on the half-life of aldicarb could not be determined by the technique used because of the short reaction time. Aldicarb completely degraded to aldicarb sulfoxide in less than 5 minutes; Lemley et al. (1984) have reported similar results. Aldicarb sulfoxide was partially oxidized to aldicarb sulfone. Reaction of hypochlorite/hypochlorous acid with thiaarenes produced mostly sulfoxide and sulfone oxidation products (Lin and Carlson, 1984). Half-lives of about 0.5 to 1 day were observed for solutions containing 1 ppm each of aldicarb, aldicarb sulfoxide, and aldicarb sulfone and 1.8 ppm chlorine in a natural water (Union Carbide, 1981).

Degradation was assumed to follow pseudo first-order kinetics, although significant decreases in free chlorine were observed at the end of some experiments. All first-order plots were linear except aldicarb sulfoxide in chlorinated water, which showed a two-step degradation process (Figure 1). The rapid decrease in aldicarb sulfoxide in the first hour after chlorination is probably due to reaction with free chlorine, while the second step is reaction with chloramines produced from aldicarb sulfoxide (Weil and Morris, 1949). Chloramine is less reactive than chlorine in tranformation of heterocylics in aqueous solution (Lin and Carlson, 1984). Half-lives for aldicarb sulfoxide were determined from the second portion of the curve.

Control experiments with each pesticide showed an increase in the corresponding hydrolysis product over time (except aldicarb, whose hydrolysis is very slow at these conditions). These products were not observed in the chlorinated mixtures. Separate experiments with the hydrolysis products 1-naphthol, 2-isopropoxyphenol, and aldicarb sulfoxide oxime in chlorinated water showed that these compounds were highly unstable with half-lives on the order of minutes. Examination of chlorinated solutions (pH 8) of carbaryl, propoxur, and aldicarb sulfoxide after one half-life degradation using purge and trap analysis did not show any measurable concentrations of volatile organic compounds. Chlorinated solutions of aldicarb sulfoxide produced several HPLC peaks that did not correspond to any of the available standards. These unknown peaks increased in size shortly after chlorination and subsequently decreased at a rate similar to the parent compound. Identification of these products is currently under investigation.

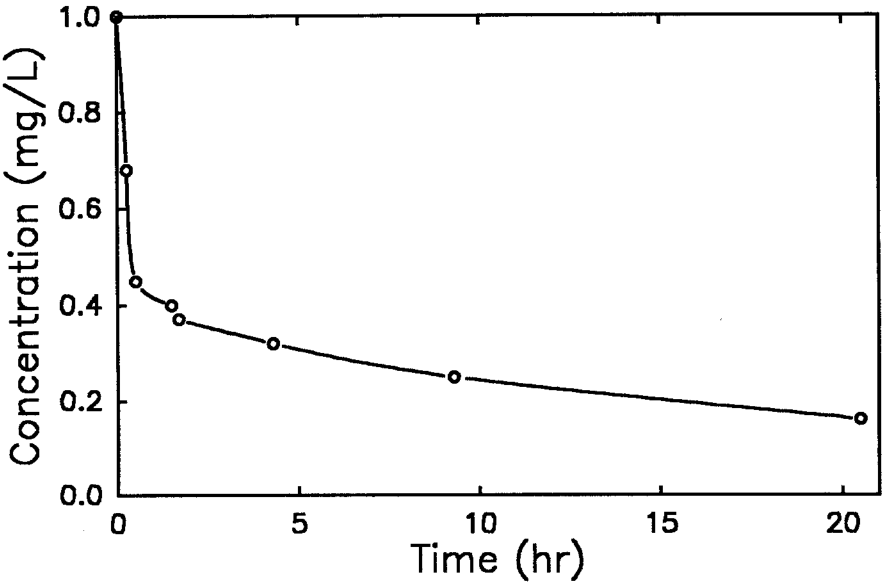

Figure 1. Degradation of aldicarb sulfoxide in chlorinated water at pH 8.

Table 1. Half-lives (in days) of carbamate and carbamoyl oxime pesticides in the absence and presence of chlorine[1].

pesticide	pH 7	pH 8
carbaryl control	10.3	1.2
carbaryl chlorinated	3.5	0.05
propoxur control	290	17.9
propoxur chlorinated	9.2	0.29
aldicarb control	years[2]	years[2]
aldicarb chlorinated	<0.03	<0.03
aldicarb sulfoxide control	100[3]	15.8
aldicarb sulfoxide chlorinated	2.0	0.5

[1] 0.01 M phosphate buffer, Temp = 26 °C, 10:1 chlorine/pesticide.

[2] estimated from Bank and Tyrrell, 1984.

[3] estimated from Lightfoot et al., 1987.

These results indicate that a water source contaminated with carbamate pesticides and treated by chlorination will contain lower concentrations of these pesticides in the effluent. Identification of these carbamate pesticide degradation products after chlorination and measurement of their toxicity will determine if chlorinated solutions of these pesticides present a health hazard and if chlorination represents a practical treatment for water contaminated with these pesticides.

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