

Sunlight Induced Photochemical Decay of Oxidants in Natural Waters: Implications in Ballast Water Treatment

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Abstract

The transport and discharge of ballast water has been recognized as a major vector for the introduction of invasive species. Chemical oxidants, long used in drinking water and wastewater treatment, are one treatment method for the control of invasive species currently being tested for use on ships. One concern when a ballasted vessel arrives in port is the adverse effects of residual oxidant in the treated water. The most common oxidants include chlorine (HOCl/OCl⁻), bromine (HOBr/OBr⁻), ozone (O₃), hydrogen peroxide (H₂O₂), chlorine dioxide (ClO₂), and monochloramine (NH₂Cl). The present study was undertaken to evaluate the sunlight mediated photochemical decomposition of these oxidants. Sunlight photodecomposition was measured at various pHs using either distilled water or oligotrophic Gulf Stream water for specific oxidants. For selected oxidants, quantum yields at specific wavelengths were obtained. An environmental photochemical model, GCSOLAR, also provided predictions in different seasons and water qualities with two different concentrations of chromophoric dissolved organic matter, at latitude 40 °, of the fate of HOCl/OCl⁻, HOBr/OBr⁻, ClO₂ and NH₂Cl. These data can be used for input into environmental fate models of ballast water treatment oxidants.

Introduction

The transport and discharge of ballast water by ships has been recognized as a major vector for the introduction of invasive species (1-5). In both freshwater and marine environments, invasive species have had negative environmental (ecosystem) and economic impacts (e.g. 6, 7) and, they may cause adverse health effects via the introduction of harmful algae (8, 9) and/or microorganisms of health concern (10 - 12). A number of studies are currently being conducted to adapt existing processes or to develop new technologies which treat ballast water and thereby minimize the likelihood of additional invasions.

A ballast water treatment process must take into account a number of aspects during development (13). In addition to being effective biocides, new treatment processes must be easy and safe to use by the ships crew, meet performance and certification standards, undergo hazardous operations reviews (which may vary from ship to ship) pass both US Coast Guard and American Bureau of Shipping reviews, and importantly, not allow toxic residuals to remain in ballast water at the point of discharge.

Included in the US EPA Environmental Technology Verification (ETV) protocol outlined by Hunt et al. (13) is the environmental acceptability of any technology employed in ballast water treatment. Post-treatment water quality, including any residuals or by-products, must be assessed for threats posed to the surrounding environment of the ship, as well as meeting federal and state water quality standards.

Chemical oxidants, long used in drinking water and wastewater treatment, are being considered as an alternative for the control of invasive species on ships. The oxidants include chlorine (HOCl/OCl^-) (14, 15), bromine (HOBr/OBr^-), ozone (O_3) (9, 16), hydrogen peroxide

(H₂O₂) (8, 14, 17-19), chlorine dioxide (ClO₂) (20) and possibly monochloramine (NH₂Cl). The application of oxidants may result in different oxidant species in freshwater and seawater because of the presence of Br⁻ in seawater (67 mg L⁻¹ at a salinity of 35) (e.g., 21, 22). For example, ozone in freshwater would be the effective oxidant and would decay via base catalyzed hydrolysis or reaction with natural organic matter prior to discharge, leaving no residual upon discharge (23). Chlorine and ozone in sea water react to form bromine (as HOBr/OBr⁻) as the major oxidant (24-26). Although oxidants may persist as toxic residuals in ballast tanks, redox reactions, reactions with natural organic matter, and photochemical decomposition could greatly reduce toxicity upon discharge to receiving waters (27, 28).

The fate of any chemical discharged to a water body is determined by biological, physical and chemical processes acting on that chemical. To a first approximation biological processes are not likely to affect the oxidants considered in this study because other processes, namely chemical processes will far exceed biological processes in absolute rate of oxidant decomposition. That is, direct reactions of oxidants with organisms, was assumed to be of minimal importance in the fate of the oxidant. The exception to this is H₂O₂. Photochemical (sunlight) decay of H₂O₂ is very slow (29); however, were ballast water containing H₂O₂ to be discharged to a coastal water system (30) or in fresh water ports (31) the biologically mediated half life would be on the order of 4 – 12 hours. In ports, with near open ocean water quality, the H₂O₂ would be relatively stable with biological half-lives often in excess of 100 hours in the oligotrophic ocean (e.g. 32).

Physical processes, namely mixing, will be different for every port and variable within a port depending primarily on factors such as fresh water input dynamics, tides and winds. Mixing will have two components, vertical and lateral, to disperse the oxidant away from the ships point

of discharge. To assess the potential effect of mixing, the overall decay half-life of the oxidant has to be considered. For example, when mixing occurs faster than the photolysis half life, photolysis is the rate limiting step in the loss function of the oxidant. However, as the photolysis rate increases, then mixing becomes the rate limiting step and the photochemical loss were more important.

It has been well established that the hypohalous acids/hypohalite anions react with dissolved organic matter or transition metals (redox cycling). Some of the factors that affect the reactions of the oxidants with DOM are ammonia, bromide ion concentration and pH (33). However, the environmental photochemical fate of oxidants in sunlit waters is poorly understood and may be important in determining the discharge limits of oxidants and for use in environmental assessment models. Photochemical decay is dependent upon the light field and flux which is related to the time of day, time of the year and latitude. For example, in higher latitude ports the seasonal impact of photochemical decay processes will be more highly variable. In the summer, there are considerably longer days; however, in the winter there may be times when there is not sufficient light to photochemically degrade any of the oxidant. In determining the fate of the oxidants in various ports all of these factors must be taken into account.

The purpose of this study was to quantify the photochemical decomposition of several oxidants in aqueous solution to provide estimates of oxidant lifetimes and to better understand the environmental fate of oxidants if discharged from ballast tanks. In this study the sunlight photodecomposition of aqueous solutions of HOCl/OCl⁻, HOBr/OBr⁻, ClO₂ and NH₂Cl at various pH's was determined. Quantum yield measurements at individual wavelengths of aqueous solutions were determined in distilled water and for HOBr/OBr⁻ in Gulf Stream water to

extend the data to marine systems. Lastly, the systems were modeled to estimate the photochemically mediated decomposition of oxidants in natural waters at several depths and different dissolved organic matter (DOM) concentrations.

Experimental Methods

Apparatus. All absorption spectra were determined using a Hewlett Packard 8450A or Cary 100 spectrophotometer, and either 1 or 10 cm path length quartz cells. The quartz cells also served as the reaction vessel for sunlight decay and quantum yield studies. An Eppley (Newport, RI) radiometer (Model TUVB) and integrator (Model 411) were used for the measurement of solar radiation. Quantum yield studies were performed using an irradiation system (LH 153 lamp housing, 1000-W Hg-Xe lamp, LPS 256 SM power supply) equipped with a GM 252-20 high-intensity 0.25 m grating monochromator (Spectral Energy Corporation, Washingtonville, NY.). Irradiance was measured using an International Light research radiometer (Peabody, MA) model IL1700 (5 V bias off) with a SED033 detector and calibrated using a conventional potassium ferrioxalate actinometer (34).

Reagents. All laboratory solutions were made with Milli-Q, 18 M Ω water. Dilute oxidant solutions were made up at different pH in the following buffers: 0.01 M KH₂PO₄ for pH 5; KH₂PO₄/Na₂HPO₄ (1/1 molar ratio) for pH 7; Na₂B₄O₇·10H₂O for pH 9; and, Na₂CO₃ for pH 12. A 5.71 mM as Cl₂ (400 mg L⁻¹) hypochlorite stock solution was made by diluting an aliquot of reagent grade 5.25 % NaOCl solution. Hypobromous acid/hypobromite ion solutions were made by adding 0.01 M KBr to the HOCl/OCl⁻ working solutions insuring an excess of bromide ion. Monochloramine solutions were made at pH 8.5 (0.01 M NaHCO₃) by slowly adding HOCl/OCl⁻ to NH₄Cl with vigorous stirring. To insure excess NH₃ at all times, a 3:1 molar ratio (NH₃:HOCl) was used. The stock solutions were diluted and standardized using amperometric

titration (35). HOBr/OBr⁻ solutions in Gulf Stream water (GSW) were prepared by adding 200 μ L of 4 - 6 % NaOCl to 1 L GSW at a salinity of 35-36 and standardized using iodometric titration (35).

Sunlight irradiation. Photochemical decomposition experiments were performed by exposing solutions of oxidant in Milli-Q water or GSW to sunlight in quartz tubes, submerged flush with the surface of distilled water (25 °C) to minimize heating. The loss of oxidant was monitored either directly by the decrease in absorbance of the oxidant or indirectly by iodometric titration. Oxidant concentration during sunlight experiments were recorded simultaneously with solar flux. Half lives and decomposition rates were calculated as first order decays. The solutions were studied at pH values ranging from pH 5 - 11. The pH of the monochloramine solution was held constant at 8.5. The GSW had a pH of 8.1.

Quantum Yield Measurements. To quantify the rate of photodecomposition for each oxidant in aqueous solution and GSW, wavelength dependent quantum yields were measured with the monochromatic irradiation system and radiometer described above. Bandwidths of 10 nm were centered at 240, 253.7, 265.2, 280.4, 296.7, 313.0, 334.1, 365.0, 404.5 and 435.8 nm. An AM1 long band-pass filter was used for 404.5 and 435.8 nm to minimize effects of second-order irradiance. The loss of each compound was calculated from UV spectrophotometer spectra. The quantum yields for photodecomposition were calculated as described elsewhere (36). Light flux at specified wavelengths was determined with a ferric-oxalate actinometer (34).

Modeling of oxidant photochemical decomposition. To generalize the environmental implications of the results a photochemical model, GCSOLAR (<http://www.epa.gov/ceampubl/swater/gcsolar/>) was used to calculate photolysis rates and half lives of oxidants in waters containing natural organic matter (37). The photolysis rates were

calculated based on the assumption that the loss of oxidant was due to a primary process, not photosensitization. Inputs for this model were solar flux at sea level, given as a function of time of day, season, and latitude. The water absorbance (including chromophoric dissolved organic matter, CDOM), molar absorptivity, and quantum yields were each added to the model as a function of wavelength. In this study no mixing in the water column was assumed.

Results

Absorption spectra of oxidants. The absorption maxima (λ_{\max}) and the molar absorptivities are summarized in Table 1. The electronic absorption spectra of aqueous solutions of HOCl/OCl⁻ and HOBr/OBr⁻ vary considerably with pH (38). The wavelength of the absorption maximum for the HOCl/OCl⁻ system increased with increasing pH suggesting that the rate of sunlight mediated photochemical processes will also increase. However, above pH 9 the system is essentially OCl⁻ and the absorption maximum did not change significantly from pH 9 -12 (39). The HOBr/OBr⁻ system was also studied from pH 5 – 12 and iodometric titration was used when obtaining concentrations using the molar absorptivity became difficult, i.e. pH < 9.

The λ_{\max} of ClO₂ was 360 nm, with a much higher molar absorptivity than the hypohalite ions (36, 40). Monochloramine has a very weak absorbance at wavelengths greater than 300 nm ($\lambda_{\max} = 245$ nm) and the absorbance spectra is invariant with pH in the range encountered in natural waters.

Sunlight irradiation. The sunlight photolysis experiments showed that aqueous solutions of HOCl/OCl⁻ and HOBr/OBr⁻ undergo photodecomposition that is first order and the rate is pH dependent (Figure 1). The calculated rates and half lives for the hypohalites are shown in Table 2. (The photodegradation of HOBr/OBr⁻ in Gulf Stream water was similar to that in distilled water in both the solar simulator and natural sunlight and the first order decay of HOCl/OCl⁻;

HOBr/OBr⁻ and ClO₂ was confirmed using a solar simulator. Data not shown)

Monochloramine was shown to be quite stable in sunlight. The absorbance monitored for monochloramine concentration did not decrease significantly after four hours of sunlight irradiation, and I₃⁻ titration for monochloramine indicated no significant oxidant decomposition. Thus, an empirical sunlight decomposition rate could not be calculated for monochloramine under these relatively short-term experimental conditions. It is also unlikely that H₂O₂ would be photolyzed in sunlight received at the surface during a similar irradiation period (29-32).

Quantum yields of oxidants. To understand the photochemical fate of the oxidants in natural waters it was necessary to evaluate quantum yields of the oxidants in distilled water over a wide range of wavelengths (Table 3). For HOBr/OBr⁻ quantum yields were also determined in Gulf Stream water. Chlorine dioxide quantum yields were reported in an earlier study (36).

Discussion

Of the oxidants considered, neither H₂O₂ nor NH₂Cl had any appreciable sunlight induced decay, in the absence of natural organic matter or transition metals, on the short time scales of interest in discharging of ballast water. The hypohalous acids and hypohalite anions and Cl₂O (36) were all shown to decay on a timescale that is of importance to the short-term (hours) environmental fate of the oxidants.

Aside from halogen anion, the photoproducts were not identified in the present studies. However, primary photoproducts can be inferred to be hydroxyl and chlorine radicals from analogy with organic hypochlorite photolysis as these radicals would result from the photolysis of HOCl (41 - 45) (see supplemental material for a more detailed discussion of the photochemical mechanism of oxidant decay). At the two shorter wavelengths studied, 240 and

253.7 nm the decomposition quantum yield decreased as the pH increased. This trend was reversed for the wavelengths 265.2 and 365.0 nm, where the decomposition quantum yield increased with increasing pH. These data suggest that the sunlight photodecomposition of the OCl^- is more efficient than for HOCl . At the lower wavelengths the HOCl/OCl^- decomposition quantum yields were greater than one. This may be attributed to the efficiency of the parallel reactions involving chlorine and oxychlorine radicals (46). The hypobromite ion system showed similar trends to the hypochlorite ion system with the quantum yield increasing with photon energy.

Quantum yields reported from earlier studies of HOCl/OCl^- , obtained using steady state mercury lamp irradiations, have been included in Table 3 (41-43). Good agreement at 253.7 and 365 nm was obtained; however, for 313 nm the earlier reported quantum yield was much lower. The experimental data with all oxidants show an increase in quantum yield with decreasing wavelength and greater absorbance. Thus the lower quantum yield at 313 nm when compared to 253.7 and 365 nm as measured (41-43) does not match trends in our data for hypochlorite or any of the other oxidants studied here. Additional experiments were conducted to check the values and confirmed the higher quantum yield.

Using the quantum yields (Table 3), a model for photochemical decay (GC-SOLARS) was applied to quantitatively determine the photochemical half-life of the oxidants in distilled water and compared to sunlight decay rates that were observed (Table 4). (The photodecomposition of the HOCl/OCl^- in natural water reported earlier is presented in Table 4 for comparison (47)). The model calculations were in good agreement with those observed and further modeling was undertaken to provide estimates of photochemical decay of the oxidants, HOCl/OCl^- , HOBr/OBr^- , ClO_2 and NH_2Cl .

The GCSOLAR model has the ability to predict the decay rates at various DOM concentrations and at depth for a specified latitude and season; however, mixing in the water body is not included. Figure 2 shows HOBr photolysis rates as a function of depth in three waters of different organic carbon concentrations. For the clearest water, 0.53 mg L^{-1} as C ($44 \text{ }\mu\text{M}$), the half life is not very sensitive to depth. However, for the waters with high DOM, 6.2 and 17.6 mg L^{-1} as C, (517 and $1,470 \text{ }\mu\text{M}$, respectively), most of the light was absorbed in the first 10 cm of the water. Therefore the photochemical loss of HOBr at depth would be dependent on mixing. The half-life of HOBr/OBr⁻ was approximately 0.33 hours in the surface waters.

Figure 3 shows the effect of DOM on the photochemical decay rate of ClO₂ in water containing no bromide ion. The photochemical loss of ClO₂ is more rapid than either HOCl/OCl⁻ or HOBr/OBr⁻. In the clear water the longest half-life was 3.9 minutes at 5 m depth. The increase in DOM for the other two waters has the same effect on the decay of ClO₂; however, because the overall photochemical reactions are so much faster the longest half-life was 70 minutes.

Although the experimental decay of NH₂Cl was too slow to measure, it was possible using the model to derive half-lives in the low and high DOM waters in the summer. The results confirmed slow decay at one meter of 7.9 and 310 hours, respectively. It is clear from the half-lives that the discharge of NH₂Cl would result in a persistent oxidant. It has been well established in water treatment that the reactions of NH₂Cl are very slow with DOM and therefore it is likely that it would present a substantial adverse effect on receiving waters.

Table 5 summarizes the effect of season on the photochemical decay of HOCl/OCl⁻ in the low and high DOM water. In the winter at the surface the half-life is nearly three-fold longer

than that of the summer and with depth increased rapidly to a time where dark reactions would predominate in determining the actual environmental decay rate. The high DOM water (17.6 mg C L⁻¹; 1,470 μM) effectively absorbed all of the light even at one meter and dark reactions would predominate. Table 6 summarizes the decay half-life data for HOBr/OBr⁻ at the surface (no effect of DOM) at 40 ° latitude.

From the model data presented, the most labile oxidant was ClO₂, then HOCl, followed by HOBr. All of the half lives for oxidants doubled under winter irradiation. Monochloramine had half lives under all conditions which were at least tenfold longer than other systems.

The effect of increased DOM on sunlight photochemical half life for all of these oxidants is dramatic. In fact, except for very clear (low DOM) water and the surface of the other waters, photochemistry will have a very limited effect on the dissipation of the oxidants (see supplemental material Tables S1 - S5, for additional model results). In waters of higher DOM it is likely that the dominant decay reaction would be those expected of thermal (dark) reactions (e.g. 33, 48, 49).

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List of Figures

FIGURE 1. Sunlight decay of oxoacids and oxoanions of chlorine and bromine at various pHs in distilled water. (The irradiations were conducted in Miami, FL, Lat. 24 °N centered on solar noon when the solar flux was 0.40 watt-hr m⁻² hr⁻¹.)

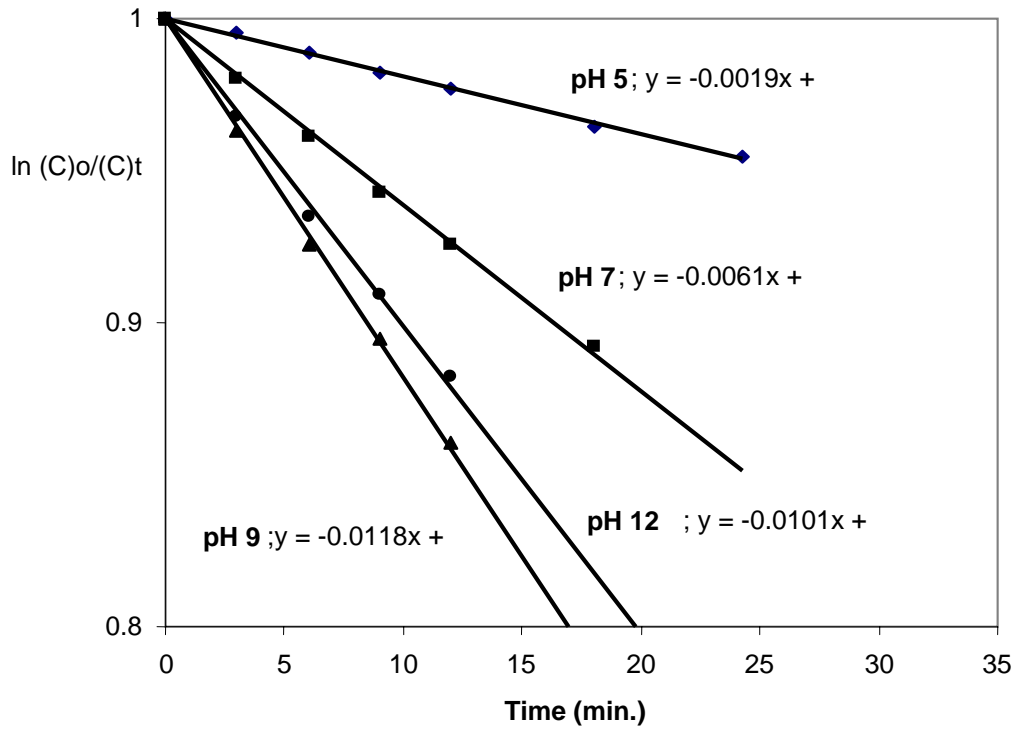
FIGURE 2. The effect of DOM on the modeled (pH = 9.0) maximum photochemical decay half-life (in hours) of HOBr/OBr⁻ in the summer (◆ DOM = 0.53 mg C L⁻¹ (44 μM); ■ DOM = 6.2 mg C L⁻¹ (520 μM); ▲ DOM 17.6 mg C L⁻¹ (1,470 μM)).

FIGURE 3. The effect of DOM on the photochemical half-life of ClO₂ in water in the absence of bromide ion (◆ DOM = 0.53 mg C L⁻¹ (44 μM); ■ DOM = 6.2 mg C L⁻¹ (520 μM); ▲ DOM

17.6 mg C L⁻¹ (1,470 μM).

FIGURE 1.

A HOCl/OCl⁻



B HOBr/OBr⁻

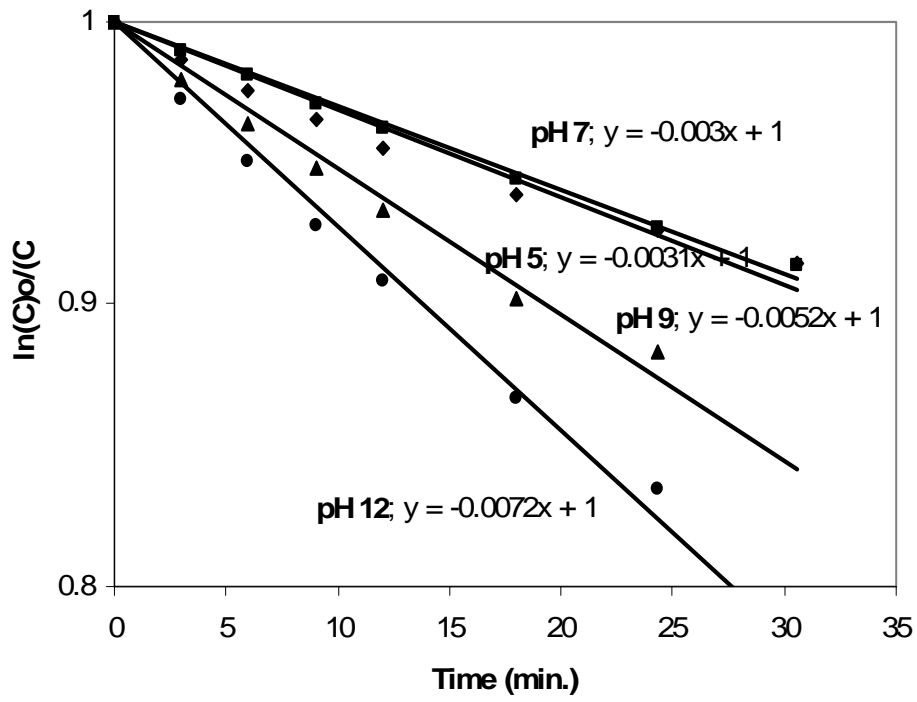


FIGURE 2

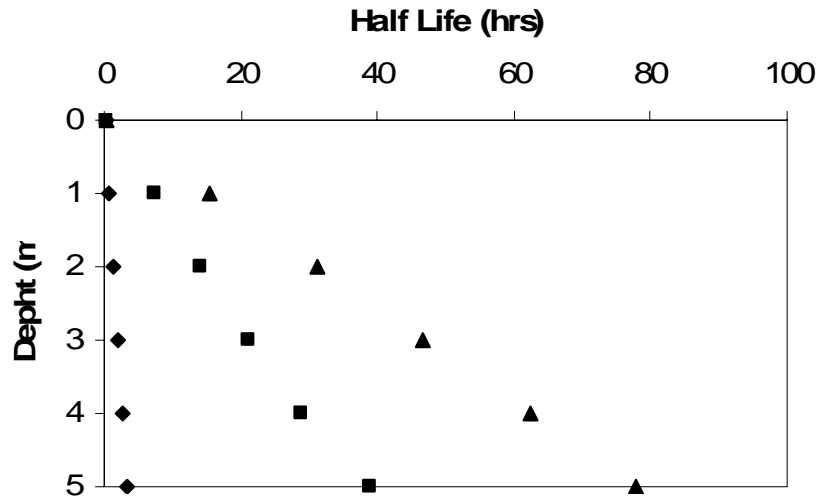
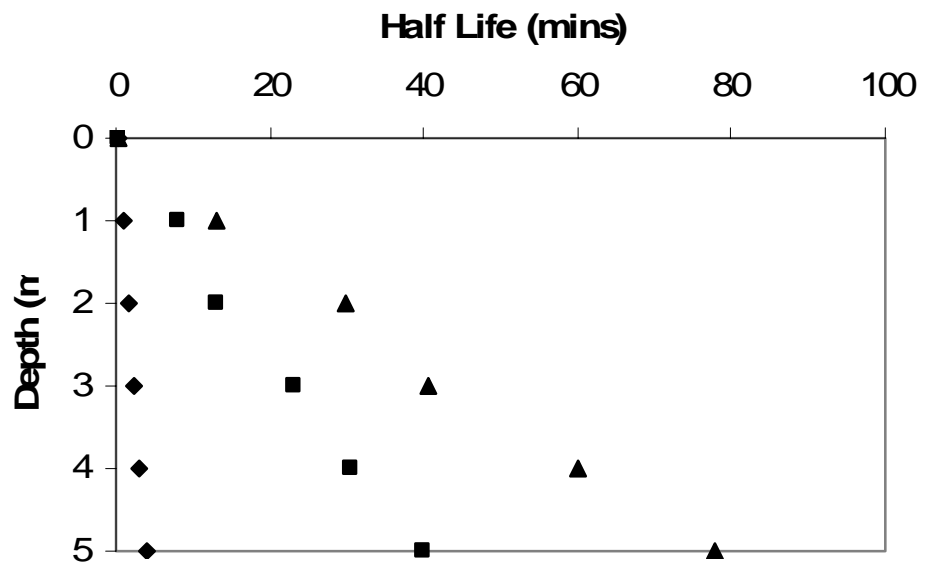


FIGURE 3.



Compound	Absorbance Maximum (nm)	Molar Absorptivity (L mol ⁻¹ cm ⁻¹)
HOCl	238	111
OCl ⁻	292	352
OBr ⁻	330	316
ClO ₂ *	360	1200
NH ₂ Cl	245	455

* Ref 36, 40

pH	HOCl/OCl ⁻		HOBr/OBr ⁻	
	k (h ⁻¹)	t _{1/2} (h)	k (h ⁻¹)	T _{1/2} (hr)
5.0	1.0	0.69	1.9	0.37
7.0	2.5	0.28	1.7	0.41
9.0	6.3	0.11	2.8	0.25
11.0	5.1	0.14	3.9	0.18
12.0	6.9	0.10	4.4	0.16

TABLE 3. Quantum yields for photodecomposition of hypohalous acids/hypohalite ions and monochloramine irradiated with Xe-Hg lamp.

Wave-length (nm)	NH ₂ Cl	HOCl/ OCl ⁻ pH 5	HOCl/ OCl ⁻ pH 7	HOCl/ OCl ⁻ pH 9	(Cl) ^a	HOBr/ OBr ⁻ pH 5	HOBr/ OBr ⁻ pH 7	HOBr/ OBr ⁻ pH 9	HOBr/ OBr ⁻ pH 12	HOBr/ OBr Gulf Stream water ^b	ClO ₂ ^c pH 7.0	ClO ₂ ^c pH 9.0
240	n/a	1.21	1.24	1.50	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
253.7	0.26	1.64	1.51	0.84	0.85	n/a	n/a	n/a	n/a	n/a	n/a	n/a
265.2	n/a	1.39	1.10	0.92	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
280.4	0.26	1.15	0.88	0.86	n/a	0.19	0.34	0.46	0.35	n/a	n/a	n/a
296.7	0.21	0.78	0.76	0.80	n/a	0.16	0.28	0.28	0.22	0.23 (0.11) ^d	1.40	1.47
313.0	0.35	0.80	0.71	0.80	0.39	0.17	0.29	0.21	0.19	0.28 (0.05)	0.98	0.86
334.1	0.85	0.69	0.61	n/a	n/a	0.20	0.24	0.15	0.14	n/a	0.90	0.90
365.0	0.87	0.73	0.55	n/a	0.60	0.10	0.18	0.10	0.09	0.11 (0.05)	0.46	0.46
404.5	n/a	n/a	n/a	n/a	n/a	0.09	0.18	0.10	0.08	0.29 (0.11)	0.13	n/a
435.8	n/a	n/a	n/a	n/a	n/a	0.06	0.10	0.11	n/a	0.17 (0.06)	n/a	n/a

^a from ref. (41-43)

^b five replicate determinations at each wavelength

^c from ref. (36)

^d determined at 300 nm

TABLE 4. Decay rates and half-lives at selected pH values for hypohalous acids/hypohalite ions from sunlight induced photodecomposition and model calculations in clear water (no DOM).

Chemical	pH	Experimental		Model Calculations	
		k (h ⁻¹)	t _{1/2} (h)	k (h ⁻¹)	t _{1/2} (h)
HOCl/OCl ⁻	7	2.5	0.28	2.2	0.31
HOCl/OCl ⁻	9	6.3	0.11	1.4	0.51
HOCl/OCl ⁻	11	5.1	0.14	2.2	0.31
HOBr/OBr ⁻	9	2.8	0.25	1.4	0.51
HOBr/OBr ⁻	11	3.9	0.18	1.5	0.45
NH ₂ Cl	8.5	negligible	negligible	0.05-0.06	11-13
HOCl/OCl ⁻	5.4		~1 ^a		
HOCl/OCl ⁻	10		~0.17 ^a		
^a (ref. 47)					

TABLE 5. The effect of season on the modeled photochemical decay half-life of HOCl/OCl⁻ in waters of different DOM concentration (decay rates for solar noon at each depth).

Depth (m)	Winter		Summer	
	DOM (44 μM) (0.53 mg C L ⁻¹)	DOM (1,470 μM) (17.6 mg C L ⁻¹)	DOM (44 μM) (0.53 mg C L ⁻¹)	DOM (1,470 μM) (17.6 mg C L ⁻¹)
0	0.438	0.438	0.157	0.157
1	1.27	31.3	0.434	10.3
2	2.36	62.5	0.792	20.7
3	3.51	93.8	1.18	31
4	4.68	nd*	1.57	nd
5	5.85	nd	1.96	nd

* = not determined

TABLE 6. Seasonal variation in modeled photochemical decay half-life of HOBr/OBr⁻ in surface water at 40 degrees latitude.		
Time of Day (hours)	Winter	Summer
504		No sun
538		32.2
605		5.38
659		1.39
732		
752	No sun	0.74
807	32.3	
839	5.4	
844		0.516
937		0.415
952	1.4	
1035		0.362
1210		0.332
1219		0.332*
1225	0.746*	
1229		0.332
1404		0.362
1455	1.4	
1502		0.415
1555		0.516
1611	5.4	
1643	32.3	
1647	No sun	0.74
1717		
1740		1.39
1834		5.38
1901		32.2
1935		No sun
* Solar noon		