Bull. Environ. Contam. Toxicol. (1987) 38:475–482
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Bulletin of Environmental Contamination and Toxicology

Chlorination Byproducts of Arabian Gulf Seawater

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Chlorine is commonly used as a disinfecting agent, as a pathogen control in municipal wastes as well as a bleach and odor suppressant in pulp and paper industries. Also it is widely used as a biocide to reduce fouling in the condensers of power generating plants, desalination plants, and other industries. Chlorination of saline cooling water results in the formation of many halogenated organic compounds. These compounds originate from the reaction of chlorine and/or bromine with the naturally occurring humic substances in the water. (Carpenter *et al.* 1980; Christman *et al.* 1983). During the last two decades, the Arabian Gulf region has witnessed tremendous industrial development. Most of the industries, such as desalination, petrochemical, paint, and metal industries are concentrated along the coastal area of the Gulf. These industries utilize huge quantities of chlorinated seawater for cooling purposes. The used cooling water is then discharged into the Gulf water. Many investigators have shown that chlorinated seawater has potentially deleterious effects on marine organisms (Brungs 1976; Davis and Middaugh 1978).

Some researchers have related the toxicity of chlorinated seawater to the residual chlorine contents of the water. This has resulted in the establishment of guidelines for reducing the chlorine levels in the discharged water (Garey 1980). However, when chlorine is added to seawater, a great proportion of it is consumed in the oxidation of the naturally occurring organic and inorganic materials of the water. Therefore, the harmful effects of the chlorinated discharges can most probably be attributed to the reaction by-products. Very little information is available about these by-products.

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Most of the work carried out in this field has dealt with the determination of the volatile compounds formed in chlorinated seawater, mainly the halomethanes. Only a few studies have discussed the identification of the semivolatile chlorinated by-products (Roger *et al.* 1978; Carpenter *et al.* 1980). However, in order to evaluate the harmful effects of these compounds on marine organisms, it is crucial to identify these by-products and to study their toxicity, degradability, bioaccumulation, and ways of transportation in the water. This paper discusses the results obtained for the identification of volatile and semivolatile organic compounds formed in chlorinated seawater from the Arabian Gulf.

MATERIALS AND METHODS

Seawater samples were collected from the Halfmoon Bay beach and brought immediately to the laboratory. To each of three 20-liter capacity glass containers supplied with side taps, 15 liters of seawater was added. Chlorination was carried out by adding 1 ml, 0.5 ml and 0.25 ml of sodium hypochlorite (Fisher Reagent Grade 4%) to the respective containers. After chlorination, the water was stirred with a glass rod and the containers were capped with aluminum foil. Water samples were collected from the side tap.

The total residual oxidant was determined in the seawater using the amperometric back-titration method (USEPA Method 330.1, 1979). The pH of the water was measured using an Orion Model 901 digital pH meter. The total organic carbon (TOC) content of the seawater samples was immediately determined after sampling by a Beckman Model 915B TOC analyzer using the EPA standard method (USEPA Method 415.1, 1979). Bromide ion concentration in the seawater was determined according to the ASTM standard method (ASTM D-1246-77, 1981). Total oxidant demand of seawater was determined by a method similar to that utilized by Hartwig and Valentine (1983).

Water samples were collected from each container periodically over a period of 10 days in 40 ml glass vials without headspace. Ten mg of sodium thiosulphate was added to each vial to stop further formation of volatile halogenated organic compounds. The samples were analyzed immediately after collection whenever possible; otherwise, they were kept in the refrigerator at 4°C until analysis. Volatile organic compounds were determined using the United States Environmental Protection Agency purge and trap gas chromatographic/mass spectrometric (GC/MS) method (USEPA Method 624 , 1982) with some modifications. A fused silica capillary column (coated with 1μm thick layer of SE-30 liquid phase) was used in place of the packed column described in the standard procedure. The capillary column was directly interfaced to the ion source of the mass spectrometer. The heating line coming from the Teckmar LCS2 concentrator was connected directly to the injection port of the gas chromatograph through the injection nut. The volatile compounds were purged for 8 minutes with helium flowing at a rate of 40 ml per minute. During the sample desorption period (100 seconds) the helium flow rate was adjusted to 15 ml/min, and the split valve, set at a splitting ratio of 10:1, was automatically activated after the sample was completely desorbed from the trap; therefore, only 1.5 ml/min of helium gas actually entered the capillary column. The gas chromatograph was programmed from 40°C to 100°C at 5°C per minute with an initial hold time of 4 minutes and a final hold time of 2 minutes. This technique has been used for more than a year in our laboratory and has proven to be very reliable. The sensitivity of the method was similar to that reported for the USEPA standard procedure. The use of this technique eliminates the need for the cryofocusing system usually utilized when purge and trap method is coupled with capillary column. Another advantage of the technique is that if the system needs to be used for syringe injection, only the septum needs to be changed.

Samples for the analysis of semi-volatile organic compounds were collected just before chlorination and 4 and 54 hours after the addition of the sodium hypochlorite to various seawater containers. Two liters of the seawater from each container were collected from the side tap and extracted with methylene chloride as follows: One liter of the sample was placed in a 2 liter capacity separatory funnel, the pH of the seawater was adjusted to 11 by the addition of few drops of 6N sodium hydroxide, and extracted with two 60-ml portions of methylene chloride (Burdick and Jackson, distilled in glass). The organic extracts were collected in a 250-ml conical flask. The pH of the aqueous phase was adjusted to less than 2 using sulfuric acid (1+1) and extracted with two 60-ml portions of methylene chloride. The second half of the sample was extracted as above. The organic extracts were combined. Traces of water in the extract were removed by elution of the extract through a chromatographic column (1.5 cm I.D. and 20 cm long) which contained about 5 grams of anhydrous sodium sulfate. The dry extract was concentrated to 1 ml in a Kuderna Danish concentrator. The methylene chloride in the concentrate was replaced with hexane by the addition of 4 ml hexane and further concentration to 1 ml. One microliter of the concentrate was injected into the GC/MS in the splitless mode. Fused silica capillary columns (30 meters long) coated with SE-30 were used for the analysis of the semi-volatile compounds on GC/MS and GC systems. A Finnigan OWA-30 GC/MS and a Varian Vista 6000 were used throughout this study. The GC was programmed from 50°C to 250°C at a rate of 5°C per minute with an initial hold time of 4 minutes and a final hold time of 10 minutes. The mass spectrometer was scanned from 45 AMU to 450 AMU in 1 second.

RESULTS AND DISCUSSION

The total organic carbon content of seawater was found to be 10 ppm. Bromide ion concentration of the seawater samples collected from the Gulf was 120 ppm. Open ocean water contains about 65 ppm bromide (Davis and Middaugh 1978). The total oxidant demand of the seawater was found to be 0.12 ppm chlorine. This value is similar to the value reported previously by Hartwig and Valentine (1983) for ocean water.

The results obtained for the volatile organic compounds formed after chlorination of the seawater indicate that bromoform ($CHBr_3$) and chlorodibromomethane ($CHClBr_2$) are the major components found after chlorination. The concentration of $CHBr_3$ was found to increase with time up to 24 hours before it levels off and remains constant for 70 hours. Also the $CHBr_3$ concentrations at the three chlorine dose levels measured were about 70-fold the concentration of $CHClBr_2$.

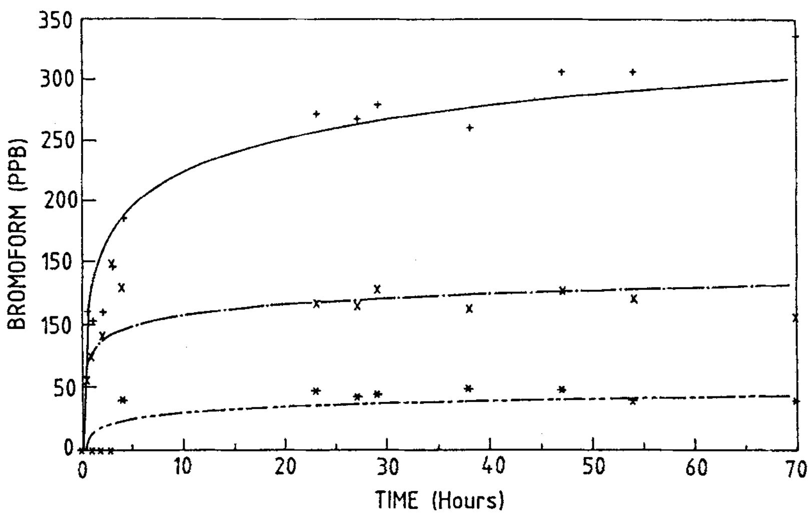

Fig. 1 Bromoform Concentrations formed in Chlorinated Seawater at Chlorine Levels of 1.2 ppm (——), 0.8 ppm (–·–), and 0.6 ppm (-----)

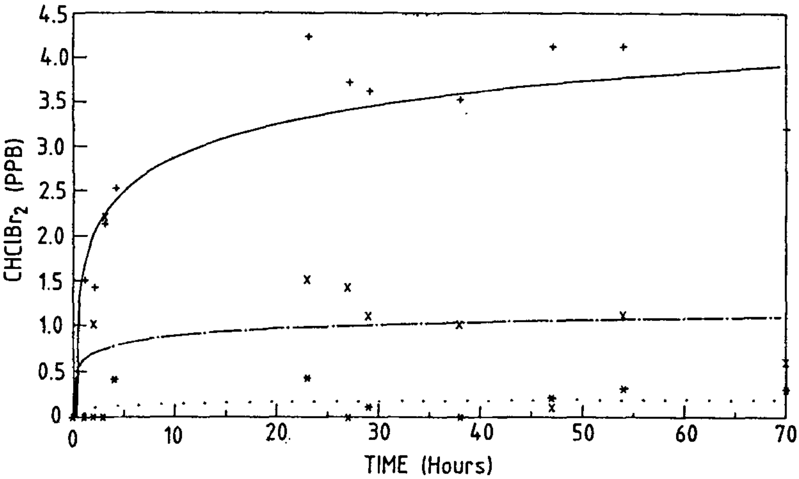

Fig. 2. Dibromochloromethane Concentrations Formed in Chlorinated Seawater at Chlorine Levels of 1.2 ppm (——), 0.8 ppm (—·—) and 0,6 ppm (·········)

Figures 1 and 2 illustrate the variations in the concentration level of these compounds as a function of time and chlorine dose. From these Figures it can be seen that the concentrations of $CHBr_3$ and $CHClBr_2$ increase as the chlorine dose increases.It was noticed that at only moderate chlorine concentration (0.8 ppm) chloroform and/or carbon tetrachloride was formed in addition to the above compounds. This may be explained as follows: at a moderate chlorine concentration (0.8 ppm), it partially reacts with the humic substances to form chloroform and carbon tetrachloride as intermediate reaction products, while the rest of the chlorine is consumed during the formation of the volatile and semivolatile by-products. However, at a lower and higher chlorine doses, most of the chlorine is consumed in the oxidation of the bromide ion present in the water to bromine, which competes with chlorine for the active sites of the precursor humic materials. In this case, only brominated compounds are formed. Stevens and Symons, (1980) have shown that bromide ions are oxidised by aqueous chlorine to species capable of producing brominated organics.

The chlorination of seawater was found to result in the formation of three major halogenated compounds. These compounds were tentatively identified by GC/MS as 2-bromocyclohexanol, 1-bromo,2-chlorocyclohexane and 1,2-dibromocyclohexane. Mass spectra obtained for these compounds are shown in Figures 3 through 5.

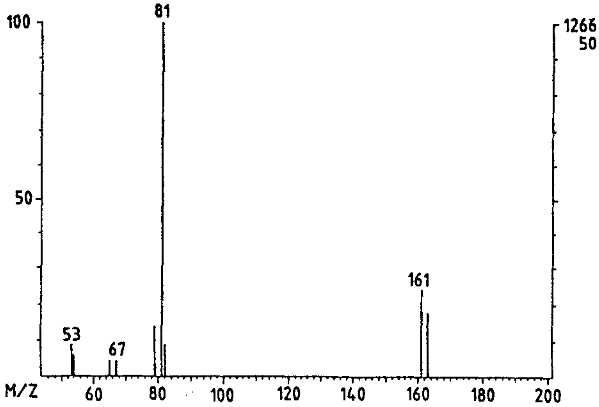

Fig. 3. Mass Spectrum Obtained for Unknown Compound Found in Chlorinated Seawater identified as 1,2-Dibromocyclohexane

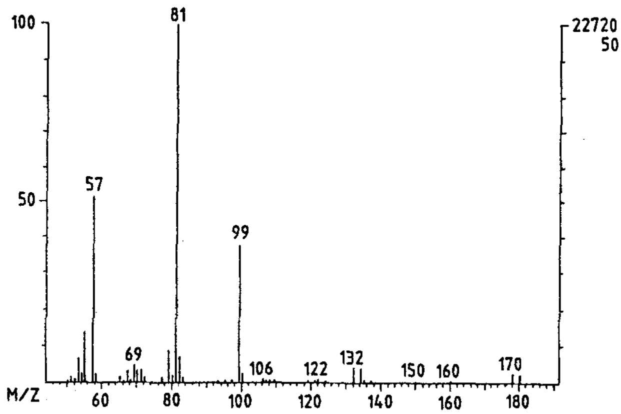

Fig. 4. Mass Spectrum Obtained for Unknown Compound Found in Chlorinated Seawater identified as 2-Bromocyclohexanol

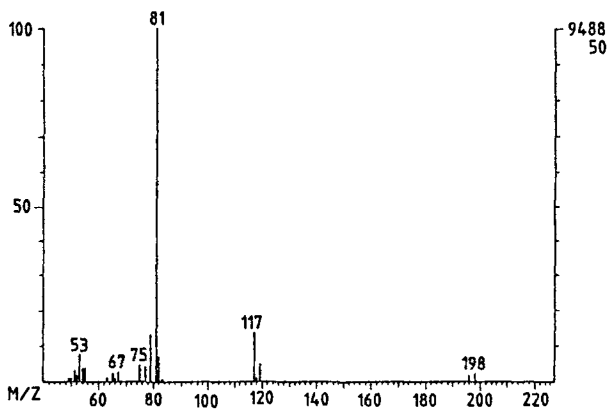

Fig. 5. Mass Spectrum Obtained for Unknown Compound Found in Chlorinated Seawater identified as 1-Bromo-2-Chlorocyclohexane

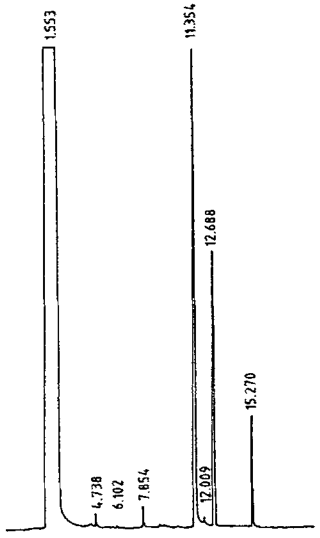

Fig. 6. Gas Chromatogram Obtained Using Flame Ionization Detector For Chlorinated Seawater After 4 Hours

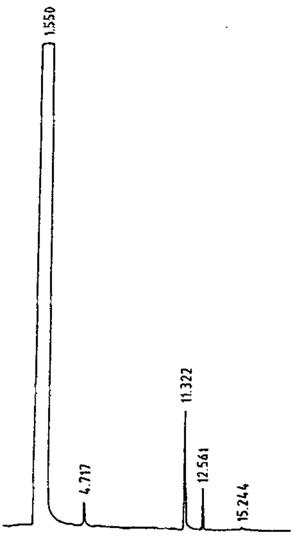

Fig. 7. Gas Chromatogram Obtained Using Flame Ionization Detector For Chlorinated Seawater After 54 Hours

Gas chromatograms obtained for these compounds 4 hours and 54 hours after chlorination are shown in Figures 6 and 7. The first two compounds were formed in relatively high concentrations as compared to the third and were found to be unstable and to degrade with time to other materials.The degradation products were not detected by FID gas chromatography. A literature review has indicated that none of these compounds has previously been reported as seawater chlorination products. Carpenter *et al.* (1980) indicated the formation of several brominated nitrogen-containing compounds in chlorinated seawater, but they did not identify them. Hartwig *et al.* (1983) showed the presence of four chlorinated benzene derivatives in seawater. Information regarding the identity of chlorinated organic compounds formed in seawater is generally scarce. The types of chlorination by-products which result from the chlorination of seawater mainly depend on the structure of the humic materials present in the water. This varies considerably from one location to another.

These reaction by-products may be environmentally more important than the extensively studied haloforms. The persistence, biological accumulation, and transfer of these compounds in the aquatic environment is not yet known. Also toxicological information regarding these compounds still needs to be acquired.

Acknowledgements. This work was supported by the Research Institute of the University of Petroleum and Minerals.

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Received July 9, 1986; accepted November 20, 1986