Incompleteness of Wastewater Dechlorination

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Dechlorination by sulfur dioxide or other S(IV) compounds is employed to protect aquatic wildlife from toxic residual chlorine in wastewater treatment plant effluents. Tests at two wastewater treatment plants show that dechlorination removes 87-98% of residual chlorine but that a remainder, which exceeds regulatory limits, is very slowly reduced. Judging from kinetic evidence, chlorinated secondary organic amines and peptides probably contribute to S(IV)-resistant residual chlorine. Most of the S(IV)-resistant fraction is extractable into octanol. Its hydrophobic character suggests that this fraction may be harmful to organisms in receiving streams. S(IV)-resistant residual chlorine has been overlooked previously because the dechlorinating agent interferes with standard analytical methods for total chlorine.

Introduction

Wastewaters in the United States are disinfected, usually with chlorine, as one of a number of measures to control waterborne disease. A drawback of this public health strategy is that chlorine and its byproducts can harm aquatic organisms living in waters receiving treatment plant effluents (1-3). Fish kills, fish avoidance, and losses of species diversity have been described near treatment plants discharging chlorinated water (4-7). To protect aquatic wildlife, the U.S. Environmental Protection Agency (EPA) in 1985 determined that total residual chlorine in freshwaters should be less than 11 μ g/L or 0.16 μ M (8). This limit is meant to be a 4-day average concentration not to be exceeded more than once in 3 yr. An acute criterion of 19 μ g/L (0.27 μ M) averaged over a 1-h period was also specified. Lower levels were specified for saltwater. These standards culminated a decade-long reevaluation of disinfection policy. Earlier standards had required more than $500 \,\mu g/L \,(7.0 \,\mu M)$ residual chlorine in wastewater effluents unless regular microbiological monitoring was performed.

To meet the new, more stringent EPA criteria, many treatment plant operators have opted to install dechlorination equipment. Ninety-five percent of the wastewater treatment plants in Maryland now dechlorinate. Recent technological literature reveals that installation of dechlorination equipment is still underway in the United States and abroad (9-13).

Dechlorination usually is accomplished with S(IV) compounds [i.e., compounds such as $SO_2(g)$ or NaHSO₃-(aq) which contain sulfur in the +IV oxidation state]. These are injected into an effluent after disinfection is complete, just prior to discharge. The objective is to reduce all chlorine-produced oxidants to nonactive halides. Chlorine-produced oxidants are operationally defined as the molar sum of chlorine byproducts that oxidize iodide at pH 4. They include not only HOCl and OCl⁻, which are the hydrolysis products of Cl₂, but also chloramines. Wastewaters contain up to millimolar concentrations of reduced nitrogen in the form of ammonia, organic amines, amides, etc. (14-16). These compounds react rapidly with chlorine to form chloramines (e.g., NH₂Cl, NHCl₂, RNHCl, R₂NCl); chloramines also oxidize iodide at acidic pH.

In most toxicological studies, it has been clear that dechlorination reduces the toxicity of disinfected wastewater effluents to aquatic wildlife (17-20). However in one detailed study (20), a small but significant increase in striped bass mortality in dechlorinated water compared to untreated estuarine water was reported. In a more recent report, the freshwater invertebrate, *Ceriodaphnia dubia*, experienced less reproductive success in chlorinated/ dechlorinated effluent than in undisinfected effluent (21). These results suggest that dechlorination does not completely remove the toxic products of chlorination.

In this paper, we report the first measurements of chlorine-produced oxidants in dechlorinated wastewaters. Key to this work was prior development of a method for

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preventing excess S(IV) in dechlorinated wastewater from interfering in the standard chlorine assay (22). Our work challenges the widely-held view that dechlorination with S(IV) is rapid and complete (23).

Methods

In order to detect residual chlorine in the presence of excess S(IV) (mostly $HSO_3^- + SO_3^{2-}$ at near-neutral pH), we bind the S(IV) to formaldehyde, forming hydroxymethane sulfonate. Then chlorine-produced oxidants are measured in the conventional way by measuring the I₂ they produce when they oxidize I⁻ at pH 4. We use the amperometric titration method for I₂ quantification. To the near-neutral pH sample, we add enough formaldehyde to give a concentration of 350 mM. A period of 2 min is allowed for the formaldehyde to combine with sulfites. Then enough potassium iodide to give 1.5 mM is added, followed by pH 4 acetate buffer. The I2 formed at this stage is titrated with phenylarsine oxide using a Brinkmann E436 potentiograph. In common practice, the analytical result is reported as the mass concentration of Cl₂ that would give an oxidizing capacity equivalent to the I2 titrated. However, in this paper, we will report results in micromolar (μM) units to facilitate comparison with S(IV) doses; to convert micromolar to microgram of Cl_2/L (\approx ppb), multiply by 71.

In blank tests, the formaldehyde method gave no detectable iodine (<0.03 μ M) in wastewaters sampled upstream of the chlorine injection point. Recovery of oxidant was tested by spiking sulfite-containing treatment plant effluents with 15-17 μ M N-chlorotrialanine, a chloramine shown by Stanbro and Lenkevich (24, 25) to react slowly with sulfite. When formaldehyde was added to the S(IV)-bearing samples before spiking with Nchlorotrialanine, recoveries of oxidizing capacity were 96% or better. When the N-chlorotrialanine was added before formaldehyde, recoveries were 86% or better. The lower recovery in the latter case is presumed to be caused by slow reaction of the test compound with sulfite before hydroxymethanesulfonate formation reaches completion. Analytical precision is estimated to be $\pm 0.03 \ \mu M$ or $\pm 2\%$, whichever is larger (26).

Effluents were analyzed on-site at two wastewater treatment plants having operating dechlorination systems. Elapsed time between collection of a sample and the beginning of the analytical protocol in the laboratory was <5 min.

The Western Branch Sewage Treatment Plant is a modern, activated sludge plant, which handles about 50×10^6 L/day of wastewater. Treatment includes nitrification to decrease ammonia. Dechlorination is accomplished by the injection of SO₂ into the effluent stream within a few meters of the discharge point.

In contrast, the Horsepen Branch plant is an older, extended aeration plant with a capacity of about 1×10^6 L/day. Because this plant is much less efficient than the Western Branch plant, much larger residual chlorine concentrations are required for disinfection. Several years ago, an activated carbon system had been installed at Horsepen Branch to dechlorinate the effluent. When this proved only partially effective, a SO₂ system was added. The activated carbon columns remained instream but were not maintained or periodically renewed.

On the day of a field experiment, analytical reagents, including Na₂SO₃, KI, and alanylalanylalanine (trialanine) solutions, were prepared from reagent-grade chemicals and



FIGURE 1. Concentrations of total residual chlorine at Western Branch in samples taken upstream and downstream of the SO_2 injection point. The residual chlorine fluctuations during the day illustrate variability typical of wastewaters. Dechlorination with SO_2 removes 90-95% of the residual chlorine in the wastewater, but the amount remaining considerably exceeds the EPA's criterion for freshwaters. Effluent characteristics: pH = 6.9; T = 18 °C; total Kjeldahl N = 1.1 mg/L.

transported to the field site in an icebox. To exclude a potentially serious analytical artifact, care was taken to minimize exposure of the KI solution to sunlight.

In the experiments with model compounds, stock solutions of selected amines were made from commercially available reagents (peptides from Sigma Chemical Co.; amines from Baker Chemical Co.). Diethylamine (Baker Analyzed grade) was redistilled prior to use. To prepare chlorinated forms of the amines and peptides, reagentgrade NaOCl was added to aqueous solutions containing the N compound of interest.

Results

Field Tests. Determinations of total residual chlorine in the effluents of the two plants are given in Figures 1 and 2. The residual chlorine remaining after treatment with SO₂ ranged from 2% to 13% but was typically about 5% of the residual chlorine present just prior to SO₂ addition. In every case, the amount of residual chlorine in the effluent after SO₂ treatment exceeded the EPA criterion of 0.16 μ M. Because these dechlorinated effluents contained excess dechlorinating agent, no residual chlorine was detectable (<0.03 μ M) by the standard amperometric method when the formaldehyde step was omitted.

As shown in Figure 2, the residual chlorine remaining after activated carbon treatment at Horsepen Branch exceeded 10% of the residual chlorine in the contact tank. This is one reason why the activated carbon method of dechlorination had been judged unsatisfactory by the plant managers.

Figure 3 shows the total residual chlorine concentration as a function of time in a sample from the chlorine contact tank of the Horsepen Branch plant. This sample was treated at the on-site laboratory with Na_2SO_3 in approximately 50% molar excess relative to the initial total residual chlorine. This sulfite dosage is in the range used for dechlorination by treatment plants. The sample was then analyzed several times during the next hour. Within the first 2 min, approximately 90% of the residual chlorine was reduced by the sulfite. The remaining residual chlorine disappeared slowly, in a manner that can be described by a first-order



FIGURE 2. Concentrations of total residual chlorine at Horsepen Branch. At this plant, water from the Cl₂ contact tank passes through activated carbon columns before being dechlorinated with SO₂. Note the much higher residual chlorine concentration used at this plant compared to that in Figure 1. Higher Cl₂ doses are required to achieve satisfactory disinfection because the plant does not denitrify its water. Effluent characteristics: pH = 6.7; T = 18 °C; total Kjeldahl N = 1.6 mg/L.



FIGURE 3. Decrease of total residual chlorine as a function of time in water from the chlorine contact tank at Horsepen Branch. The sample was treated with sulfite at the on-site laboratory. Time is measured from the moment of sulfite addition. The linear decrease indicates approximate first-order decay with a half-life of 26 min. On this log scale, the EPA criterion of 11 μ g Cl₂/L would be -6.8.

rate constant of 0.026 min⁻¹ ($t_{1/2} = 26$ min). The rate of disappearance of residual chlorine depended on the sulfite concentration, but even doubling the initial sulfite concentration did not eliminate all residual chlorine from a fresh sample within 1 h.

Hydrophobic Characteristics. Experience with the bactericidal properties of hydrophilic organic chloramines, such as chlorinated amino acids, has led to the common view that organic chloramines are relatively nontoxic (27). However, some hydrophobic organic chloramines are more toxic than NH₂Cl and nearly as toxic as HOCl to fish (28). Thus, the hydrophobicity of residual chlorine fractions has toxicological significance. To explore hydrophobicity in the S(IV)-resistant oxidant fraction, we attempted to extract

TABLE 1

Extraction of Chlorine-Produced Oxidants from Horsepen Branch Water into 1-Octanol^a

sample	concn (µM)
initial oxidant in water oxidant after dechlorination ^b oxidant in water after extraction	$27.6 \pm 1.1 \\ 3.2 \pm 0.3 \\ {}^{<}0.7$
oxidant in octanol after extraction ^c	3.4 ± 0.3

 a A volume of 0.35 L of water was extracted with 0.1 L of octanol. b Oxidant determined by formaldehyde method 2 min after the addition of 60 μM Na_2SO₃. c Determined by back-extracting into thiosulfate solution; volume corrected for comparison with other values in the table.

TABLE 2

Calculated Half-Lives for First Dechlorination Step for Selected Chloramines under Pseudo-First-Order Conditions (i.e., S(IV) \gg Chloramine); pH 7, S(IV) = 10 μ M, 25 °C

base compd	monochloru	dichloro	trichloro
NH ₃ CH ₃ NH ₂ alanine trialanine	0.072 min ^a 0.26 min ^c 0.97 min ^c 15 min ^c	17 ms ^b 4.1 ms ^b fast ^c	22 µs ^b

^{*a*} Data from Yiin et al. (*31*); for comparison with other values in this column, acid catalysis by 0.01 M $H_2PO_4^-$ is assumed. ^{*b*} Yiin and Margerum (*32*). ^{*c*} Stanbro and Lenkevich (*24*).

the oxidant from Horsepen Branch effluent into octanol. We chose octanol simply because octanol—water partition coefficients (K_{ow}) are used in pharmaceutical and environmental sciences as a measure of hydrophobicity.

In this experiment, water from the chlorine contact tank at Horsepen Branch was dechlorinated in the laboratory with Na_2SO_3 for 2 min. Then the sample was shaken with octanol in a separatory funnel. After 15 min for phase separation, the aqueous phase was analyzed for residual chlorine, and the octanol phase was back-extracted with a standardized thiosulfate solution. Iodometric determination of the thiosulfate loss served to quantify the amount of oxidant in the octanol phase.

The results are shown in Table 1. Some difficulties with phase separation were encountered owing to surfactants in the wastewater. As a consequence, the precision of the amperometric titrations was adversely affected. However, within experimental uncertainty, it appears that nearly all the S(IV)-resistant oxidants could be extracted into octanol. The back-extraction results, employing thiosulfate, demonstrate that the oxidant consists of substances that were dissolved in the octanol, not simply reduced by it.

Discussion

Chemical Interpretation. How can the observations above be explained chemically? According to published kinetic data (29, 30), S(IV) reduces free chlorine (i.e., HOCl + OCl⁻) to chloride extremely rapidly. The same conclusion applies to NHCl₂ and NCl₃, calculated half-lives for which are shown in Table 2. Di- and trichloramine are dechlorinated in a stepwise manner, one chlorine at a time, and the half-lives in Table 2 refer to the first dechlorination step under assumed conditions of pH 7 and S(IV) = 10 μ M.

For NH₂Cl, the lifetime is somewhat longer (Table 2), but still short relative to mixing processes at treatments



FIGURE 4. Calculated half-life of NH₂Cl with respect to dechlorination by S(IV). Kinetic data from ref 31. Pseudo-first-order conditions assumed (i.e., S(IV) \gg NH₂Cl). Half-lives are upper limits because no provision is made for general acid catalysis other than by H₂O, H₃O⁺, and HSO₃⁻.

plants provided the pH is near neutral or below. Unlike NHCl₂ and NCl₃, dechlorination of NH₂Cl is subject to general acid catalysis (31), so the half-life shown in Table 2 depends upon the bulk composition of the solution. To be consistent with the rest of the values in the monochlor-amine column of Table 2, the value reported is for a 0.02 M phosphate buffer solution.

Figure 4 shows that higher pH values as well as lower S(IV) concentrations favor longer lifetimes for NH_2Cl . In alkaline wastewaters, such as those treated for phosphorus removal, the lifetime of NH_2Cl could be long enough to make it a toxic agent in receiving waters. (This could be avoided by compensating for higher pH with higher S(IV) doses.) Nevertheless, the wastewaters discussed in this paper (Figures 1–3) had slightly acidic pHs, making the predicted half-life of NH_2Cl shorter than 10 s. Thus, NH_2Cl and the other inorganic chloramines are not plausible candidates for the long-lived residual chlorine observed in the field experiments.

Table 2 shows that organic monochloramines are longer lived than NH_2Cl . The lifetime appears to increase with the size of the organic group attached to the amine, suggesting steric inhibition. According to the mechanism proposed by Yiin et al. (31), dechlorination of a monochloramine requires that the electron pair on the amine be accessible to a general acid at the same time that the Cl on the amine is accessible to sulfite. Organic groups on the amine undoubtedly make achieving this complex reactive configuration more difficult, leading to steric inhibition.

In the experiment shown in Figure 3, the pH was 6.7, and the excess S(IV) (after the initial reduction of the fast-reacting oxidant fraction) was approximately 20 μ M. The observed half-life of the residual oxidant (26 min) is long enough that none of the compounds in Table 2 provides an entirely satisfactory model for the observed rate of dechlorination, but the tripeptide comes close. Given the current limitations in our understanding of both general acid catalysis and amine chemistry in wastewaters, peptides and protein fragments must be regarded as plausible contributors to the slowly dechlorinated oxidant in wastewater effluents. However, in an extraction experiment, we found that *N*-chlorotrialanine was negligibly extracted into octanol. Thus, most of the sulfite-resistant oxidants in



FIGURE 5. Gradual loss of total residual chlorine in a solution initially containing 38 μ M monochlorinated disthylamine when treated with HSO₃⁻/SO₃²⁻ (pH 7).

Horsepen Branch water are more hydrophobic than tripeptides.

The suggestion that steric inhibition slows the rate of dechlorination of organic monochloramines hints that chlorinated secondary (2°) amines also may be contributors to the residual chlorine fraction that reacts slowly with S(IV). To test this, we undertook an exploratory investigation of the rate of dechlorination of N-chlorodiethylamine. Figure 5 shows the results of an experiment in which N-chlorodiethylamine was prepared by treating $38 \,\mu M$ diethylamine with 38 μ M of NaOCl for 5 min. Then pH 7 sulfite solution was added, and the residual oxidant was measured periodically by the formaldehyde method. The loss of oxidant occurs in an approximately first-order manner with 3-5min half-lives. It can be estimated that in the presence of the lower excess S(IV) prevailing in our Horsepen Branch experiment (Figure 3) N-chlorodiethylamine would decay at a rate similar to that observed in the field experiment.

We also conducted exploratory experiments with several other amines. *N*-Chloro-*n*-butylamine, a 1° structural isomer of *N*-chlorodiethylamine, was reduced by sulfite too quickly for its rate to be characterized by our titrimetric method. Thus, in a comparison of two molecules of identical molecular weight, the 1° amine reacts much faster than the 2° amine. On the other hand, *N*-chlorodicyclohexylamine and *N*-chloro-*N*-ethylaniline, both 2° amines, reacted slowly with S(IV), suggesting that slow reaction with S(IV) is a general characteristic of chlorinated 2° amines.

It is unlikley that Horsepen Branch or other treatment plants contain greater than micromolar concentrations of a single 2° amine, such as diethylamine. However Scully et al. (14) have quantified >0.1 μ M of several 2° amines in wastewaters, and more compounds probably await discovery. The common amino acid proline, which contains a 2° amine structure, will almost certainly be found in biologically treated wastewaters at low concentrations. Thus, it seems reasonable to propose that wastewaters contain a suite of dilute 2° amines, which along with peptides contribute collectively to the S(IV)-resistant oxidant observed in dechlorinated effluents.

Regulatory Implications. Environmental regulatory agencies face the dilemma of finding a disinfection policy that will achieve the conflicting goals of protecting public health and preserving aquatic wildlife. There can be no

question that dechlorination removes most of the total residual chlorine from disinfected wastewaters. As a consequence, it reduces the toxicity of disinfected wastewater effluents to aquatic wildlife (17-20). However, according to the evidence in this paper, some residual chlorine, apparently hydrophobic in character and thus probably of concern toxicologically, remains in dechlorinated effluents. Our limited results warrant a substantially larger survey of wastewater treatment plants.

In the plants we have examined, the amount of residual chlorine in dechlorinated effluents considerably exceeds EPA criteria for receiving waters. At Western Branch, an effluent dilution factor of 5 in the receiving stream would bring the residual chlorine concentration within the EPA limit, even assuming no further decay of the oxidative compounds after discharge. On the other hand, at the less efficient Horsepen Branch plant, a dilution factor of about 20 would be needed.

It is worth remembering that effluent dilution not only reduces oxidant concentrations but also reduces S(IV)concentrations. In the cases where dechlorination kinetics have been studied, reaction rates are first order in S(IV). This means that lifetimes of residual oxidants will increase in inverse proportion as S(IV) is diluted until the point is reached where the inherent instability of the oxidant compounds themselves controls lifetimes. At the present time, SO_2 dechlorination systems are being installed at treatment plants that were not originally designed for them. In general, SO_2 is injected immediately prior to discharge, and time is not provided for dechlorination reactions to reach completion before dilution.

Because we have observed an S(IV)-resistant oxidant in every case in which we have looked so far and because kinetic literature and exploratory experiments suggest that common types of chlorinated organic amino compounds are likely to react slowly with S(IV), especially at high pH, we predict that the incompleteness of dechlorination is widespread. The implication is that many plants employing dechlorination are failing to meet the EPA limits for total chlorine. This prediction can be tested using the formaldehyde modification of the standard amperometric titration method, as described in this paper and ref 22.

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