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Production and Loss of Dissolved Gaseous Mercury in Coastal Seawater

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The formation of dissolved gaseous mercury (DGM, mainly composed of elemental mercury, Hg⁰) in the surface ocean and its subsequent removal through volatilization is an important component of the global mercury (Hg) cycle. We studied DGM production and loss in the coastal waters of the Gulf of Mexico using 4-26 h in situ incubation experiments. DGM production was only induced in the presence of sunlight. Once produced, DGM was rapidly lost from solution (with a first order rate constant of k = 0.1h⁻¹), apparently as a result of oxidation. Furthermore, laboratory experiments showed that dissolved gaseous Hg⁰ could be rapidly oxidized in the presence of chloride. In the field, most DGM production (about 60%) was associated with the dissolved and colloidal Hg(II) phases. Spiking of samples with inorganic Hg(II) prior to in situ incubation greatly increased DGM production rates, suggesting that photoreducible Hg(II) complexes were limiting DGM production. Diurnally, DGM seems to be formed through photoproduction in the morning; DGM production halts when substrate is exhausted, and DGM levels decrease afterwards, presumably by oxidation of Hg⁰.

Introduction

The oceanic production and subsequent transfer to the atmosphere of dissolved gaseous mercury (DGM) is a crucial part of the global mercury (Hg) cycle (1). Oceanic evasion of 10 Mmol Hg yr⁻¹ accounts for about 30% of the current total annual flux of Hg to the atmosphere. By comparison, values for direct anthropogenic Hg emission to the atmosphere range from about 18 to 23 Mmol $yr^{-1}(2, 3)$. DGM is mainly composed of elemental Hg⁰ in the surface ocean (4, 5), in freshwater lakes (6), and in estuaries (7). Other volatile Hg species (in particular dimethylmercury) may be present at depth in the ocean. Both laboratory culture experiments and incubation experiments with natural seawater have suggested that biologically mediated reduction of Hg(II) to Hg⁰ contributed to DGM production (8). This reduction could be linked to light-dependent biological processes (9, 10). Alternatively, photochemical DGM production could also be important (11-14).

We investigated the effect of solar radiation on DGM production in seawater samples collected along the coast of

the Gulf of Mexico, on the shores of Galveston Island, TX. The Texas coastal region is characterized by relatively little cloud cover and high temperatures year round, both factors being important in photochemical and photobiological studies.

We assessed the effect of ultraviolet radiation (UV_A: 320–400 nm; UV_B: 280–320 nm), visible radiation (400–700 nm), substrate availability, and filtration on DGM production. Furthermore, the importance of DGM loss by oxidation was investigated. Laboratory experiments by Yamamoto (15) have recently shown that elemental mercury oxidation is stimulated by chloride ions in a dose- and time-dependent manner. We therefore hypothesized that oxidation should be a significant mechanism controlling DGM levels in seawater.

Experimental Section

Water samples were collected into 2-L FEP Teflon bottles (Nalgene) using a peristaltic pump equipped with freshly acid-cleaned Teflon and Masterflex tubing. Plastic gloves were worn at all times. Samples were taken from a fishing pier on the Seawall of Galveston Island from a depth of 1 m, about 200 m offshore. The samples were analyzed for DGM content within 5 min of the end of incubation during time series experiments and within 6 h for other incubation experiments. During the 6-h lag between collection and analysis, some DGM may have been lost by oxidation. Therefore, for experiments with such lags, our DGM production rates represent conservative estimates and are probably lower then actual rates.

For analysis of dissolved gaseous mercury (DGM) in seawater, 2 L of sample was slowly decanted into a glass bubbler and purged for 45 min with ultra high-purity nitrogen stripped of ${\rm Hg^0}$ by passage over Au traps, at a flow rate of 1 L min $^{-1}$. The gas stream coming out of the bubbler was dried using a ${\rm K_2CO_3}$ column. Mercury compounds volatilized by the purging were trapped on a gold-coated sand column. The mercury on the column was desorbed by pyrolysis at a flow rate of 60 mL min $^{-1}$ and quantified by gas-phase atomic fluorecence spectrometry.

The effect of solar radiation on DGM production was evaluated by incubating water samples in situ for 5 h in February 1996 under the following treatments: (1) absence of light (black FEP Teflon bottles, Nalgene); (2) presence of solar radiation (transparent FEP Teflon bottles, Nalgene); (3) absence of UV_B radiation (transparent Teflon bottles wrapped in Mylar, Dupont); (4) absence of UV radiation (transparent bottles wrapped in UV Lee filters Model 226, U.K.). The wavelength cutoff of UV Lee filters was determined using an Optronics 752 Spectroradiometer connected with an underwater optical sphere with a 3-m fiber optic cable. The filters were placed 10 cm underwater during measurements. Cut off values ranged from 390 to 400 nm. These filters transmitted 0.3% of incoming UV_B, 4.9% of incoming UV_A, and 80.0% of visible light. For Mylar filters, cutoff values for Mylar were measured by Lean and Perin (unpublished) and ranged from 315 to 323 nm. Transparent FEP Teflon bottles absorbed 2.5% of total incident radiation ($\lambda = 280-700 \text{ nm}$) and 0.7% of photosynthetically active radiation (PAR, $\lambda = 400-700$ nm). The influence of Teflon on UV_A ($\lambda = 320-400 \text{ nm}$) and UV_B $(\lambda = 280-320 \text{ nm})$ absorption was greater, causing a decrease in irradiance of 18% and 34%, respectively.

Water samples in black and transparent Teflon bottles were exposed to sunlight for different time intervals to investigate the relative importance of DGM loss vs DGM photoproduction (0, 1, 2, 3, 4, 5, 6, 7, 24, and 25 h). Incubations were conducted in plastic tubs placed over dark surfaces on the ground. To ensure a constant temperature during incubation, water in the tubs was continuously renewed using

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TABLE 1. Effect of Visible and UV Radiation on DGM Production in Seawater^a

treatment during incubation	DGM concn (fM)	p value of ANOVA for treatment effect	Tukey <i>HSD</i> comparison ^b	% of total Hg being photoreduced/h ^a
black	71 \pm 4	0.012	а	
no UV	$\textbf{95} \pm \textbf{6}$		a b	0.3
no UV _B	111 \pm 19		bс	0.5
transparent	123 ± 0		С	0.7

 a Samples were incubated for 5 h (February 14, 1996) in transparent bottles, black bottles, transparent bottles wrapped in Mylar (no UV_B treatment), and transparent bottles wrapped in UV Lee filters (no UV treatment). Results of an ANOVA testing for treatment effect are indicated. Standard deviations based on three replicates are shown. b Significant differences (p < 0.05) between treatments are indicated by different letters. c Based on a total Hg concentrations of 1.5 \pm 0.2 pM.

a flow-through system. Additional experiments were conducted where DGM levels were measured in black and transparent bottles incubated for 0–6 h. Some transparent bottles were put in the dark after a 1-h incubation in the sun to observe DGM loss after a short exposure to sunlight. Also, to investigate the possible role of Hg(OH)₂,⁰ a photolabile Hg(II) complex commonly found in natural waters (12), a time series of DGM levels in distilled water incubated in black and transparent bottles was measured.

To assess if DGM production was limited by substrate, water samples were spiked with 22, 44, and 66 pM Hg(II) and incubated for 3 h.

The effect of particulate matter on DGM production was determined by conducting 7-h incubation experiments (in black and transparent FEP Teflon bottles) using filtered seawater samples (filtration with 0.45-mm MSI polypropylene filter capsule, Westborough, MA). Furthermore, DGM levels in filtered and unfiltered samples incubated under sunlight were measured at different time intervals (0–5 h; March 11 and 18, 1996).

To study dark oxidation independently from photoreduction, seawater and river water samples were spiked with 8 nM dissolved gaseous elemental Hg (Hg 0), and the loss of Hg 0 and total Hg in the dark were followed over 7 h. Inorganic Hg, Hg(II), was calculated by difference between Hg 0 and total Hg. The effect of chloride on Hg 0 oxidation was evaluated using river water (Choptank River, NJ), spiked with 0.5 M chloride and seawater (Seaside Park, NJ). The stock solution of dissolved gaseous Hg 0 was prepared by bubbling N $_2$ gas saturated with Hg 0 vapor through Milli-Q water (Millipore). The N $_2$ was saturated with Hg 0 in a U-shaped glass tube containing 0.1 mL of liquid elemental Hg.

One possible caveat to this work is that Teflon is permeable to $\mathrm{Hg^0}$. It could be argued that any observed decline in DGM levels with time is due to a loss of Hg through the walls of the experimental vessel. To rule out this possibility, DGM levels were measured in seawater samples in glass and Teflon bottles for a 24-h incubation. There was no significant differences (*t*-test: t=4.30; p=0.263; N=3 per treatment) in DGM concentrations between Teflon bottles (137 \pm 13 fM) and glass bottles (149 \pm 4 fM). Therefore, Teflon permeability to $\mathrm{Hg^0}$ is not responsible for the rapid loss of DGM concentrations observed in this study.

Results and Discussion

Effect of visible, UV, and UV_B Radiation on DGM Photoproduction. Samples incubated in transparent bottles yielded DGM levels that were significantly higher than those in black bottles (Table 1). Samples only exposed to visible or to visible and UV_A radiation also yielded significantly higher DGM levels.

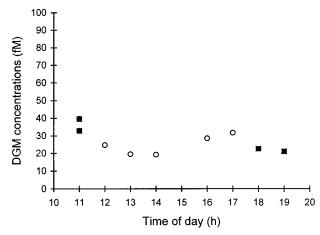


FIGURE 1. Time series measurements of DGM levels in Milli-Q water kept in black (■) and transparent (○) bottles on April 2, 1996.

Visible, UV_A, and UV_B radiation contributed approximately 46, 31, and 23% of total DGM production, respectively. These results show that DGM production can be photoinduced in seawater. The rate of DGM photoproduction in these coastal waters is quite low (in transparent bottles, 10 fM h⁻¹) as compared to some temperate freshwater systems (11–85 fM h⁻¹; 13, 14). But, normalized to the total Hg concentration, DGM production in seawater (0.7% h⁻¹; Table 1) is faster than in Florida lakes ($<0.2\% h^{-1}$; 16) at a similar latitude. This may result from the fact that, compared to Florida lakes, the small total Hg pool in seawater contains a larger proportion of Hg not complexed to DOC and easily reducible (17). It is also possible that part of the DGM photoproduction observed in this study is linked to the recently discovered photodegradation of methyl and ethyl mercury by singlet oxygen in seawater (18).

Time Series of DGM Production and Loss. Previous work has clearly demonstrated that DGM production can be photoinduced in lake water (11, 13, 14), but similar studies with natural seawater have yet to be conducted. Moreover, recent laboratory experiments have shown that the presence of chloride ions may promote Hg⁰ oxidation (15). Hence, seawater media may also be subjected to DGM loss through oxidation. We evaluated the importance of theses processes with time series measurements of DGM in Teflon bottles exposed to sunlight. First, a control experiment was conducted using Milli-Q water to verify the possible role of photolabile Hg(OH)₂⁰ (12). DGM levels in black and transparent bottles remained in the 30 fM (range: ± 10 fM) with no correlation to solar radiation (Figure 1). Note that typical total Hg levels in our Milli-Q water (~1 pM) are similar to total Hg levels in unfiltered seawater samples taken near the shore of Galveston Island (1.5 \pm 0.2 pM). Thus, DGM photoproduction in fresh or saltwater is not the result of a direct photolysis of inorganic Hg complexes such as Hg(OH)₂, which are present in distilled water at neutral and basic pH. One caveat to this test is that some of the Hg in Milli-Q water may be complexed with DOC since our Milli-Q water has submicromolar levels of DOC.

Time series measurements of DGM in seawater held in transparent bottles increased by 3-fold during the first hour of incubation in sunlight and then decreased rapidly (23 fM h^{-1}) during the next hour (Figure 2). A slower decrease was observed during the following 5 h (2 fM h^{-1}). Twenty-four hours later, DGM levels at midday were high as compared to the first day. DGM levels in black bottles remained low (20 fM) and showed no change in concentration during the experiment (Figure 2).

When the experiment was repeated 4 days later (Figure 3), DGM levels in transparent bottles increased at a rate of 67 fM h⁻¹ during the first 3 h and declined afterwards, at a rate

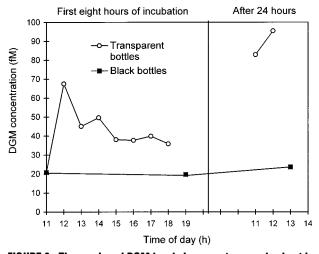


FIGURE 2. Time series of DGM levels in seawater samples kept in black and transparent bottles. The samples were collected nearshore (Galveston Island) on February 29, 1996.

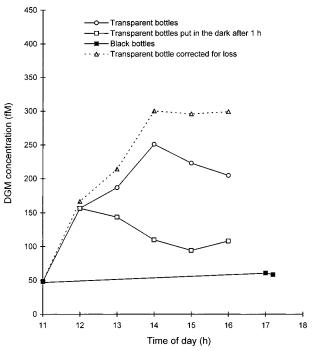


FIGURE 3. Time series of DGM levels in seawater samples kept in black and transparent bottles and incubated in sunlight. Some transparent bottles were placed in the dark after the first hour of incubation. The samples were collected nearshore (Galveston Island) on March 4, 1996.

of 23 fM h $^{-1}$. Some transparent bottles were placed in the dark after the first hour of incubation. DGM levels in these bottles declined at a rate of 21 fM h $^{-1}$ during the first 3 h of dark incubation and reached a plateau at about 100 fM. DGM levels in black bottles remained constant at about 50 fM. Differences in DGM levels between this experiment (weather: sunny with some clouds) and the one reported on Figure 2 (weather: rainy, overcast) may result from differences in solar radiation.

Quantitative examination of the data from Figures 2 and 3 shows that the kinetics of DGM loss are approximately first-order, with a mean rate constants of $k = 0.10 \pm 0.01 \; h^{-1}$. It is unlikely that zero- or second-order kinetics apply here since the respective rate constants for these orders vary widely over the range of initial DGM concentrations (19). Note that rates for experiments under sunlight should be considered net rates for both oxidation and reduction. However, since observed

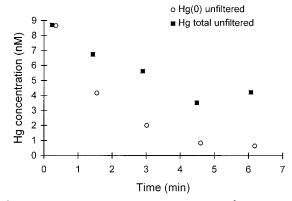


FIGURE 4. Time series of dissolved gaseous Hg⁰ and total Hg concentrations in seawater samples after an 8.7 nM addition of Hg⁰. Samples were kept in the dark.

rates in sunlight are similar to those obtained for bottles placed in the dark (after 1 h of exposure to sunlight), photoreduction was presumably relatively unimportant (probably due to substrate limitation) during this phase of the experiment.

These results suggest that DGM is indeed produced by photoreduction in seawater and can also be rapidly oxidized in saltwater. This is particularly significant for it contrasts with the results from freshwater systems where DGM loss was either not detectable (11) or relatively slow (13). These findings support the laboratory study of Yamamoto (15), where it was shown that, due to the presence of chloride, Hg oxidation was more important in seawater than in fresh or distilled water.

The plateau reached by DGM levels (corrected for loss, assuming first-order kinetics; Figure 3) indicates that photoreduction completely stops after 3 h of incubation. Since solar radiation was still intense at that time (14:00), DGM production may have been limited by the amount of substrate available for photoreduction, which would thus be a small fraction of the total Hg. However, the high DGM concentrations observed after 24 h in transparent bottles (Figure 2) indicate that the pool of photoreducible substrate can be replenished during the night. The kinetics of production of reducible species is thus much slower than the kinetics of photoreduction.

In the dark bottles (Figures 2 and 3), DGM levels did not significantly decrease over time. This may indicate that a steady state was reached between light-independent reduction and oxidation. It is also possible that oxidation of Hg(II) is induced by sunlight, since loss of DGM was only observed in bottles either continuously exposed to solar radiation or recently placed in the dark (after a 1-h incubation under sunlight). It further indicates that adsorptive losses of Hg⁰ were low.

Oxidation of Hg^0 . Past laboratory experiments on Hg oxidation in seawater were conducted with liquid Hg droplets in water as sources of Hg^0 , and only Hg(II) was measured (15). To test whether these data are pertinent to natural environment, we examined the oxidation of dissolved gaseous Hg^0 in the presence of chloride, but in the absence of Hg droplets.

Dissolved gaseous Hg^0 was rapidly oxidized in the dark in unfiltered seawater (Figure 4) and river water samples salted with 0.5 M chloride (Figure 5B). The apparent first-order constant for Hg^0 loss or Hg(II) production varied between 0.1 and 0.4 h^{-1} (Table 2). By comparison, very little oxidation was detected in filtered river water with no chloride added (Figure 5A). In these experiments, Hg^0 loss not only includes oxidation but also volatilization from solution. In fact, total Hg decreased over time (first-order k: $0.07-0.10 h^{-1}$; Table 2) as a result of Hg^0 volatilization in the headspace of the sample. For each of these experiments, only one sample was

TABLE 2. Kinetics Constants k for DGM Oxidation, Assuming Zero-Order, First-Order, and Second-Order Kinetics^a

treatment	initial [DGM] (fM)	<i>k</i> (in fM h ⁻¹) zero-order	<i>k</i> (in h ⁻¹) first order	<i>k</i> (fmol ⁻¹ h ⁻¹) second-order	see
		Experiments at Envi	ronmental Levels of DGN	Л	
light	68	4.2	0.09	$5.8 imes 10^{-3}$	Figure 2
light	251	23.1	0.10	4.5×10^{-4}	Figure 3
dark	157	14.6	0.12	$9.3 imes 10^{-4}$	Figure 3
dark	227	18.2	0.09	1.8×10^{-3}	N/A
mean \pm SD	178 \pm 82	$\textbf{15.0} \pm \textbf{8.0}$	$\textbf{0.10} \pm \textbf{0.01}$	$\textbf{2.2} \pm \textbf{2.4} \times \textbf{10}^{-3}$	
CV (%)	46	53	10	108	
		Experiments	with Hg ⁰ Addition		
		A: River Wate	er (+ 0.5 M Chloride)		
Hg ⁰ loss	$8.3 imes 10^6$	$1.0 imes 10^6$	` 0.21	$4.9 imes 10^{-8}$	Figure 4
Hg(II) prod	$8.3 imes 10^6$	$4.6 imes 10^5$	0.33	$2.8 imes 10^{-7}$	ŭ
Hg volatil	$8.3 imes 10^6$	4.6×10^5	0.07	1.1×10^{-8}	
		B: :	Seawater		
Hg ⁰ loss	$8.7 imes 10^6$	$1.0 imes 10^6$	0.44	4.0×10^{-7}	Figure 5
Hg(II) prod	8.7×10^{6}	4.1×10^5	0.42	$1.9 imes 10^{-6}$	ŭ
Hg volatil	8.7×10^6	$5.9 imes 10^5$	0.10	4.1×10^{-4}	

^a For experiments at environmental levels of DGM, DGM oxidation was measured in bottles continuously exposed to sunlight ("light" treatment) or in bottles kept in the dark after a 1-h exposure to sunlight ("dark" treatment). For experiments with DGM addition, kinetics constants for Hg⁰ loss, Hg(II) production, and Hg volatilization were measured in the dark after spiking (no exposure to sunlight). CV coefficient of variation; SD, standard deviation; N/A; not available.

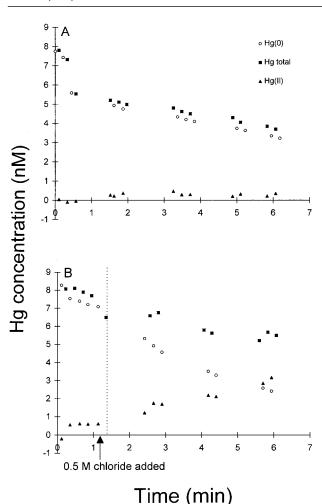


FIGURE 5. Time series of dissolved gaseous Hg^0 , total Hg, and Hg(II) concentrations in (A) filtered river water and (B) unfiltered river water with 0.5 M chloride. 8.3 nM Hg^0 was added at the onset. Hg(II) was obtained by the difference between Hg^0 and total Hg.

followed over time, and data points represent subsamples from the sample being studied. This contrasts with most of the other experiments presented in this paper where each data point is associated with a different bottle.

TABLE 3. Effect of Hg(II) Addition on DGM Levels in Transparent Bottles Incubated at Midday for 3 h^a

amt of Hg(II) added (pM)	DGM concn (fM)
22	$\textbf{920} \pm \textbf{60}$
44	$\textbf{1440} \pm \textbf{200}$
66	2040 ± 40

^a Samples were collected nearshore on Galveston Island on April 5, 1996.

These results clearly indicate that Hg^0 is being oxidized in the dark to Hg(II) in the presence of chloride and that oxidation may be as important as volatilization in the depletion of the Hg^0 pool in seawater. Furthermore, since no headspace was left in the bottles incubated *in situ* at environmental levels (Figures 2 and 3), volatilization could not be involved in these cases. Oxidation of Hg^0 is thus the likely mechanism of DGM loss

Hg(II) Availability as a Limiting Factor of DGM Production. DGM levels obtained after incubation increased with the amount of Hg(II) added to the samples prior to incubation, suggesting that DGM production was limited by the amount of available photoreducible substrate (Table 3). Therefore, organomercurial compounds are not the only potential source of substrate for reduction.

While, under natural conditions, maximum DGM levels after a 3-h incubation were lower than 300 fM (Figure 2), here DGM production ranged between 920 and 2040 fM after Hg-(II) spiking, after a 3-h incubation. This corresponds to a conversion of total Hg of 3–4% per 3-h incubation. These rates are lower than those obtained in temperate and arctic regions (up to 27% in a 4-h incubation; 13, 14). One explanation for this difference may be that DGM oxidation is more important in subtropical environments as compared to temperate areas.

Effect of Particulate Matter on DGM Production. Due to resuspension of sediments and high productivity, suspended particulate matter in coastal regions is much higher than in the open ocean. To determine the influence of the particulate phase on DGM photoproduction, filtered and unfiltered samples were incubated and compared. In a first experiment, after a 7-h incubation under daylight, DGM production was 40% lower in filtered than in unfiltered

TABLE 4. Effect of Filtration (0.45 mm) of Seawater Samples Collected near the Shore of Galveston Island on Januarary 23, 1996^a

type of bottle	treatment before incubation	DGM concn (fM)	p value of ANOVA for treatment effect	Tukey <i>HSD</i> comparison ^b	hourly DGM production (fM h ⁻¹)
black	none	69 ± 6	< 0.001	а	
transparent	none	171 \pm 11		b	15 \pm 2
black	filtration	$\textbf{36} \pm \textbf{5}$		С	
transparent	filtration	101 \pm 16		d	9 ± 2

^a Samples were incubated 7 h prior to analysis. Standard deviations based on three replicates are shown. ^b Significant differences (p < 0.05) between treatment are indicated by different letters.

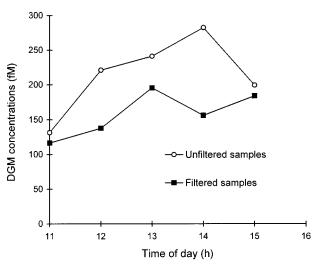


FIGURE 6. Time series of DGM levels in filtered and unfiltered seawater samples collected nearshore of Galveston Island on March 11, 1996.

samples (Table 4). DGM concentrations in filtered samples kept in transparent and black bottles were respectively 41% and 48% lower than their unfiltered counterparts.

In another experiment (Figure 6), unfiltered samples again yielded higher production rates of DGM than filtered ones, during the first 3 h, confirming the contribution of particulate matter in DGM production. After 4 h of incubation, DGM levels became relatively similar in both treatments because of an important DGM loss in filtered bottles. However, since the observed decrease in the unfiltered samples is based on only one point, we do not consider that this experiment convincingly shows the presence of oxidation of Hg⁰.

These results indicate that the majority (\sim 60%; Table 4) of sunlight-induced DGM production was associated with dissolved and colloidal Hg phases. Colloidal Hg (1 kDa, 0.45 mm) in Galveston can account for as much as 77% of the filtrate (<0.45 mm) (20). Consequently, it is likely that photochemical processes are responsible for most of the observed DGM production. However, other processes associated either with particles or with photosynthetic organisms must also be important since 40% of the DGM production involved particles larger than 0.45 mm. Filtration may be removing a readily exchangeable or a photolabile particulate-Hg pool or a biotic component (e.g., bacteria and algae) that can reduce Hg(II).

This suggests that photoinduced DGM production in seawater is the result of more than one mechanism. Near-shore water samples used in this study contained relatively high levels of particles (suspended particulate material in Galveston Bay: $7-16 \text{ mg L}^{-1}$; 20) as compared to the open ocean, and particulate matter may be less important offshore.

Mechanism of DGM Loss. Our work and other laboratory studies suggest that DGM loss is likely the result of Hg⁰ oxidation, since Hg⁰ is the predominant volatile species in most natural waters. At this point, we have insufficient information to propose a specific Hg oxidation mechanism

involving chloride mediation. Chloride ions may stabilize oxidation products (e.g., Hg(II)) and therefore promote the oxidation reaction (15). The oxidants involved in this oxidation may be organoperoxy compounds (21), O_3 (22, 23), OH^{\bullet} (3, 24) and/or O_2 (25). Since, in the present study Hg oxidation was observed in the dark, the most likely oxidant would be O_2 . DGM loss may also result from nonoxidative processes. For instance, if dimethyl mercury represents a significant fraction of DGM (which is unlikely; 4, 5), degradation of dimethyl mercury to monomethyl mercury or other nonvolatile species would decrease DGM levels. Adsorption and complexation of volatile species can also induce some DGM loss, athough the constant DGM levels observed in black bottles suggest that adsoptive losses are low.

Analytical and Biogeochemical Implications. Our results strongly support the view that Hg⁰ does not always behave as a conservative element in aquatic systems but may be rapidly oxidized. From an analytical perspective, it is therefore very important to analyze seawater samples for DGM immediately after collection (i.e., during the 0.5 h). It would be even better to measure DGM *in situ*. Some storage protocols, such as cooling, could be tested to minimize these problems. Furthermore, in view of the very dynamic nature of DGM, it is important to study the temporal variations of DGM levels over short time intervals

From a biogeochemical perspective, Hg⁰ oxidation may have to be considered in future modeling of sea-air transfer. Previously, only reduction, diffusion, advection, and the availability of reducible substrate were considered as important parameters controlling DGM levels (26). The relative importance of Hg oxidation vs Hg volatilization in controlling DGM levels in seawater will depend on the rate at which DGM degases from the water column as compared to residence times and the depth of the photoreduction influence (i.e., light penetration). To illustrate, with a piston velocity of 5 m day⁻¹ (typical of the equatorial region; 27) and an atmospheric gaseous mercury concentration of 2 and 40 ng m⁻³ in the water (about 200 fM; see Figures 3 and 6), we calculate a flux out of the water of 8 ng m⁻² h⁻¹. By comparison, the loss of DGM resulting from oxidation (firstorder $k = 0.1 \text{ h}^{-1}$) at the same initial DGM concentration (40 ng m⁻³) would be 4 ng m⁻² h⁻¹ for a 1 m deep water column (half of the evasional flux) and 40 ng m⁻² h⁻¹ for a 10 m deep water column (five times the evasional flux).

Therefore, in shallow coastal waters, such as Gulf Coast estuaries, evasion of DGM may be more important than oxidation. DGM photoproduction will be favored since light may penetrate the entire water column (although in some cases light penetration may be diminished by high loads of suspended particulate matters). Also, DGM degassing may be promoted by turbulence, warm temperatures, and proximity of the air—water interface. In contrast, DGM production in offshore water can occur at greater depth, and DGM degassing will be less important than *in situ* degradation of DGM. Note, however, that the present study deals only with coastal seawater rich in suspended solids and allochtonous matter. No oxidation of Hg⁰ has yet been reported in the open ocean.

Acknowledgments

We thank Greg Mierle, David R. S. Lean, William H. Schroeder, Dawn Bazely, Mike Mozurkiewich, and three anonymous reviewers for helpful comments. Laboratory and field assistance by Mary C. Stordal, Ron Lehman, Laura McKenzie, Susan Gonzalez, Irene Shaperdoth, and Anne Kraepiel are acknowledged. This research was supported by an EPRI grant (FAEMCMP project) to G.A.G., by grants from EPA and ONR to F.M.M.M., and by a Canada—U.S. Fulbright postgraduate scholarship and an NSERC fellowship to M.A.

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Received for review April 25, 1997. Revised manuscript received September 9, 1997. Accepted September 15, 1997.

ES9703685

[®] Abstract published in Advance ACS Abstracts, October 15, 1997.