Description of a dimethylmercury automatic analyzer for the high-resolution measurement of dissolved gaseous mercury species in surface ocean waters

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Abstract

Our understanding of the significance of dimethylmercury (DMHg) to the mercury (Hg) the global ocean biogeochemical cycle is unclear because of the lack of detailed DMHg measurements in the water column. To our knowledge, 30-years of published studies have generated no more than 200 DMHg data points in the ocean surface waters and marine boundary layer (MBL). To improve the precision and reduce the uncertainty in determining DMHg in surface seawater, we developed a simple and robust DMHg automatic analyzer (DAA). This DAA system couples the main sampling and analytic steps, including a continuous flow chamber, with dual Carbotrap pre-concentration, a gas chromatographic column, a cold vapor atomic fluorescence spectrometry and a data logger for signal integration. We compared the operation, performance, and reproducibility between our DAA and the traditional manual analytic method. Its advantages include the ease of operation, the high time resolution and precision (30 min sampling; < 5% relative variation) and long-term stability (two weeks). The DAA can determine DMHg in both the MBL and surface seawater. The estimated detection limits for DMHg with the DAA in atmosphere and in surface seawater are 10 pg/m^3 and 0.2 fM, respectively. The successful DAA field measurement in coastal waters indicates that it can help detect the low DMHg concentration in surface seawater and the time series DMHg data helped our understanding of the DMHg behavior (sources and sinks) and its flux into the MBL. The comparison of DMHg concentration in various oceans also suggests that the coastal region had the lowest averaged DMHg; up to an order of magnitude lower than other ecosystems.

Keywords

Dimethylmercury, Dissolved gaseous mercury, Automatic analyzer, High time resolution, Marine boundary layer, Coastal waters

Synopsis

This study describes a newly developed dimethylmercury (DMHg) automatic analyzer and presents the first high-resolution DMHg observations in the surface ocean, demonstrating its usefulness for examining DMHg behavior and its role in the global biogeochemical cycling of mercury.

Introduction

Dimethylmercury (DMHg), a volatile, toxic and organic form of mercury (Hg), appears to be relatively ubiquitous in marine waters and has been found in deep hypoxic oceanic waters, upwelling waters, coastal waters and the mixed layer, primarily under upwelling conditions, in all oceans globally.[1-11] From the Hg cycling perspective, DMHg could be formed by Hg methylation in water column and/or in benthic sediment through biotic and abiotic processes which are, however, still unclear in terms of their importnace.[12-14] Although current understanding of the sources of DMHg in oceanic waters is limited, the degradation of DMHg may be an important source of monomethylmercury (MMHg) in the marine environment and the marine boundary layer (MBL) atmosphere, and in wet deposition.[9, 15, 16] From a human health perspective, MMHg is the most bioaccumulative form of Hg in marine food webs and the form which impacts human Hg exposure through seafood consumption.[17, 18] Previous studies suggest that DMHg ranges from 30% to 80% of the total methylated Hg pool (both MMHg and DMHg) in ocean waters, which means degradation of DMHg to MMHg could also indirectly contribute to the marine food web MMHg accumulation.[6, 15] In addition, it has been suggested that DMHg could evade from the surface ocean as a gas or within sea spray into the MBL atmosphere.[19-21] The evaded DMHg, after decomposition to MMHg, can be absorbed by water vapor contributing to the methylated Hg compounds in the rain in coastal regions, in the snow in polar regions, or in open ocean locations, and could be an important MMHg source.[21-23] However, due to the limited data on DMHg levels in surface waters and the MBL, it's difficult to understand the behavior and importance of DMHg's role within the global Hg biogeochemical cycle.

Based on our knowledge, the past 30-years of published studies have generated no more than 200 data points of DMHg within the surface ocean/MBL and no more than 1000 data points of DMHg from the entire water column in all oceans.[1-11, 24] The reasons for the limited dataset of DMHg are that: 1) DMHg is not stable after collection in bottles and degrades within hours and so needs to be analyzed on board or immediately after collection; and 2) DMHg concentrations are generally low and near current detection limits in surface water and much of the interior ocean, except for some atypical regions (i.e., Arctic, Antarctic, low oxygen zones and upwelling waters).[15, 25] Given its low concentration, and the traditional manual analytic method for its measurement includes several steps, such as collection of a large volume of seawater and pre-concentration of DMHg to improve the detection limit (DL) prior to the analysis. However, this

may also increase the uncertainty and operational bias. Furthermore, the long purging time during the preconcentration step may also promote DMHg degradation in the purging bottle. Thus, in many ocean studies of Hg speciation, analysis of DMHg is not done and samples are acidified for later analysis of methylated Hg. Acidification converts the DMHg into the more stable MMHg and allows for the determination of total methylated Hg.

To briefly summarize, the traditional manual analytic method for determination of DMHg is based on sparging a water sample with pre-concentration on a solid phase absorbent, either a Tenax© or Carbotrap© trap, followed by thermal desorption, gas chromatographic (GC) separation, decomposition of Hg species to elemental Hg (Hg^0) and detection.[26] Several detection methods for quantifying Hg^0 have been successfully tested and used with this manual method, such as cold vapor atomic absorption spectrometry (CVAAS),[27, 28] cold vapor atomic fluorescence spectrometry (CVAFS),[26] and inductively coupled plasma mass spectrometry (ICPMS).[29, 30] However, despite the detection methods used, this traditional manual analytical method requires intensive effort, and is not suitable for continuous or semi-continuous measurement. In addition, there is potential bias of the results from this manual method, primarily due to: 1) purging gas leaks; 2) trap contamination; and 3) operational failure, (i.e., trap overheating and degradation, baseline drift, biased calibration spikes). Additionally, the DL in previous studies varies widely from 2 fM to 25 fM, although these previous studies all use the traditional manual method.[5, 24, 25, 31] Therefore, a new method is urgently needed for improving the precision and the DL in determining DMHg in the ocean, to confirm or refute its importance in the global Hg cycle by determining its concentration at a high resolution in both time and space.

In this study, we describe a simple and robust DMHg automatic analyzer (DAA), which is newly developed and tested in laboratory and field. This DAA is based on the automation of the existing manual method. This method minimizes the uncertainty of conventional procedures, minimizes the labor requirements of the manual analysis and improves the accuracy and DL of DMHg determination. More specifically, the advantages of our DAA include: 1) the ease of operation (program controlled); 2) its high time resolution (30 min collection per data point); and 3) its high precision (< 5% relative variation), low DL (0.2 fM in water) and long-term operational stability (two weeks). The DAA is applicable to the determination of DMHg in both the atmosphere and the surface seawater to allow for examination of air-sea exchange at the

MBL/seawater interface. The estimated detection limits for DMHg using the DAA in the atmosphere and in surface seawater are 10 pg/m^3 and 0.2 fM, respectively. The successful field measurement with our DAA indicates that the high-resolution measurements and low DL can help us detect the temporal variability in low DMHg concentration in surface seawater. With a time-series of DMHg data, we also demonstrate how such data can lead to a better understanding of DMHg behavior and its flux from surface seawater to the atmosphere.

Materials and Methods

Caution: Dimethylmercury is a volatile and extremely toxic organic Hg compound. It has been shown to cause human death through contact with the skin from one droplet of a concentrated dimethylmercury solution.[32, 33] Additionally, nitrile and other material gloves can be penetrated by dimethylmercury liquid as it should be considered as an organic compound. Therefore, we do not recommend working with concentrated or pure solutions. All work needs to be performed under the protection of an evacuated fume hood with extreme caution and suitable protective equipment. However, given the extremely low concentrations of dimethylmercury in the environment (fM), there is no danger from making these environmental measurements.

Experimental apparatus. The design of the DAA is shown in Figure 1a, in contrast to the traditional manual analytic method, which is depicted in Figure 1b. For measuring dissolved gaseous Hg species (DGHg) in seawater, which includes both Hg^0 and DMHg, a continuous counter-flow chamber has been coupled with the DAA. This approach has been used in many studies of DGHg.[34-36] The principle of the continuous flow chamber is that the opposite flow of gas in the chamber can facilitate the exchange and rapid equilibration of dissolved gaseous Hg species between the aqueous and gaseous phase.[34] A similar approach is used in most studies of dissolved gases in environmental waters. To briefly summarize, the continuous flow chamber contains a seawater filled jacketed outer cylinder made of acrylic, which helps maintain the temperature of the inner cylinder filled with seawater to that of the environmental sampled water. The water flow is into the inner chamber followed by the outer chamber. Pressurized air (Hg free) is directed by Teflon tubing to glass frits (70-100 μm porosity, Ace Glass, MilliporeSigma Corp.) mounted into the bottom of the inner cylinder at a flow rate of 1.1 to 1.2 L/min. The glass frits disperse the pressurized air into fine bubbles which contacts the seawater increasing the

contact area between the air and seawater and increasing the efficiency of equilibration of the gases in the seawater with the sparging air. The seawater flows into the inner cylinder from above and exits at the bottom of the inner cylinder at a flow rate of 10 to 15 L/min. The ratio of water to air flow determines the response time of the system to changes in water concentration.[32] The height of seawater at the outflow port of the outer cylinder determines the seawater level at the inner cylinder and keeps it relatively stable. In addition, a temperature sensor (HOBO MX2201, Onset Computer Corp.) was installed in the inner cylinder to record the seawater temperature. After gaseous Hg species reach equilibrium between the aqueous and gaseous phase, the gaseous Hg species are then collected onto the sampling trap from the outgoing air. This continuous flow chamber has been successfully used for determining dissolved Hg^0 in surface seawater and its flux in previous studies in the Pacific, Atlantic, Arctic and coastal oceans.[35-37]

The outgoing air from the continuous flow chamber is dried using soda lime (4-8 mesh, Alfa Aesar) and directed into the DAA and a Tekran 2537B for determining DMHg and Hg^0, respectively (Figure 1a). As with the traditional manual method, the outgoing air from the continuous flow chamber passes through a Carbotrap with removes organic Hg compounds primarily (Figure 1b). The manual method requires changing the Carbotrap every 2 hr at the typical 1 L/min flow rate to minimize the breakthrough of DMHg from the Carbotrap.[38] For the DAA, dual Carbotrap tubes (Carbotrap B, 20-40 mesh, Supelco) are designed to allow the alternation between the adsorption and desorption of DMHg with each sampling cycle. For example, while Carbotrap A is sampling, the outgoing air from the continuous flow chamber passes through the Carbotrap A for adsorption of DMHg and then passes into Tekran 2537B for determining of Hg^0. At the end of the sampling cycle for Carbotrap A, the sampling air flow switches to Carbotrap B and initializes the sampling cycle for Carbotrap B. Then Carbotrap A enters the desorption cycle with a continuous argon (UHP, Airgas Inc.) purging flow at 60 ml/min controlled by the mass flow controller (MFC). The Carbotrap A is also heated to 250 °C for 30 sec using the nichrome resistance wire coil, wrapped around the trap. The argon carries any desorbed Hg species from Carbotrap A to the isothermal gas chromatographic column (GC; Teflon tube, 1 m length, ¼ inch OD; packed with Chromosorb WAW-DMCS 60-80 mesh, 15% OV-3, Supelco), maintained at the temperature of 38 ± 1 °C. The Hg species are separated by the GC column based on their molecular weight, and all forms are decomposed to Hg^0 in the

pyrolyzer column after the GC column. The pyrolyzer column is a quartz tube (15 cm length, ¼ inch OD; packed with quartz wool) which is heated and kept at 700 ± 50 °C by a nichrome resistance wire coil inside a thermally insulated oven. After the Hg species are converted to Hg^0 by the pyrolyzer, the produced Hg^0 passes through the CVAFS commercial detector – a Tekran 2500 is used in this application. The voltage information from the CVAFS and the peak area is recorded and integrated by a PeakSimple Chromatography Data System (Model 333, SRI Instruments Inc.). The algorithm of the peak integration includes two steps: 1) location of the peak start and end points by fitting the whole voltage information spectrum using a log normal distribution equation; and 2) integrating the peak area between the peak start and end points. Additional algorithm details of peak integration system are included in the Supporting Information (S1; Figure S1). The entire cycle from thermal desorption of the Carbotrap to peak data acquisition is about 5 min. The entire sampling cycle is designed to be 30 min, which represents a total of 30 L of air passing through the Carbotrap at 1 L/min flow rate. The sampling cycle and desorption cycle is controlled by a programable script which mainly commands the solenoid valve (NResearch Inc.), the nichrome resistance wire and the cooling fan during switching between each Carbotrap. For calibrating the DAA, with either Hg^0 or DMHg, there is an injection port for manually injecting gaseous Hg species prior to the port V2 (shown in Figure 1a). All tubing and connectors are Teflon with ¼ inch OD, unless elsewhere stated. The DAA setting and analytical parameters are summarized in Table 1. The use of DAA improves the analytical efficiency by allowing analysis without supervision and also allows high time resolution measurement.

Laboratory validation. The solid phase adsorbent for DMHg used in the DAA is the commercial Carbotrap B, which has a high and stable recovery about 100 ± 0.3% for DMHg.[38] However, a known issue for the Carbotrap material is the potential breakthrough of DMHg, which usually occurs with increasing sampling volume causing loss of the analyte from the trap. Therefore, the volume of air that can pass through the adsorbent without any significant loss of analyte needs to be determined. The breakthrough volume of the Carbotrap was determined by the traditional manual method as shown in Figure 1b. From previous studies, it has been demonstrated that the seawater in the continuous flow chamber has a relative stable DMHg concentration over short timescales. While increasing the sampling air volume from 10 to 400 L,

adsorbed DMHg on the Carbotrap was measured by the GC-CVAFS system. Additional details of the breakthrough sampling period study are included in the Supporting Information Figure S2. The breakthrough recovery was calculated from this data, and compared with previous studies as shown in Figure 2a, which demonstrated that the larger sampling volumes used resulted in a lower recovery of DMHg. The fitted regression curve indicated that the sampling volume should not be larger than 90 L to ensure a good recovery (> 95%).

The retention time of DMHg in the DAA was determined by injecting DMHg vapor directly into the system. The DMHg vapor was obtained by sampling the headspace of a diluted DMHg solution with a glass syringe (Hamilton Comp.). The diluted DMHg solution was handled carefully in an evacuated fume hood. The retention time for Hg^0 and DMHg were 75 sec and 160 sec, respectively. The detection limit (DL), determined as 3 times of the standard deviation of multiple analysis of a known amount of DMHg, is 0.3 pg for the DAA. According to the chosen sampling duration of 30 min at 1 L/min, the DL for the atmosphere is 10 pg/m^3. The calibration of the DAA can be implemented in two ways: 1) by injecting known amounts of DMHg vapor; and 2) by changing the Carbotrap with a gold trap and injecting known amounts of Hg^0 vapor. The calibration curve was found to have a similar response in terms of the peak area and Hg mass for both DMHg injection and Hg^0 injection (< 10% relative variation). Therefore, we assumed that, for the DAA system, the peak area response would be the same in the GC-CVAFS for the two gaseous Hg species, because DMHg is thermally decomposed to Hg^0 prior to the detection. Due to the toxicity of DMHg, it is impossible to transport and use the DMHg standard to calibrate the DAA in the field. Instead of using a DMHg standard, it is much safer to transport and use a Hg^0 standard to calibrate the DAA. The DAA was calibrated every three days to evaluate the stability of the DAA, as shown in Figure 2b. The result of this multiple calibration suggested that the DAA system could run stably (< 5% relative variation) without extra care and supervision for more than two weeks.

Field measurement. Prior to the field measurement, the DAA system blank was determined by pumping tap water into the continuous flow chamber. The calculated blank for the dissolved DMHg was below the DL, while the calculated blank for dissolved Hg^0 was < 7 fM. The field measurement site was located within the Rankin Lab, a flowing seawater facility at the

University of Connecticut, Avery Point campus, which is on the east side of Long Island Sound and connected to the North Atlantic, as shown in Figure 3a.

The seawater was pumped from the surface waters of Long Island Sound (< 5 m depth) into the continuous flow chamber at a flow rate of 10-15 L/min to ensure that equilibrium is rapidly obtained and that the water is not depleted of DMHg.[34] The outgoing air at a flow rate of 1.0-1.2 L/min passed through both the DAA and Tekran 2537B for quantifying both the dissolved DMHg and Hg^0, respectively. The ratio of the seawater flow and air flow was set around 10, which has been tested in the lab experiments and also used in the previous cruises.[34-37] After quantifying the different amounts of Hg species on the trap, each component of dissolved gaseous Hg species can be recalculated from its corresponding concentration in the outgoing air using the following equations and Henry's Law:

$$Hg^0_{diss} = \frac{Hg^0_{air}}{H_{Hg^0}}$$

$$DMHg_{diss} = \frac{DMHg_{air}}{H_{DMHg}}$$

where Hg^0_{air} and $DMHg_{air}$ represent corresponding Hg species concentration in the outgoing air and H_{Hg^0} and H_{DMHg} are the dimensionless Henry's law constant for Hg^0 and DMHg, respectively. The Henry's law constant is temperature dependent, and the detailed calculation can be found in Supporting Information Table S1. The estimation of gas exchange flux could also be carried out using the following equations

$$F_{Hg^0} = k_{w,Hg^0}\left(Hg^0_{diss} - \frac{C_{air,Hg^0}}{H_{Hg^0}}\right)$$

$$F_{DMHg} = k_{w,DMHg}\left(DMHg_{diss} - \frac{C_{air,DMHg}}{H_{DMHg}}\right)$$

where C_{air,Hg^0} and $C_{air,DMHg}$ represent corresponding Hg species concentrations in the ambient atmosphere and k_{w,Hg^0} and $k_{w,DMHg}$ are the mass transfer coefficient for Hg^0 and DMHg, respectively. The mass transfer coefficient is both temperature and wind speed dependent, and again the detailed calculation of their values for Hg^0 and DMHg can be found in Supporting Information Table S1. As the Carbotrap can potentially absorb a small amount of Hg^0, which is quantified because of the GC separation of species, the calculation of the Hg^0 amount required consideration of both the Hg^0 absorbed by the Carbotrap and gold trap. The raw data of

measured dissolved Hg^0 and DMHg amounts has been converted to a 5-hour moving average to minimize the impact of the outlier values and demonstrate the longer-term trends. The atmospheric Hg^0 concentration at the sampling site was measured by a Tekran 2537X, while the atmospheric DMHg concentration at the sampling site was found to be under the DL. Therefore, the DMHg flux calculation was based only on the dissolved DMHg concentration in surface seawater. In addition to comparing and evaluating the collected data for both DMHg and Hg^0, the DMHg measurements in Long Island Sound were also been compared with previous studies in Arctic, Pacific and Atlantic to quantitatively illustrate the DMHg distribution in surface waters globally. The implications of its concentration and flux are evaluated within the context of the global Hg biogeochemical cycle.

Auxiliary data. In order to understand the extent to which environmental factors influenced the dissolved gaseous Hg species, several environmental parameters (i.e., surface seawater temperature, atmospheric temperature, wind direction and wind speed) were monitored by the weather station located at University of Connecticut, Avery Point campus, near the Rankin Lab. Environmental parameters collected are summarized and shown in Supporting Information Figure S3.

Results and discussion

Validation of the DAA. Several optimizations of the DAA system have already resulted in improved accuracy, higher reproducibility, a low DL, and long-term continuous analysis.

The solid phase adsorbent for DMHg used in the DAA is the commercial Carbotrap B, which has a high and stable recovery about 100 ± 0.3% for DMHg.[38] The breakthrough issue for Carbotrap B was quantified and is shown in Figure 2a, with a comparison to previous studies. The calculated overall breakthrough recovery fitted a polynomial curve ($R^2 = 0.96$, $p < 0.001$***), illustrating that increasing sampling volume would cause a lower recovery. We conclude that, for a good recovery (> 95%), the sampling volume should not be larger than 90 L, or 90 min for a sampling rate at 1 L/min. Here, the sampling time in our study is much shorter (30 min).

The gaseous Hg species are identified by their retention times after the GC column separation. The performance of the peak separation is dependent on: 1) the carrier gas flow rate;

and 2) the GC column temperature. Optimization of the DAA showed that the good separation of peaks is achieved with a carrier flow of 60 ± 2 ml/min and a GC column temperature of 38 ± 1 °C. Therefore, the optimized retention time for Hg^0 and DMHg was determined as 75 sec and 160 sec, respectively (as shown in Supporting Information Figure S1).

The estimated DL for DMHg with the DAA in atmosphere and in surface seawater are 10 pg/m^3 and 0.2 fM, respectively. The DLs in previous studies have varied widely from 2 fM to 25 fM.[5, 24, 25, 31] Thus, our DAA is a substantial improvement with a 10 times lower DL. In addition, the calibration can be easily done by injecting Hg^0 vapor into the DAA system (changing Carbotrap to gold trap is required). Due to the toxicity of DMHg, it will be much safer to carry and use Hg^0 standard to calibrate the DAA on the filed measurement. Based on our continuous calibrations (every three days), the DAA is stable with the averaged variation of 100 ± 3% (as shown in Figure 2b; < 5% relative variation) without supervision for more than two weeks.

Field measurement. The sampling site is located at the eastern end of Long Island Sound, near the mouth of the Thames River (Figure 3a). The seawater exchange, and mixing between fresh river water and salty seawater may drive a higher Hg methylation potential and the formation of DMHg in the vicinity of the sampling location, as found by Schartup et al.[39] Also, there is the potential for Hg methylation within the sediment and its transport to the water column at the shallow sampling location through porewater diffusion or sediment resuspension.[40] Previous studies that have investigated dissolved methylated Hg in the Long Island Sound water column have focused mostly on MMHg, not DMHg, over the past 20 years.[41, 42] Therefore, the understanding of the role of DMHg flux in the Hg biogeochemical cycling in the coastal region like Long Island Sound represents a knowledge gap. Data on DMHg in the open ocean is also limited.

Here, we present the high time resolution continuous measurements of gaseous Hg species in both the surface seawater and atmosphere in Long Island Sound. Dissolved DMHg and Hg^0 in surface seawater were determined with a resolution of 30 min and 5 min, respectively, and averaged 2.7 ± 0.7 $pmol/m^3$ (n = 333) and 95.0 ± 16.3 $pmol/m^3$ (n = 2016), respectively, as shown in Figure 3b and Figure 3c. The estimated air-sea exchange flux for DMHg and Hg^0 were calculated as 0.12 ± 0.14 $pmol/m^2$-hr (n = 333) and 4.79 ± 3.80 $pmol/m^2$-hr (n = 2016) as shown in Figure 3d and Figure 3e. The magnitude of dissolved Hg^0 was about 30

306 times higher than dissolved DMHg in surface seawater at this location. Gosnell, et al. [43]
307 measured a concentration of total methylated Hg in eastern LIS of 15 ± 9 pmol/m^3, which
308 suggests that the relative amount of DMHg is small compared to MMHg at this location. This is
309 consistent with other studies that suggest that unless active upwelling of deeper water is
310 occurring, which can be elevated in DMHg, surface water DMHg values are low due to its loss
311 via gas evasion and also due to some sorts of biotic and abiotic degradation. Overall, given the
312 potential production of MMHg from DMHg photodegradation in either surface waters or in the
313 boundary layer atmosphere, DMHg concentration and flux should be considered a potential
314 mechanism influencing the MMHg pool in local environment, primarily in the atmosphere
315 through its contribution to MMHg dry and wet deposition.[41, 42]
316 The time series data of dissolved DMHg showed a relative stable trend compared to
317 dissolved Hg^0 in surface seawater. Dissolved Hg^0 can be photochemically produced in surface
318 seawater from dissolved divalent Hg, and the observed daily trends of dissolved Hg^0 support this
319 contention as a diurnal cycle in concentration is evident (Figure 3c).[44, 45] Conversely, the relative
320 constant dissolved DMHg concentration in surface seawater suggests a stable DMHg source
321 under the surface layer that is not influenced by changes in solar radiation. No strong evidence
322 for photodemethylation of DMHg is found in the data. Further investigation is needed to
323 determine the sources of DMHg in this region. The reason for the elevated concentration of
324 measured dissolved DMHg on Nov 28 is also not known.
325 The air-sea exchange fluxes of both DMHg and Hg^0 varied similarly and were largely
326 determined by the wind speed as the ambient temperature was relatively consistent over the
327 sampling period, and the change in Hg^0 concentration was relatively small compared to the
328 differences in wind speed (Supporting Information Figure S3). Due to the supersaturation of
329 DMHg and Hg^0 in surface seawater, the air-sea exchange flux was always positive, so that the
330 atmosphere was a relative sink for DMHg and Hg^0 During the wintertime, the coastal region of
331 Long Island Sound can have strong offshore wind during the daytime and higher ambient
332 temperature (surface seawater and atmosphere) due to the solar radiation. Therefore, the trend of
333 air-sea exchange flux could be driven by these changes, i.e. an increasing trend after sunrise with
334 the highest value at midday and the lowest values after sunset.
335

Global comparison and implication. This study has shown the globally first high-resolution time series data of dissolved DMHg in surface seawater and its air-sea exchange flux. To compare our DMHg measurement with previous studies for the surface ocean (depth < 5 m; Figure 4a), we have extracted previous DMHg data from studies completed in Arctic (red symbol), Pacific (green symbol) and Atlantic (orange symbol) which are representative the polar region, subpolar region, open ocean, upwelling region and coastal region. The dissolved DMHg concentrations of the western Arctic (WA)[4], Canadian Arctic Archipelago (CAA)[11], North Pacific (NP)[7], central tropical Pacific (CTP)[10], Monterey Bay California (MBC)[2], North Atlantic (NA)[5], North Atlantic by Mason (NAM)[9], South Atlantic (SA)[8] and Long Island Sound (LIS) averaged 15.8 ± 20.9 fM (n = 16), 39.6 ± 59.9 fM (n = 23), 15.6 ± 7.8 fM (n = 5), 9.8 ± 9.7 fM (n = 12), 73.3 ± 86.9 fM (n = 15), 43.0 ± 43.3 fM (n = 11), 25.2 ± 45.0 fM (n = 9), 5.3 ± 5.5 fM (n = 6) and 2.6 ± 0.7 fM (n = 438), respectively. In addition, by computing the Tukey Honest Significant Difference of each set of normalized cruise data, four significant different groups of dissolved DMHg were classified as shown in Figure 4b (letter a to d; pairwise confidence level 95%; data shown in Supporting Information Table S2). There was no clear pattern for surface dissolved DMHg in the oceans. However, there were some interesting observations illustrated by the data: 1) higher surface dissolved DMHg in CAA than in the WA, 2) equatorial Pacific and equatorial Atlantic generally showed higher dissolved DMHg likely due to the potential Hg supply from the intermediate and deep ocean, 3) the MBC showed the highest dissolved DMHg among all regions, which also suggested the DMHg production at depth and supply to surface, as suggested by others[2], and 4) coastal region (excluding MBC) apparently had the lowest dissolved DMHg among all regions by a factor of 5 to 10. However, as all previous studies used the traditional manual method, and had higher DL, this may have hindered the accurate determination of DMHg in the surface waters. Indeed, the concentration level of dissolved DMHg in LIS would have been mostly undetectable using the traditional manual method but mostly detectable with our DAA. The successful field measurement with the DAA allowed detection of the low DMHg concentration in surface seawater and such time series of DMHg data should help us better understand the DMHg behavior and its flux from surface seawater to the atmosphere MBL.

Supporting Information

Detailed descriptions of the algorithm of the peak integration used in the DAA; detailed descriptions of the parameter for air-sea exchange flux calculation of Hg0 and DMHg; detailed descriptions of a summary of previous published data used in the global comparison in this study; an example of the peak signal from the data logger (black line) and the fitted curve using a log normal distribution (red line) with the marked start and end points (vertical blue line) for Hg0 and DMHg peak, respectively; a case of the Carbotrap deployment for measuring breakthrough; detailed descriptions of ancillary surface seawater and atmospheric data for the field measurement at coastal Long Island Sound including surface seawater temperature and wind speed, from top panel to bottom panel, respectively.

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Table 1. *The dimethylmercury automatic analyzer settings and the analytical parameters used and validated in this study.*

Sampling cycle	
Seawater inflow	10 – 15 L/min
Pressurized air	1.1 – 1.2 L/min (Hg free)
Temperature sensor	HOBO MX2201 (1 Hz, ±0.5 °C)
Drying tube	Soda lime (5.0 g, 4 – 8 mesh)
Sample trap	Carbotrap B (0.1 g, 20 – 40 mesh)
Sampling duration	30 min
Desorption cycle	
Carrier gas	Argon (UHP)
Carrier flow rate	60 ± 2 ml/min
Desorption temperature	250 ± 10 °C (30 sec)
GC column	Teflon tube (1 m length, ¼ inch OD)
GC column temperature	38 ± 1 °C
Pyrolyzer column	Quartz tube (15 cm length, ¼ inch OD)
Pyrolyzer temperature	700 ± 50 °C
Retention time of Hg^0	75 sec
Retention time of DMHg	160 sec
Desorption duration	5 min
Detector and data logger	
Detector	CVAFS (Tekran 2500)
Data logger	PeakSimple (Model 333)
Peak integration	LabVIEW or other software

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measurement (blue line). (e) The air-sea exchange flux of Hg^0 in surface seawater calculated based on the DAA measurement (red line). The environmental parameters associated with this field measurement are summarized and shown in Supporting Information Figure S3.

Figure 4. Global dimethylmercury (DMHg) measurements in the surface ocean mixed layer (<5 m) from the past 30-years of published studies. (a) Summarized DMHg measurement completed in the Arctic (red symbol), Pacific (green symbol) and Atlantic Oceans (orange symbol). The abbreviations are: western Arctic (WA), Canadian Arctic Archipelago (CAA), North Pacific (NP), central tropical Pacific (CTP), Monterey Bay, California (MBC), North Atlantic (NA), North Atlantic, data by Mason (NAM), South Atlantic (SA) and Long Island Sound (LIS). (b) Comparisons of dissolved DMHg concentration in surface seawater in the global ocean. Different letters (a to d) denote significant differences between locations for the normalized data; that is, for two groups with different letters, their mean values are significantly different at the $p < 0.05$* level (Tukey Honest Significant Difference). Previous published data and the references for each study are provided in Supporting Information Table S2.

Graphical Abstract

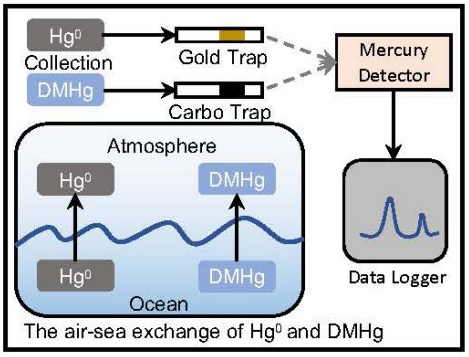


Figure 1

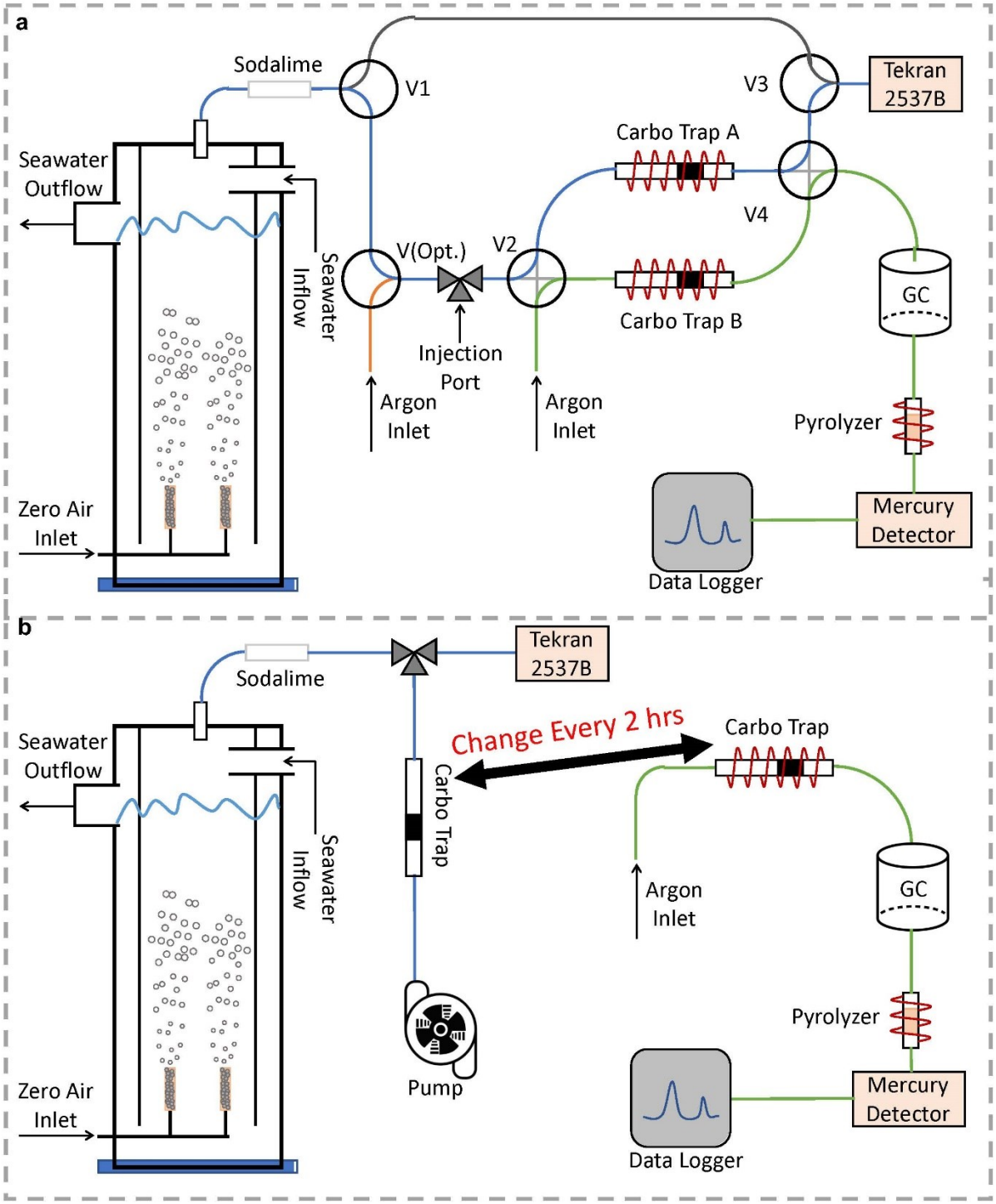
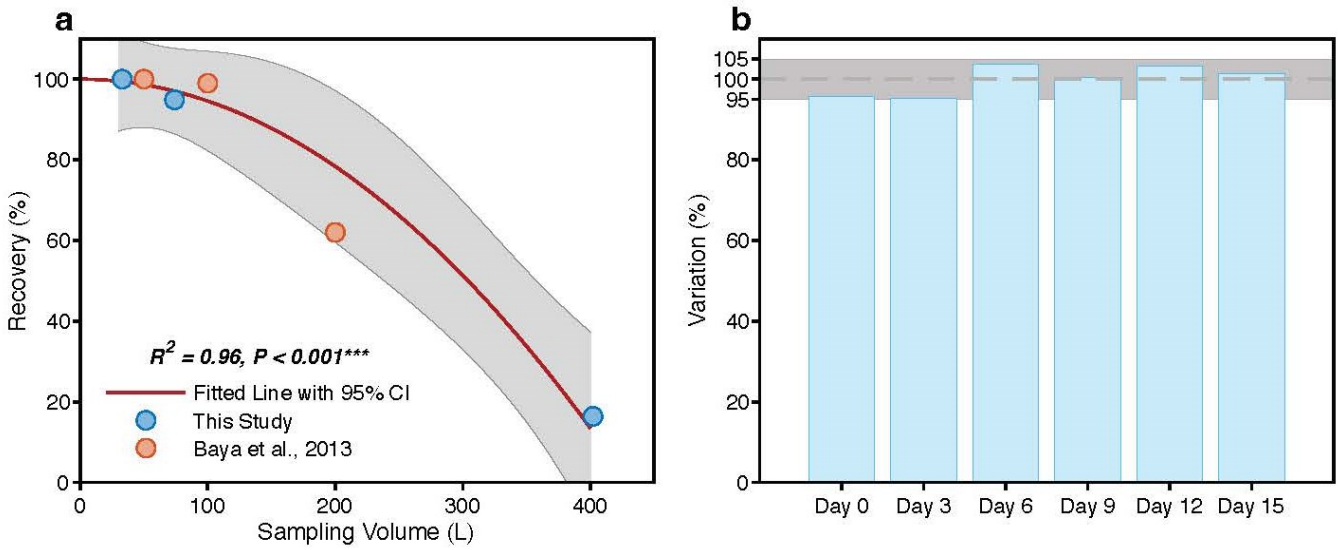

a
Sodalime
V1
V3
Tekran
2537B
Carbo Trap A
Seawater
Outflow
V4
V(Opt.)
V2
Seawater
Inflow
GC
Carbo Trap B
Injection
Port
Argon
Inlet
Argon
Inlet
Pyrolyzer
Zero Air
Inlet
Mercury
Detector
Data Logger
b
Tekran
2537B
Sodalime
Change Every 2 hrs
Carbo Trap
Seawater
Outflow
Carbo Trap
Seawater
Inflow
Argon
Inlet
GC
Pyrolyzer
Pump
Zero Air
Inlet
Mercury
Detector
Data Logger

Figure 2


a
Recovery (%)
100
80
60
40
20
0
0
100
200
300
400
Sampling Volume (L)
R^2 = 0.96, P < 0.001***
Fitted Line with 95% CI
This Study
Baya et al., 2013
b
Variation (%)
105
100
95
80
60
40
20
0
Day 0
Day 3
Day 6
Day 9
Day 12
Day 15

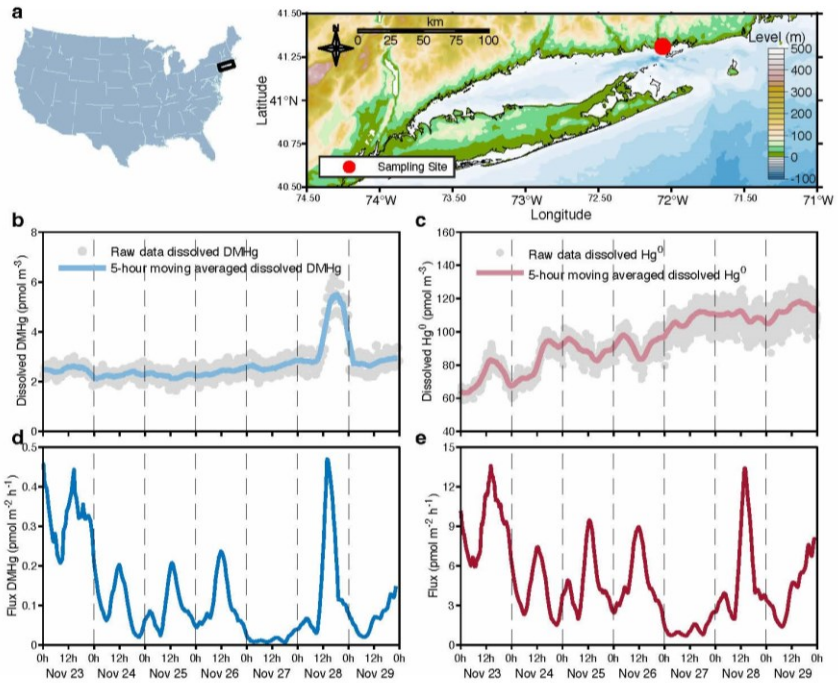


Figure 3 (Double-column)

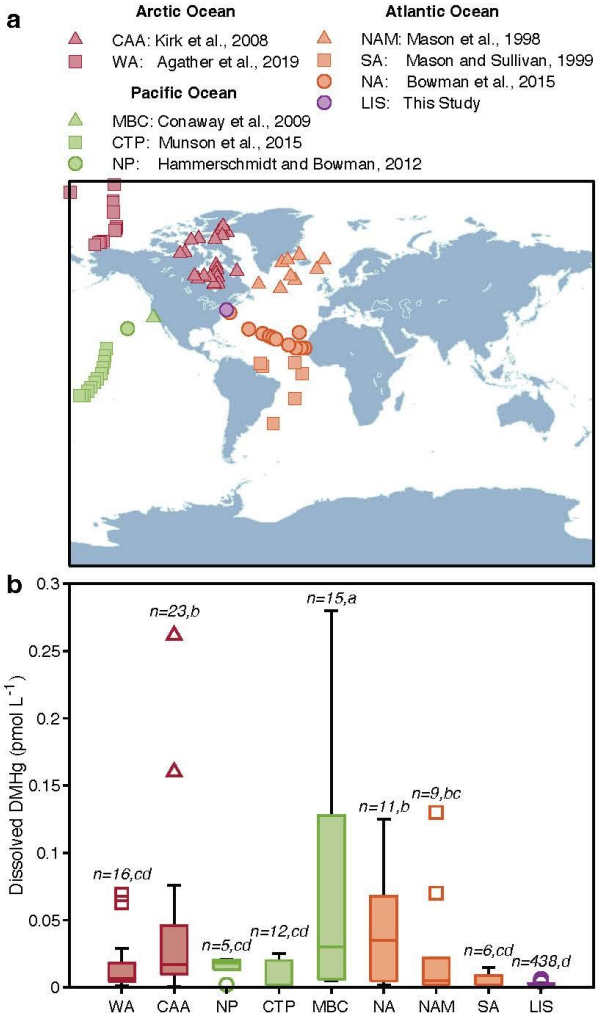


Figure 4 (Single-column)