



Project Summary

Reaction Products from the Chlorination of Seawater

James H. Carpenter, Carroll A. Smith and Rodney J. Zika

A general study of the reaction products from the chlorination of seawater is reported. The results include the following:

Some analytical methods in widespread current use underestimate the residual oxidants in chlorinated seawater by as much as 70% depending upon the detail of the procedures.

The chlorination of seawater in the presence of light produces substantial quantities of bromate ions which can influence standard analytical procedures and represents an unknown factor in estuarine and coastal waters. The toxicity of bromate ion and the possibility of bromate as a persistent source of brominated compounds in coastal waters needs to be determined.

The copper complexing capacity of Biscayne Bay, Florida water was found to be substantially reduced with the addition of chlorine. Analysis was made by anodic stripping voltammetry on water samples after successive additions of copper sulfate solution. The chlorination of seawater may, therefore, produce toxicity and growth reduction through the indirect mechanism of copper release and/or reduced binding capacity.

Laboratory chlorination of water from the intake of the Port Everglades, Florida power plant produces bromoform levels comparable to that found in the plant discharge. These results are in contrast to results reported in the literature for a power plant on the Patuxent estuary in Maryland, so that bromoform production appears to be site-specific.

Chloroform extracts of chlorinated Biscayne Bay water are found to contain halogenated compounds which are new and different, and which pose unusual analytical problems. Studies using GC/ECD, GC/MS, HPLC, ¹H NMR, differential pulsed polarography and other techniques on natural extracts and synthesized compounds are reported.

This Project Summary was developed by EPA's Environmental Research Lab, Gulf Breeze, Florida, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Measurement of residual chlorine in seawater has been a recent subject of study with the increasing recognition of the responses of aquatic organisms to low levels of "residual chlorine" (1,2). Measurement of the residual oxidants in the waters discharge from wastewater treatment plants and electricity-generating plants has become important in order that the environmental impact of the discharges can be properly assessed and regulated. The large number of power plants has led to much greater input of chlorinated waters. The wastewater collection systems of many coastal communities contain some seawater as a result of infiltration with brackish ground waters, and chlorine added as a disinfectant during treatment reacts with the seawater constituents during treatment and in the receiving water. We find that the analytical methods in

widespread current use can underestimate the residual oxidants in chlorinated seawater by as much as 70%, depending on the details of the analytical procedures.

The addition of chlorine to waters containing sea salts leads to reaction with the natural bromide ion (65 mg/L in ocean water) to produce a mixture of hypobromous acid and hypobromite ion at pH 8 (3). If ammonia is present, a mixture of monobromamine and monochloramine may be formed (4). In addition, reaction with organic compounds may produce a variety of brominated substances. Thus, the determination of "residual chlorine" actually corresponds to the estimation of the sum of this complex mixture and is better termed "chlorine-produced oxidant determination."

A general study of the reaction products from the chlorination of seawater was carried out with special emphasis on waters in the Florida Current and in Biscayne Bay, Florida. The study extended to several critical aspects of the chemistry of the chlorination of seawater. Analytical procedures for the determination of "residual oxidants" in chlorinated seawater were examined critically (5). The chemistry of hypobromous acid-hypobromous ion in seawater was investigated with the finding of bromate formation in sunlight (6). The copper complexing capacity of the organic fraction of seawater and the effects of chlorination on it were investigated by anodic stripping voltammetry (7). A local conventional power plant was examined for the production of bromoform with chlorination and the persistence of residual oxidants were compared with other investigators (7). Chloroform-soluble halogenated compounds were extracted from chlorinated Biscayne Bay water and examined with a variety of chemical techniques, including GC/ECD, GC/MS, HPLC, NMR and fluorescence (8).

Results

The results and conclusions resulting from this study are summarized as follows:

1) Analytical methods for the determination of "residual chlorine" (more correctly termed "residual oxidants") developed for fresh water use cannot be applied to saline waters without critical examination.

2) Some analytical methods in widespread current use underestimate the

residual oxidants in chlorinated seawater by as much as 70% depending upon the details of the procedures. A technique is described that is shown to be applicable to seawater.

3) The chlorination of seawater in the presence of light produces substantial quantities of bromate ions which can influence standard analytical procedures and represent an unknown factor in estuarine and coastal waters (Figure 1). The toxicity of bromate ion and the possibility of bromate as a persistent source of brominated compounds in coastal waters needs to be determined.

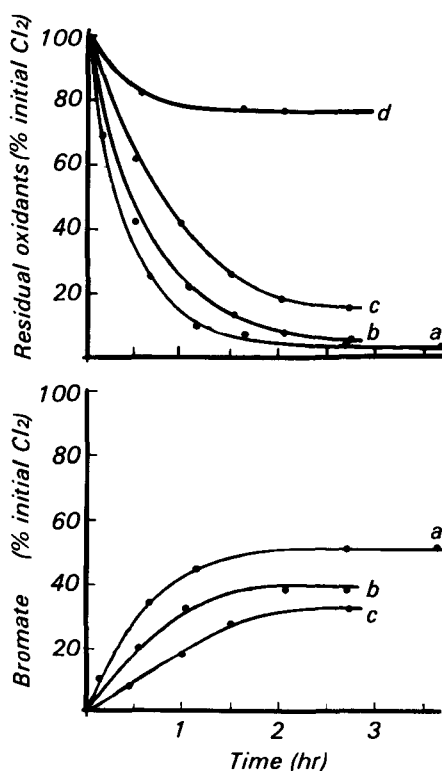


Figure 1. (A) Disappearance of residual oxidants with time and (B) concomitant appearance of bromate in chlorinated seawater (4.2 to 4.9 ppm of Cl₂) as a function of exposure to sunlight. The conditions were: (curve a) full midday sunlight, (curve b) 65 percent of full sunlight, and (curve c) overcast, 20 percent of full sunlight. Curve d shows residual-oxidant disappearance in the dark at 40°C. No bromate production was observed in the dark.

4) The copper-complexing capacity of Biscayne Bay (Florida) water was found to be substantially reduced by the addition of chlorine (Figures 2 and 3). Analysis of water samples after successive additions of copper sulfate solution was made by anodic stripping voltammetry. The chlorination of seawater may, therefore, produce toxicity and growth reduction through the indirect mechanism of copper release or reduced organic binding capacity for copper ion or both.

5) Laboratory chlorination of water from the intake of the Port Everglades (Florida) power plant produces bromoform levels comparable to that found in the plant discharge. Bromoform was found in the plant discharge in contrast to the observation by others of the absence of bromoform at the Chalk Point power plant on the Patuxent estuary in Maryland.

6) Chloroform extracts of chlorinated Biscayne Bay water were found to contain halogenated compounds, primarily brominated, that could be resolved by gas chromatography (Figure 4). Bromoform at 3.7 min overlaps another smaller peak at 3.8 min. The peak at 2.7

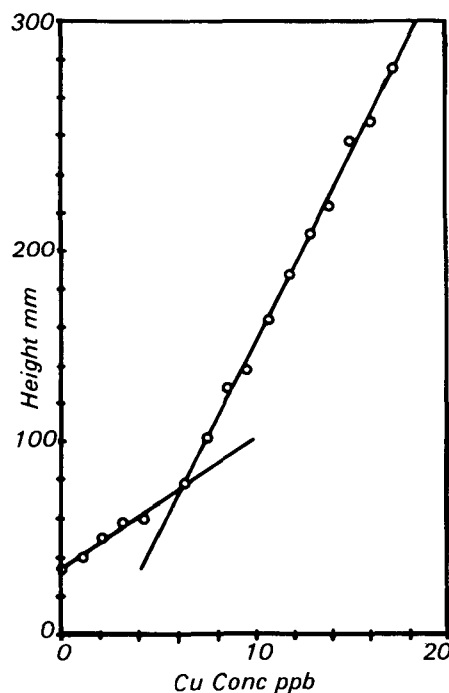


Figure 2. Anodic stripping current variation with copper added to a sample of Biscayne Bay water, showing copper-complexing capacity of 6 ppb.

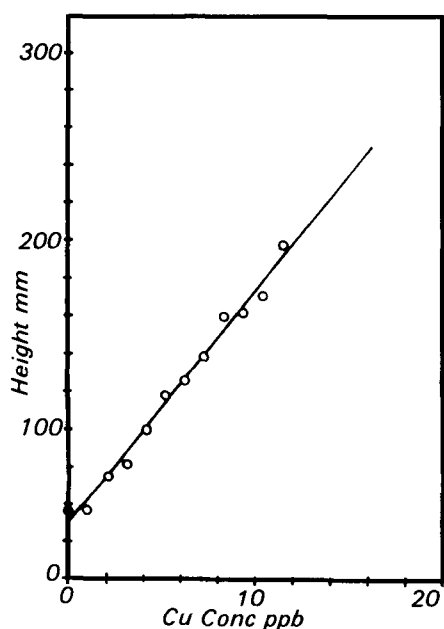


Figure 3. Anodic stripping current variation with copper added to a chlorinated (5 ppm Cl₂) sample of Biscayne Bay water, showing a loss of complexity capacity.

min gave a mass spectrum that corresponds to methylisobutyl ketone. Other peaks that were large enough to provide adequate mass spectral signals were all halogenated compounds, as shown by the characteristic M, M+2 couplets in the mass spectra. Compounds represented by the two major peaks at 4.2 min and 5.9 min were studied further, due to their high abundance in the chloroform extracts of Bay water, which may be expected to contain the lipophilic halogenated compounds that are potentially subject to substantial bioaccumulation. Studies using GC/ECD, GC/MS, HPLC, ¹H NMR, differential pulse polarography and other techniques were carried out on the natural extracts, as well as on synthesized compounds that gave the same mass spectra as the natural compounds. Work to date, described in detail in the project report, has led to partial characterization of these previously undetected and unknown chlorination products. The compounds were found to be reactive with the reductant, sodium thiosulfate, added to Bay water at pH 8 and therefore probably represent a significant part of the "chlorine-produced oxidants." Since

such oxidants commonly are biologically active, the tentative inference can be made that these compounds, which were discovered in this study, may play a substantial role in the environmental impact from the introduction of chlorine into brackish and marine waters.

Recommendations

1) Determine the uptake of compounds found to result from the chlorination of seawater, using standard test organisms and other controlled-exposure facilities.

2) Develop techniques for determining an appropriately selected series of haloamines in seawater at trace levels and examine chlorinated coastal waters for these compounds, using HPLC with fluorescence detection at sub-picomolar levels.

3) Utilize polarography (e.g., differential pulse, in conjunction with HPLC/fluorescence measurements), to determine electroreducible compounds in natural saline waters before and after chlorination.

4) Study the formation, decomposition and reactivity kinetics of haloamines, utilizing sophisticated stop-flow reaction techniques. New instrumentation that makes such work feasible has recently been developed by collaboration of our staff with Tracor Northern Inc. and Update Instrument Inc. Complete UV-visible-near IR spectra can be measured at 5 millisecond intervals, so that rapid reactions and observations of fleeting intermediates can be followed. Low concentrations of reactants can be used because of the signal-averaging capabilities of the system; for example, 200 spectra can be measured over a time period of one second and these data averaged. Freeze-quench and continuous flow modes are also features of this new instrument and may be particularly useful for the study of haloamines.

5) Study the reactivity of haloamines with other substrates in living organisms *in vitro* and *in vivo*. Mutagenesis is of particular concern and can be explored with the Ames test. Coupling reactions with RNA would be particularly interesting and could be sought by using C-14 tagged amines.

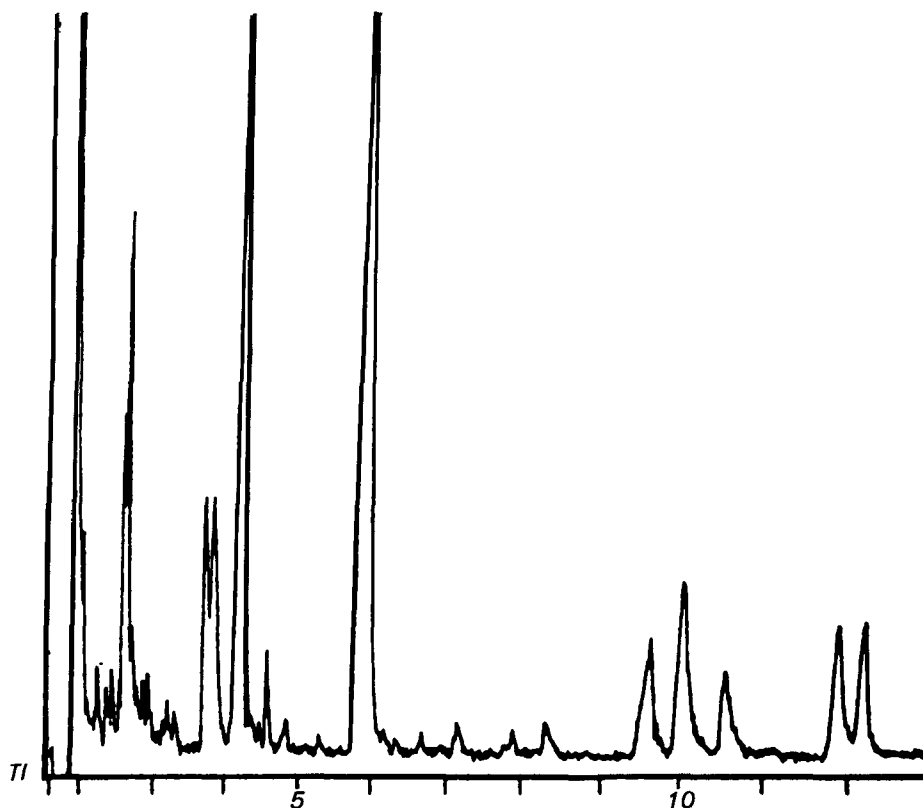


Figure 4. Total ion chromatogram of chloroform extract of chlorinated Biscayne Bay water, total ion abundance vs. elution time, minutes.

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W. P. Davis is the EPA Project Officer (see below).

The complete report, entitled "Reaction Products from the Chlorination of Seawater," (Order No. PB 81-172 280; Cost: \$8.00, subject to change) will be available only from:

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