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Detection of Sewage Organic Chlorination Products That Are Resistant to Dechlorination with Sulfite

WILLIAM A. MACCREHAN,*,† JAMES S. JENSEN,‡,§ AND GEORGE R. HELZ‡

Analytical Chemistry Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, and Water Resources Research Center, Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

Most of the 36 billion gal of treated sewage wastewater discharged daily into the environment in the United States is disinfected via chlorination. To minimize toxicity, dechlorination with sulfite or sulfur dioxide is often performed. Although dechlorination is considered instantaneous and complete, several studies have found residual toxicity of chlorinated/dechlorinated effluent to aquatic life. We investigated chlorination/dechlorination of the organic nitrogen components of sewage wastewater using both iodometric titration and a novel LC method. For LC, a postcolumn reaction with iodide rendered submicromolar chloramine concentrations detectable with amperometry. Using a gradient-elution LC separation, the retention and dechlorination behavior of a suite of model amines was determined, representing primary and secondary aliphatic, peptide, and protein-N. Chlorination/dechlorination experiments on freshly collected, tertiary-treated wastewater showed a fraction of the organic N-chloramines are dechlorinated slowly by sulfite with half-lives of >20 min. Chromatographic retention and kinetic behavior of the sewage N-chloramines was consistent with the behavior of the model peptides and proteins. Proteolytic hydrolysis markedly increased the "peptide" fraction observed upon chlorination of the wastewater. These results suggest that peptides and proteins contribute to slow dechlorination of sewage and may be a factor in the toxicity noted for chlorine-disinfected wastewater.

Introduction

Most municipal sewage treatment facilities are required to disinfect wastewater before discharge into the environment. Chlorination, via addition of either chlorine gas or hypochlorite ion, is the most common approach. To help protect aquatic wildlife from the toxic effects of "residual chlorine" in treated wastewater, the United States Environmental Protection Agency (EPA) established a criterion (*1*) for total residual chlorine of less than 0.16 μmol/L (0.011 mg/L as Cl_2). In working toward meeting this stringent criterion, many sewage wastewater treatment plants in the United States have installed equipment for dechlorination. Before discharge, the residual chlorine level in the wastewater is reduced by the addition of either sulfur dioxide or sulfite in stoichiometric excess. Since the dechlorination process is considered instantaneous (*2, 3*), the wastewater is typically discharged without additional delay.

Historically, the residual chlorine levels of dechlorinated wastewaters have not been accurately measured. The standard amperometric titration method (*4*) for residual chlorine suffers from an interference by sulfite. In this titration, residual chlorine stoichiometrically converts iodide to iodine, which is then titrated. However, Nweke and Helz (*5*) showed that the excess sulfite used for dechlorination reduces the iodine formed in the titration reaction directly, providing an incorrectly low value for residual chlorine. The modified amperometric titration method (*5*) eliminates this error via complexation of excess sulfite with formaldehyde before determining the residual chlorine. Using this method, the discharge of a sewage treatment plant employing dechlorination was found to often substantially exceed the EPA criteria for residual chlorine (*6*). The authors also found that the effective rate of sewage dechlorination by sulfite was bimodal. Although 90% of the chlorine is removed in the first 2 min of sulfite contact, about 10% was slowly dechlorinated with an effective rate constant of approximately 0.026 min^{-1} ($t_{1/2}$ = 26 min).

Although sulfite dechlorination dramatically reduces the acute toxicity of chlorinated wastewater, several studies have noted residual toxic effects to aquatic organisms. In controlled experiments with chlorinated/dechlorinated waters, acute mortality and reduced reproductive success was noted for *Ceriodaphnia dubia* (*7*), and mortality was noted for *Daphnia magna* (*8, 9*) and the eggs and larvae of *Morone saxatilis* (*10*). Residual chlorination products, persistent at levels higher than indicated by the standard titration method, may help account for these toxic effects. Of particular interest are the chlorination products of peptides and proteins, which are now known to be slowly dechlorinated (*6, 11*).

In this paper, we move toward a more complete understanding of the chemical events that occur during wastewater chlorination/dechlorination processes in sewage treatment. Using effluent collected from two processing facilities, the modified titration method was used to estimate total residual chlorine in controlled chlorination and dechlorination experiments. A reverse-phase liquid chromatographic method, based on electrochemical detection following a postcolumn reaction with iodide, was developed to monitor the behavior of organic N-chlorination products. In principle, this detection system responds to the same type of reactive chlorine compounds as the iodometric titration. Specific attention was given to the formation, possible identity, and kinetic behavior of dechlorination-resistant wastewater organic nitrogen components.

Experimental Section

Reagents. Mobile phase acetonitrile and trifluoroacetic acid (TFA) were HPLC grade. Water was purified by distillation, deionization, and cartridge filtration. A stock solution of TFA was prepared at a concentration of 1 mol/L, then adjusted to pH 2.88 with sodium hydroxide, and used to prepare the mobile phases. The TFA concentration in the final chromatographic solvents was 0.05 mol/L. At the beginning of each day, the mobile phases were degassed under vacuum at 50 °C in an ultrasonic bath. The postcolumn reagent was

* To whom correspondence should be sent. Phone: (301)975-3122; fax: (301)977-0587; e-mail: william.maccrehan@nist.gov.
† National Institute of Standards and Technology.
‡ University of Maryland.
§ Present address: Pharmaceutical Delivery Systems, Parke Davis, Morris Plains, NJ 07950.

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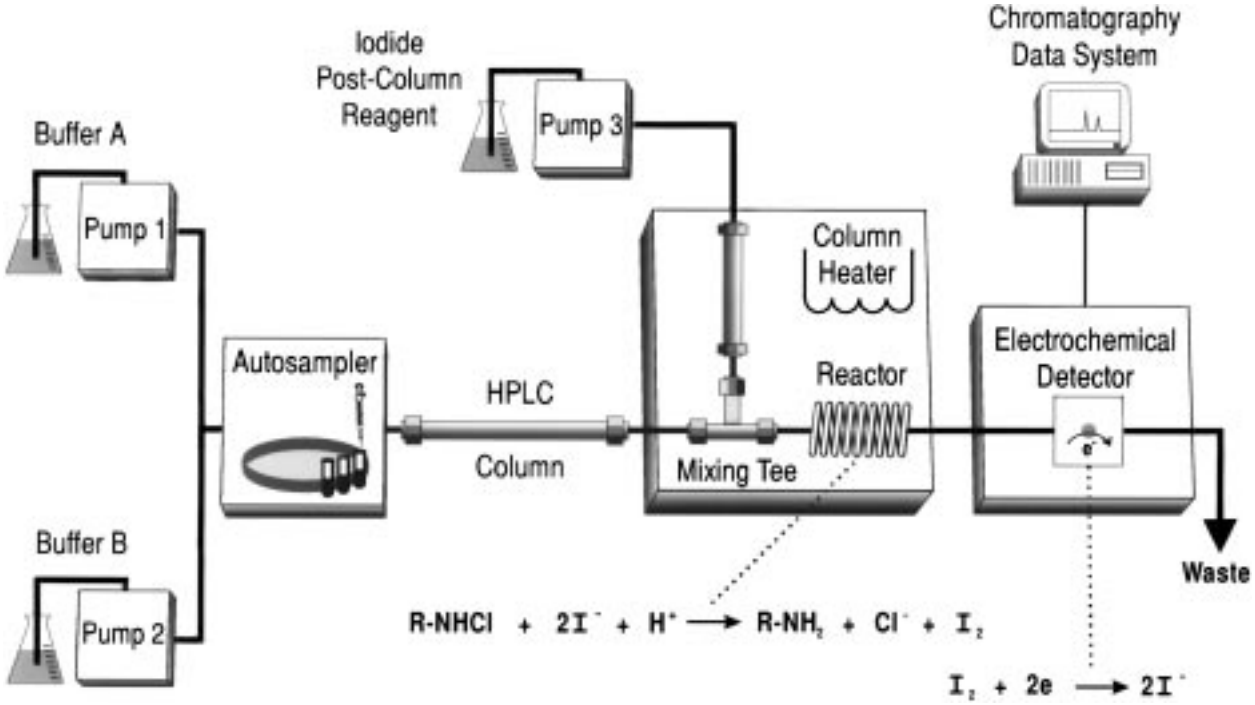

FIGURE 1. Liquid chromatograph/postcolumn electrochemical detection system for the detection of N-chloramines.

made up with Suprapur-grade potassium iodide (EM Science, Gibbstown, NJ), sodium acetate (analytical reagent, Mallinckrodt, Paris, KY), and glacial acetic acid (Suprapur, Matheson, Coleman and Bell, Norwood, OH). The postcolumn reagent was made fresh daily and stored in a brown bottle.

Sodium hypochlorite solution (reagent grade, Johnson Matthey, Inc., West Deptford, NJ) and cartridge-purified distilled water were used to prepare stock solutions of aqueous chlorine. Stock solutions were standardized weekly using the amperometric titration method at pH 4 (*4*). A Metrohm 716 DMS (Metrohm, Herisau, Switzerland) titrator was used with a phenylarsine oxide titrant (Fisher Scientific, Springfield, NJ), standardized using the iodate/iodide reaction (*4*). The modified amperometric titration was used to determine total residual chlorine in the presence of excess sulfite (*5*, *6*, *12*). Sodium sulfite solutions were prepared gravimetrically from purified water and Na_2SO_3 (reagent grade, J. T. Baker). The sulfite solutions were made fresh daily and used immediately. The peptides glyclyglycine (gly_2), alanylalanine (ala_2), tetraalanine (ala_4), hexaalanine (ala_6), leucylalanine (leu-ala), and phenylalanylglycine (phe-gly) and the amino acids leucine and phenylalanine were all obtained from Sigma Chemical Co. (St. Louis, MO), and purity was verified by thin-layer chromatography (*8*). Piperidine and *n*-butylamine (Sigma), insulin (from hog pancreas) (Fluka Chemical Corp, Milwaukee, WI), and proteinase K (Sigma) were used without further purification. Active and inactive proteinase K enzyme were added at a concentration of 0.4 μmol/L to BARC wastewater and allowed to react for 24 h at room temperature before analysis. Inactive enzyme was prepared by denaturation at 100 °C for 10 min.

Chromatography. The LC system for the detection of N-chloramines is diagramed in Figure 1. A two-pump, gradient-elution liquid chromatograph was used with a variable volume autosampler that allowed for injection volumes to 2 mL. A 500-μL injection volume was used for all chromatograms shown in the figures. The mobile phase composition was as follows: A, 100% water, 0.05 mol/L trifluoroacetic acid (TFA), pH 2.88; B, 90:10 acetonitrile:water (v/v), 0.05 mol/L TFA buffer. The solvent composition program was 100% A from 0 to 5 min, linear gradient to 100% B from 5 to 30 min, and hold at 100% B from 30 to 40 min before return to 100% A.

The analytical column was an octadecylsilyl bonded-phase silica, Bakerbond C18, 4.6 × 250 mm, 5-μm spherical particles, product 7098-00 (J.T Baker, Phillipsburg, NJ) protected with a guard column (2.2 × 30 mm) packed with pellicular C-18 silica (Waters, Bondapak C18 corasil, 37−50 μm particles). A mixing tee was used to introduce the postcolumn reagent. The iodide reagent was 0.02 mol/L KI in 0.30 mol/L sodium acetate/acetic acid buffer at pH 4.0. Flow was provided by an HPLC pump with an internal pulse dampener. The postcolumn reactor consisted of fluoropolymer tubing (0.50 mm × 5.0 m) crocheted to minimize band spreading. The LC mobile phase was delivered at 1.0 mL/min, and the postcolumn reagent was at 0.50 mL/min. The residence time in the reactor was approximately 40 s. An LC column temperature controller was used to maintain the temperature of a reagent back-pressure column and the postcolumn reactor coil at 50 °C.

Iodine produced in the postcolumn reaction was detected by reductive amperometry (BAS model LC-4A detector) at a glassy carbon electrode using an applied potential of −100 mV against an Ag/AgCl reference electrode. Early experiments showed that the postcolumn reagent I^- interfered with the reference electrode via the formation of AgI, so the reference electrode was isolated by a double junction filled with saturated KCl and refreshed weekly. A back-pressure regulator was used at the detector outlet. A computerized chromatography data system was used to process and output the data.

Sewage Samples. Sewage wastewater samples were collected from two treatment facilities that employ chlorination/dechlorination as part of the normal effluent processing. The Beltsville Agricultural Research Center (BARC) system utilizes an aerobic activated-sludge reactor, and the Fort Meade (FM) process utilizes a multistage sludge reactor combining nitrification/denitrification steps (*8*). Samples were collected from the process stream at a point just prior to the chlorination step. Samples were transported to the lab and stored in a refrigerator at 4 °C. All chlorination/dechlorination experiments were performed within 24 h of

sample collection. Calibrated amounts of sodium hypochlorite, standardized by amperometric titration, were added to produce a known chlorine dose. After 1 h of chlorine reaction time, the residual chlorine level was determined by amperometric titration against standardized phenylarsine oxide (Fisher Scientific) (*4*). Then sulfite was added in 1.5-fold stoichiometric excess to measured residual chlorine value. For the BARC samples (pH 7.54), the 60 μmol/L hypochlorite (4.4 mg/L as Cl_2) dose typically produced a 1-h residual of 18 μmol/L OCl^- (1.3 mg/L as Cl_2) to which a 27 μmol/L dose of sulfite was added. The FM samples (pH 7.41) had corresponding levels of 60 μmol/L OCl^- dose, 26 μmol/L 1-h residual, and 40 μmol/L sulfite dose. For some samples, the time course of dechlorination was monitored using the modified amperometric titration that removes interference of sulfite with formaldehyde (*5*, *6*). Separate subsamples were dosed identically for liquid chromatographic analysis.

Results and Discussion

Analytical LC Method. Although there are many analytical methods for the determination of chlorinated organic compounds with C−Cl bonds, there are few methods for the determination of chlorine-produced oxidants such as organic N-chloramines. Methods based on derivatization/fluorescence of the N-chloramine functionality have been developed (*13*, *14*). However, these approaches provide poor selectivity against interference from free amines that are present in excess in chlorinated sewage wastewater. A method with high selectivity for N-chloramines using liquid chromatography/electrochemical detection was proposed by Jersey (*15*). Following a reverse-phase separation, N-chloramines were determined using a postcolumn reaction with iodide. The iodine formed enhances detection because it has a lower reduction potential at a glassy carbon electrode than the parent N-chloramines (*15*).

For this study, the sensitivity of the iodine postcolumn electrochemical detection approach was enhanced by the careful choice of a low pH, by controlling the concentration of iodide, and by heating the postcolumn reactor (*8*). Despite this optimization, stoichiometric conversion of organic N-chloramines to iodine was not obtained. *N*-Chloropiperidine and *N*-chloroleucylalanine provided molar response factors that differed by 2-fold (*8*). Stoichiometric conversion would be highly desirable, as this would permit calibration of the sewage N-chloramine content against a stable standard such as *N*-chlorosuccinimide. We believe iodide/iodine may not be an ideal electrochemical mediator for the "on-line" detection of N-chloramines. The substoichiometric response in the flow reactor may be the result of insufficiently fast reaction of I^- with some N-chloramines (*16*). However, the current I^-/I_2 postcolumn detection method provides good N-chloramine selectivity and sensitivity for components that contribute to residual chlorine. The detection limits for a 500-μL injection of the N-chloramines of piperidine and leu-ala were estimated to be 1.7×10^{-7} and 0.8×10^{-7} mol/L, respectively, based on a peak height three times the baseline noise. This sensitivity is adequate for process monitoring; however, the technique would be of limited utility in studying the fate of these compounds after dilution in receiving streams.

Model Compound Measurements. A gradient elution LC solvent program was developed that provided resolution of N-chloramines possessing a wide range of hydrophobicities. The retention of a series of possible sewage N-chloroalkylamines, -amino acids, -porphyrin, and -peptides has been tabulated (*8*). In all cases tested, the N-chloramine has greater reverse phase retention and hence more hydrophobic character than the parent amine. The N-chloramine hydrophobicity may facilitate cellular membrane accumulation and transport of these compounds contributing to the toxic effect on aquatic life.

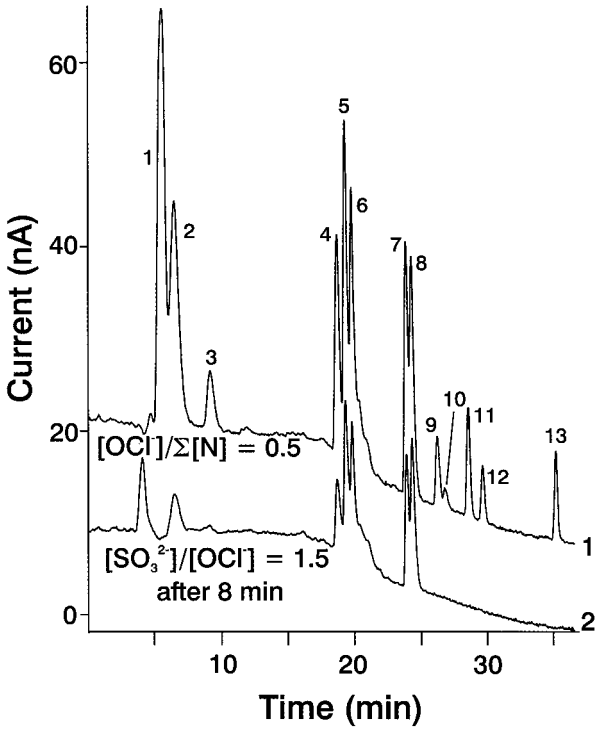

FIGURE 2. Chlorination/dechlorination of a model amine mixture. Upper trace: Sample in 1.0 mmol/L phosphate buffer, pH 7.1; total amine concentration of 25 μmol/L; 12 μmol/L OCl^- added; and a contact time of 10 min. Lower trace: As in panel A with 18 μmol/L SO_3^{2-} added and a contact time of 8 min. Peak identification: (1) monochloramine, (2) unidentified, (3) *N*-chloroglycylglycine, (4) *N*-chloroalanylalanine, (5) *N*-chlorotetraalanine, (6) *N*-chlorohexaalanine, (7) *N*-chloroleucylalanine, (8) *N*-chlorophenylalanylglycine, (9) *N*-chloroleucine, (10) *N*-chlorophenylalanine, (11) *N*-chloro-*n*-butylamine, (12) *N*-chlorpiperidine, and (13) *N,N*-dichloro-*n*-butylamine (tentative).

The chlorination/dechlorination behavior of a mixture of some model peptides and amines was investigated chromatographically. Approximately 2 μmol/L each of ammonia, gly-gly, ala-ala, tetra-ala, hex-ala, leu-ala, phe-gly, leu, phe-ala, butylamine, and piperidine ($\Sigma[\text{amines}]_{\text{total}} = 25\ \mu$mol/L) were chlorinated using a substoichiometric OCl^-/N ratio of 0.5 with a reaction time of 10 min, producing the chloramine mixture in Figure 2, trace 1. This low OCl^-/N ratio minimized the formation of dichloramines or other side product oxidation reactions. Both inorganic and organic N-chloramines formed rapidly. This product mixture was then dechlorinated for 8 min with excess sulfite at a SO_3^{2-}/OCl^- ratio of 1.5, shown in Figure 2, trace 2. Dechlorination occurs rapidly for the N-chloramines derived from ammonia, an amino acid (leucine), and primary and secondary alkylamines (butylamine and piperidine, respectively). As previously determined in kinetic studies (*8*, *11*, *17*), the dechlorination rates of some N-chloropeptides (ala-ala, tetra-ala, hex-ala, phegly, leu-ala) are slow on the time scale of this experiment. The "peptide" elution window of 15−25-min retention time under these LC conditions includes all of the slowly dechlorinated model peptides. It is likely that the chloramines of structurally similar peptide and protein organic-N may contribute to the slow dechlorination previously observed in wastewater effluents (*6*).

The chlorination/dechlorination of a model protein was studied to represent the behavior of protein-N known to be present in treated sewage wastewater (*18*, *19*). Free and combined amino acids have been estimated to be 10% of the

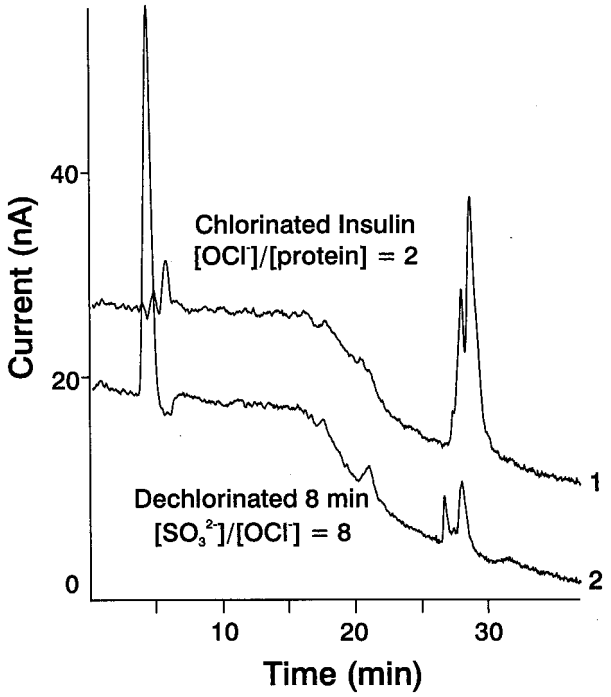

FIGURE 3. Chlorination/dechlorination of porcine insulin. Upper trace: 2 μmol/L insulin in 1.0 mmol/L phosphate buffer, pH 7.7, with 4 μmol/L OCl^- added and a contact time of 40 min. Lower trace: as in panel A with the addition of 32 μmol/L SO_3^{2-} and a contact time of 8 min.

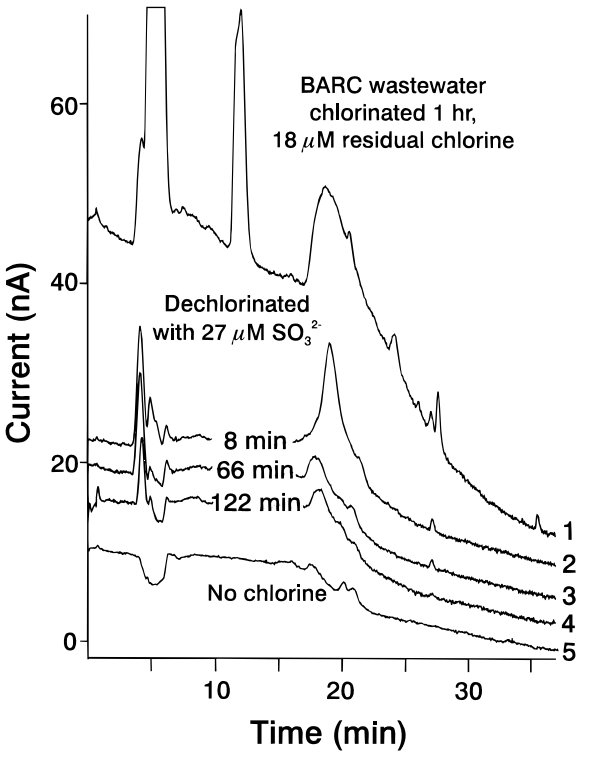

FIGURE 4. Chlorination/dechlorination behavior of sewage wastewater. Trace 1, BARC sewage (pH 7.54) with the addition of 60 μmol/L OCl^-, measured 1-h residual chlorine − 18 μmol/L; trace 2, dechlorination of trace 1 with 27 μmol/L SO_3^{2-} with a contact time of 8 min, measured residual chlorine 1.6 μmol/L; trace 3, as 2 with a contact time of 66 min; trace 4, as in trace 2 with a contact time of 122 min; trace 5, BARC sewage without the addition of OCl^-.

total soluble organic nitrogen in an activated sludge treated wastewater (*20*). Porcine insulin (MW = 5777) was selected as a model protein because it is known to accept chlorine preferentially at the two terminal amino acid residues (glycine and phenylalanine) of this dimeric polypeptide (*21*). Chlorination at a molar ratio of 2:1 OCl^-/protein, with an equilibration of 40 min, produced the chromatographic result in Figure 3, trace 1. Note the formation of two distinct protein N-chloramine products with retention times in the 25−30-min range. Dechlorination with excess sulfite (SO_3^{2-}/OCl^- = 8) and a contact time of 8 min is shown in Figure 3, trace 2. The reproducible change in retention noted for the freshly chlorinated versus slowly dechlorinated form of the protein may be the result of the tertiary structural changes associated with partial conversion of some of the hydrophobic N-chloramine sites on the protein back to the hydrophilic amine form via the dechlorination process.

Sewage Wastewater Measurements. Wastewater was collected from two municipal wastewater treatment plants at points just preceding the chlorination process. Chlorination and dechlorination were performed in the laboratory on fresh samples. Measured doses were used to control residual oxidant concentrations, contact times, and dechlorination agent concentrations to levels that were typical of process conditions.

Chromatographic analysis of the initial products formed by chlorination of the wastewater from the BARC plant is shown in Figure 4, trace 1. Monochloramine, dichloramine, and excess hypochlorite elute in under 15 min and are rapidly removed upon the addition of sulfite at a 1.5 stoichiometric excess over the titrimetrically measured residual chlorine level. The 1-h residual chlorine values were 18 μmol/L (1.3 mg/L as Cl_2) before dechlorination and 1.6 μmol/L (0.11 mg/L as Cl_2) after 8 min of dechlorination. A prominent broad "peak" that elutes in the retention time window of 15−25 min is likely to represent a number of N-chloramine compounds that are not chromatographically resolved. This elution window corresponds to that observed for the model peptide compounds. The compounds comprising this broad peak are slowly dechlorinated by sulfite, as shown in Figure 4, traces 2, 3, and 4, for contact times of 8, 66, and 122 min, respectively. Some residual oxidant is noted even after the contact time of 122 min. The dechlorination rate obtained for the broad peak is consistent with results from kinetic studies of a series of model peptides (*11*). Thus, both the chromatographic retention time and the observed rate of dechlorination consistently point to the presence of peptides in the wastewater as contributing to slow dechlorination.

An additional chromatographic peak at 27 min was also observed to be slowly dechlorinated. This retention time corresponds well to the elution range of the model protein. The selectivity of the analysis scheme for determining active chlorine is shown in Figure 4, trace 5. This largely featureless chromatogram was obtained from a wastewater sample without the addition of hypochlorite.

An estimation of the total concentration of slowly dechlorinated N-chloramines can be made by measuring the total peak area under all peaks eluting after 15 min. Assuming that the peak response for *N*-chloroleucylalanine can be used for rough calibration, the dechlorination-resistant N-chloramine fraction, as determined by LC, was estimated to be 0.8 μmol/L (0.06 mg/L as Cl_2) after 8 min of contact with excess sulfite. This is in rough agreement with the titrimetric residual value of 1.6 μmol/L (0.11 mg/L as Cl_2). Residual chlorine values estimated by both methods clearly exceed the EPA criterion of 0.011 mg/L for residual chlorine. Several factors contribute to this lack of exact agreement between the titration and LC experiments: (i) unlike the titration, the LC postcolumn reaction time may be too short (40 s) for complete reaction, providing a less than stoichiometric detector signal; (ii) the calibration of the LC signal with *N*-chloroleucylalanine may not provide high accuracy;

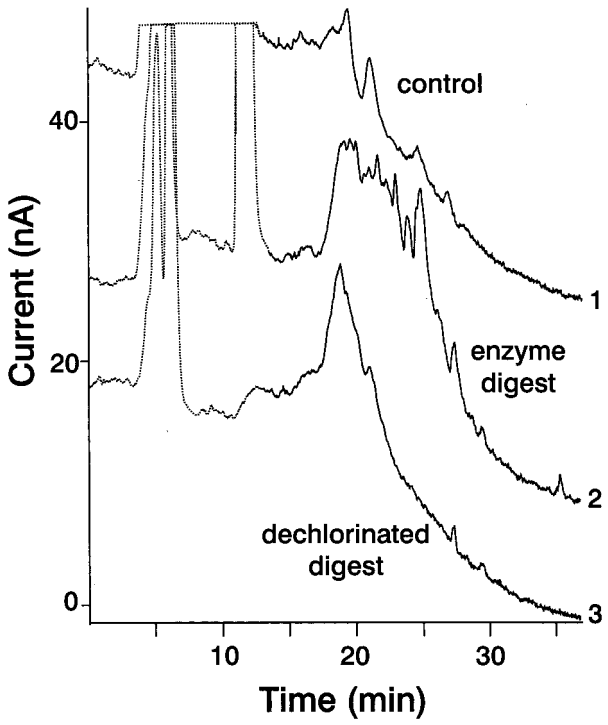

FIGURE 5. Chlorination/dechlorination of wastewater sample treated with proteolytic enzyme. Trace 1, BARC wastewater (pH 7.19) with addition of 0.4 μmol/L deactivated proteinase K, 94 μmol/L OCl^- added; trace 2, as in trace 1 except active enzyme added 24-h before 94 μmol/L OCl^-, followed by a contact time of 1 h; trace 3, as in trace 2 with the addition of 60 μmol/L SO_3^{2-} and a contact time of 8 min.

(iii) some decomposition of the N-chloramines may occur on the stainless steel and silica surfaces of the LC system; and (iv) sewage N-chloramines detected by the titration may not elute under the LC conditions chosen. Replication of this chlorination/dechlorination experiment on samples collected on three separate occasions at the BARC facility produced chromatograms retaining the same pattern of chromatographic peaks as shown in Figure 4 and that varied only within a factor of 2 in peak area.

A sample of wastewater from the FM treatment facility was also collected and chlorinated/dechlorinated to evaluate differences that might be attributed to a different process chemistry (*8*). When compared to the BARC wastewater, a less prominent dechlorination-resistant N-chloramine peak was observed in the retention window of 15−25 min that corresponded to the retention of peptides. Two additional peaks at 27 and 29 min retention (that corresponded to the retention range found for protein) were noted.

To investigate the possibility that proteinaceous material contributes to the dechlorination-resistant fraction of the sewage N-chloramines, we chromatographically analyzed a BARC sewage sample (pH 7.19) after the addition of a proteolytic enzyme of low sequence specificity, proteinase K. An analogous hydrolysis occurs during the bacterial treatment process, via exocellular enzymes that reduce the size of the high molecular weight proteinaceous material to amino acid and peptide fragments suitable for transport through the cell membrane. As a control, thermally denatured proteinase K was added to the wastewater in the same concentration as active enzyme. Figure 5, trace 1 shows the N-chloramines in the native sewage, as well as any chlorination products associated with the addition of inactive enzyme. Figure 5, trace 2 is the sample after 24 h of enzymatic digestion of the sewage sample, revealing the formation of a number of N-chlorinated hydrolysis products with the retention time in the range of peptides. Dechlorination of the digested sample for 8 min (trace 3) shows enhancement of the broad peak with retention (15−25 min) associated with peptides. For this dechlorination experiment, SO_3^{2-} was added at twice the stoichiometric amount to the residual chlorine value previously determined for the undigested sewage. These results indicate that the treated sewage at BARC does contain protein that may contribute to dechlorination-resistant N-chloramines observed. Interestingly, the peak at 27 min remains after the proteolytic hydrolysis and dechlorination.

Thus, in addition to the formation of inorganic chloramines, chlorination of effluents from two treatment plants also produced a large number of moderately hydrophobic, iodide-oxidizing compounds. Although the addition of excess sulfite rapidly dechlorinated the inorganic chloramines, the concentration of compounds with longer chromatographic retention decreased slowly over the period of 1 h. Chlorination/dechlorination of model peptides and a protein yielded products with chromatographic retention times and rates of removal that were consistent with those observed in sewage. In addition, pretreatment of sewage with a proteolytic enzyme increased the concentration of components eluting in the peptide elution window. Given these lines of evidence, it appears likely that peptides and protein fragments constitute a major fraction of the slowly dechlorinated components in sewage. It is reasonable that biologically treated wastewater would contain peptide and protein fragments produced during microbial digestion of the proteinaceous material in raw wastewater. In view of the findings in this paper, an exploratory investigation of the toxicity of chlorinated peptides/proteins to aquatic ecosystems now seems justified.

Acknowledgments

Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose. This work was partially supported by the Maryland Water Resources Research Center with a grant from the U.S. Geological Survey.

Note Added in Proof: While this paper was in review, another method for the post-column reaction detection of amino acid and peptide *N*-chloramines was published (*22*).

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