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INVESTIGATION OF HALOGENATED COMPONENTS FORMED FROM CHLORINATION OF ESTUARINE WATER

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ABSTRACT

Chlorination of power plant cooling water is extensively used as a means of controlling biofouling. This practice presents the potential for formation of halogenated organic compounds hazardous to man and his environment. Accordingly, the organic composition resulting from the chlorination of relatively pristine estuarine waters of the northern Olympic Peninsula is currently under investigation. Organic matter is extracted by passing large volumes of seawater over columns of XAD-2 macroreticular resins. Examination of ether extracts from the resin columns using capillary gas chromatography has revealed the presence of halogenated methanes, as well as other electron-capturing components, that are not found when unchlorinated seawater is sampled. Examination of the unrefined chlorinated seawater extracts using gas chromatography/mass spectrometry has revealed a complex mixture which generally was not separable into individual components, even when high efficiency WCOT capillary columns were used. As an aid to the GC/MS investigations, the concentrated XAD-2 column ether extracts were further fractionated using high speed liquid chromatographic techniques. The samples were first separated into molecular weight fractions using a microstyragel column, and then further separated into fractions of increasing polarity using a water-deactivated silica gel column. Fractions were thus obtained which give baseline separation of components and which are more amenable to GC/MS investigation.

INTRODUCTION

Halogenated organic compounds in drinking water[1] and in treated waste waters[2,3] have been studied over the past several years. However, the potential for formation of organohalogen products in chlorine-treated power plant cooling waters has received attention only recently. About 100,000 tons of chlorine were used to treat cooling waters from electricity generating plants in 1975[4] and this use of chlorine will probably increase as additional conventional and nuclear power plants are brought into service. Jolley et al.[5] recently provided evidence that chlorinated organics were present in samples of chlorinated cooling waters of fresh water origin, and suggested that in estuarine waters, organobromine compounds would be formed.[6]

Our studies are part of an interdisciplinary program designed to investigate the formation of halogenated organic compounds in both fresh and saline cooling waters, and to determine their toxicity and biological availability to aquatic organisms. Much of our initial experimentation was directed toward isolating and identifying halogenated components formed in seawater under conditions similar to those used in cooling water treatment, particularly those halogenated compounds that might be expected to be absorbed and biomagnified in the lipids of aquatic biota. Thus, for these studies, we investigated the nonpolar, presumably lipophylic organohalogens formed in seawater. The procedures used to identify these compounds would specifically exclude more polar component types such as halogenated phenols, amines, and nitrogen heterocycles that are being investigated using other methodologies.

EXPERIMENTAL

Samples of chlorinated seawater were obtained from a continuous flow apparatus located at the Battelle-Northwest Marine Research Laboratory at Sequim, Washington. The apparatus was designed to simulate conditions of current power plant cooling water treatment practice. The waters of Sequim Bay are relatively pristine, containing about one mg/liter organic carbon. Chlorination as NaOCl was carried out at between one and two mg/liter chlorine and the seawater was sampled approximately two hours after treatment.

Organic components were concentrated by forcing chlorinated and unchlorinated seawater through columns of XAD-2 resin using a positive displacement pump. The procedures used were recently reported[7] and are similar to those discussed by Glaze et al.[8] Samples taken for study were usually several hundred liters in volume. Because of the large volumes involved, we did not destroy the active chlorine prior to resin adsorption in these experiments, although procedures for continuous additions of reductant are being implemented.

Ether extracts of the XAD-2 columns were dried over sodium sulfate, subsampled and mixed with an ether solution of 1,3-dibromopropane as internal standard. The samples were analyzed for haloforms using a Hewlett-Packard 5840A gas chromatograph equipped with a 30 meter wall-coated open tubular capillary column containing OV101 as liquid phase. The sample was injected at 1:10 split ratio at a temperature of -20°C and after seven minutes, the temperature was raised at 8°C/min to 65°C. Detection was by electron capture.

The procedures used for the analysis of seawater extracts for components other than haloforms involved a number of preliminary separation steps prior to gas chromatographic analysis. Gel permeation chromatography was first used to remove material having molecular weight greater than 800. Silica gel chromatography using hexane, then hexane-ether, was used to separate the sample into two fractions. Fraction A contained nonpolar components (e.g., hydrocarbons and halocarbons) and Fraction B contained components of intermediate polarity (e.g. ketones and esters). Both fractions were investigated by capillary gas chromatography. Temperature programming was from 65°C to 250°C at 4°C/min. Four detection systems were used: flame ionization, electron capture, electron impact mass spectroscopy, and chemical ionization mass spectroscopy. The separation and gas chromatographic techniques used to study the nonhaloform halogenated organics were described at a recent symposium on capillary chromatography.[7]

RESULTS AND DISCUSSION

Haloform Formation

Our initial analyses for haloforms were performed on XAD-2 extracts obtained from several hundred liters of seawater. An electron capture gas chromatogram obtained from one of these samples is given in Fig. 1. The principle component

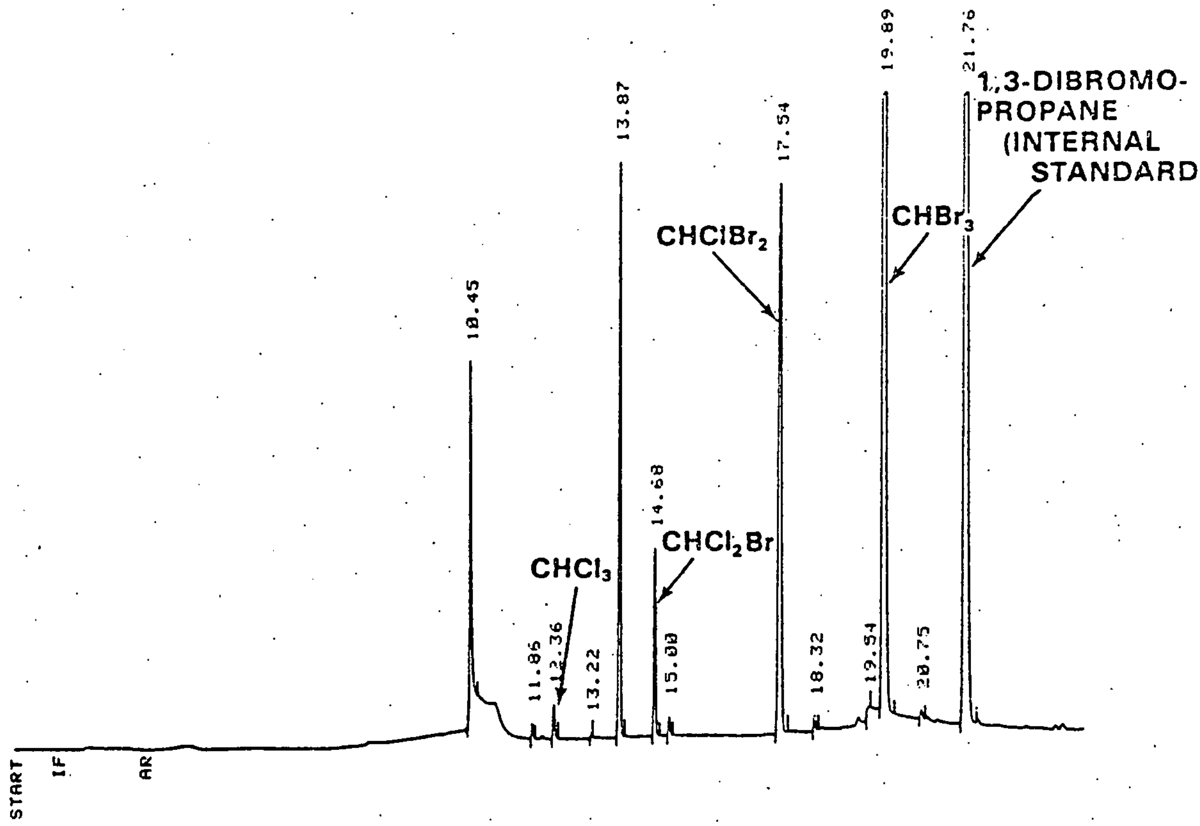

FIGURE I. Electron capture capillary chromatogram of XAD-2 concentrate from chlorinated seawater.

found in all seawater samples was bromoform. Smaller quantities of dibromochloromethane and traces of dichlorobromomethane were found. Interestingly, chloroform was not present in significant concentrations. The first two experiments on Table I give results from the analyses of large volume samples using different quantities of XAD resin. Since the quantity of bromoform adsorbed appeared to be a function of the quantity of resin used, it was apparent that the large sample volumes were overloading the resin with bromoform. Table I shows the results obtained from a third experiment in which two XAD-2 columns were connected in series and nine liters of chlorinated seawater sampled. The results indicate that about 30 μg/l $CHBr_3$ were formed in the Sequim Bay seawater under the chlorination conditions used. Seventy-nine percent of the bromoform was trapped on the upper column. This would indicate an adsorption efficiency somewhat lower than that recently reported by Glaze et al.[8] (87%), probably because we employed a higher sample-to-resin ratio. It is of some interest that bromoform was found in all unchlorinated seawater samples analyzed and probably represents environmental concentrations.

TABLE I. Analysis of XAD-2 extracts of seawater for halomethanes

EXP #	Chlorine Addition	Sample Vol. (l)	Volume of Resin (ml)	$CHCl_2Br$ (µg/l)	$CHClBr_2$ (µg/l)	$CHBr_3$ (µg/l)
1	Yes	238	8.0	<0.01	0.13	2.11
	No	231	9.0	nd*	nd	0.04
2	Yes	425	15.5	nd	0.44	8.33
	No	510	15.6	nd	nd	0.01
3	Yes	9.0	8.0 (Top)	nd	0.14	23.39
	Yes	9.0	10.8 (Bottom)	nd	nd	6.33

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*not detected

Formation of Other Halogenated Components of Low Polarity

The liquid chromatographic separations applied to the XAD-2 extracts were critical to the overall analytical procedure. Fractionation of the organic material using gel permeation chromatography indicated the presence of material in excess of 800 molecular weight. Direct injection of the extracts into the gas chromatograph resulted in pyrolysis of the sample in the injection port. Chromatograms obtained on unrefined samples indicated poor resolution of individual components, even on chromatographic columns having as high as 100,000 effective theoretical plates. The poor resolution was reflected in preliminary runs made with capillary GC/MS in which all but the most prominent chromatographic peaks gave uninterpretable spectra indicative of multicomponent composition. The cleanup steps applied to the extracts gave samples which yielded baseline separations of most component peaks.

Capillary chromatograms obtained from Fraction A (nonpolar components) and B (components of intermediate polarity) using the flame ionization detector are shown in Fig. 2. These two fractions were derived from the XAD-2 extract of over 600 liters of chlorinated seawater. Final volume of the fractions was adjusted to less than 50 µl prior to GC analysis. The chromatographic peaks denoted by asterisks or numbers represent components that met two criteria: 1) exhibited response from the electron capture detector, and 2) gave chemical ionization mass spectra having peaks characteristic of bromine isotope ratios. A component was required to meet both of these criteria to positively designate it as bromine-containing. The identities of numbered peaks in Fig. 2 are listed on Table II.

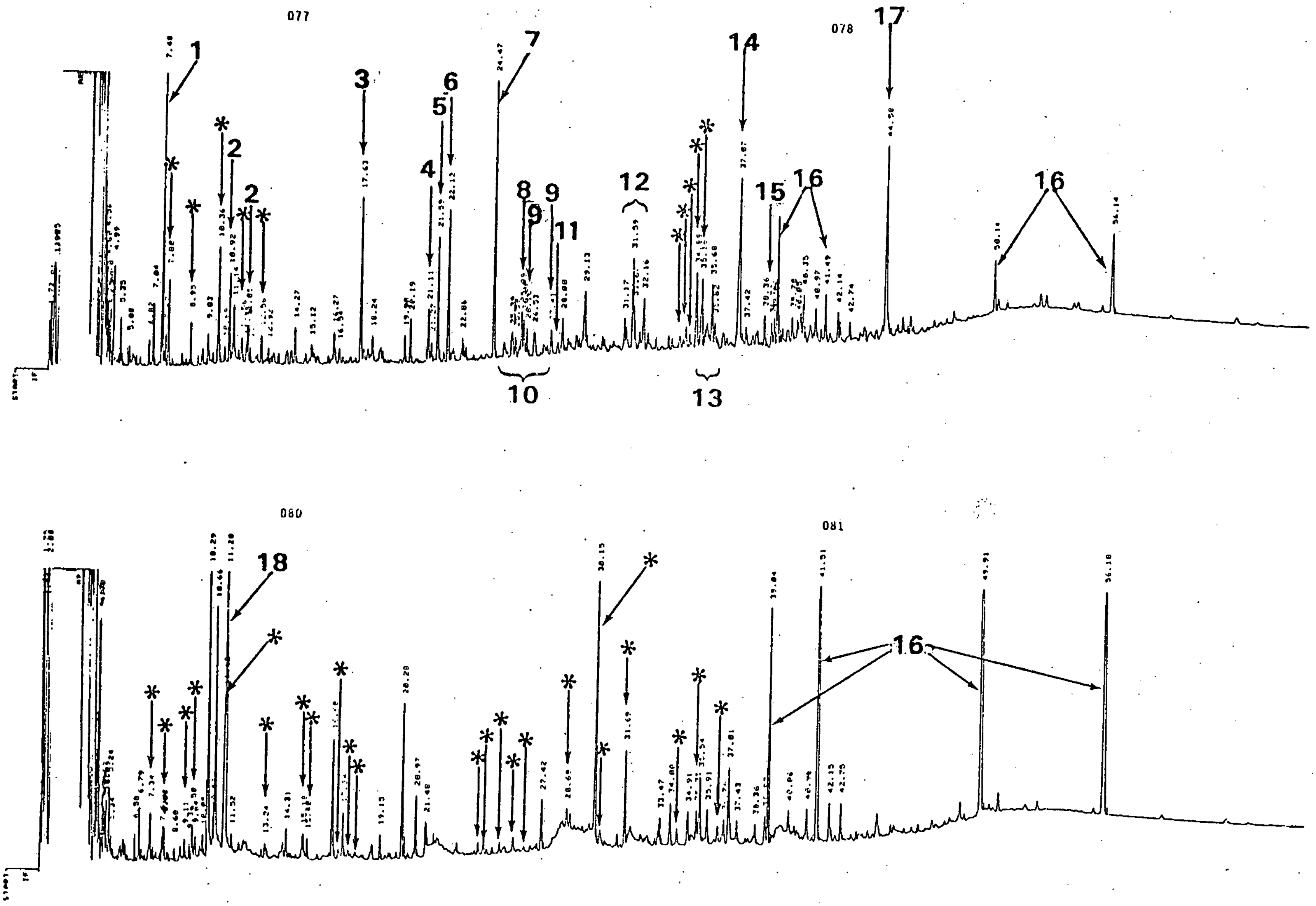

Fig. 2. Above, gas chromatogram of Fraction A from XAD-2 extract of seawater using flame ionization detector; Below, chromatogram of Fraction B. Chromatographic peaks denoted by an asterisk represent unidentified bromine-containing components (confirmed by GC/MS and electron capture). Peaks denoted by numbers have been identified and are listed by number on Table 1.

TABLE II. Components identified by GC/MS in Fractions A and B obtained from XAD-2 extract of seawater*

1. Bromoform
2. Trimethylbenzene
3. Naphthalene
4. Bromotrimethylbenzene
5. 2-Methylnaphthalene
6. 1-Methylnaphthalene
7. Biphenyl
8. Bromotetralin
9. Bromotetramethylbenzene
10. Dimethylnaphthalenes
11. Bromonaphathalene
12. Bromomethylnaphthalenes
13. Bromobiphenyls and Bromodimethylnaphthalenes
14. Phenanthrene
15. Bromotrimethylnaphthalene
16. Phthalate Esters
17. Pyrene
18. Bromoacetal

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*Hydrocarbons were identified by comparison of spectra with authentic samples; identities of brominated components were assigned solely on the basis of spectral interpretation.

Many of the components identified in Fraction A are aromatic hydrocarbons. At first these components were thought to arise from petroleum contamination of the seawater samples since oil pollution studies are a part of ongoing research at the Sequim Laboratory. However, these same hydrocarbons were found in all samples studied, including those derived from fresh water sources. Procedural blanks performed by extracting freshly packed XAD-2 resin columns and subjecting the extracts to all the steps of the analytical procedure did not contain these hydrocarbons. Our present belief is that these components are initially present in the XAD-2 polymer matrix in an unextractable form and are released during the sampling operation, possibly because of fracturing of the resin particles as the bed is compacted. This belief is reinforced by the observation that the resin contains aromatic hydrocarbons as impurities when received from the supplier. These impurities must be removed by exhaustive soxhlet extraction. The above observations also led us to conclude that the brominated aromatic components in Fraction A are formed by reaction of bromine with the hydrocarbon impurities during sampling. While the concentrations of these experimental artifacts represent only a few nanograms per gram of XAD-2 resin, they appear in concentrations comparable to other halogenated components in Fractions A and B which, although unidentified, do appear from their spectra to arise from the chlorination of seawater.

On the basis of our results thus far obtained, the concentrations of non-polar and presumably lipophylic halogenated components generated by the low level chlorination of relatively pristine seawater appear to be very low, in the nanogram per liter range, with the exception of the haloforms. Identification of halogenated components at these concentrations is proving to be a difficult task, particularly since brominated standards are lacking and many of the components under investigation give singularly uninformative spectra under electron impact conditions. Although destruction of active chlorine prior to XAD adsorption should eliminate brominated artifacts, continued problems with contaminants can be expected since many substances are ubiquitous in the environment at these levels.

Acknowledgments

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