Development of a novel on-line flow injection mercury analyzer to determine gaseous elemental mercury over the northern South China Sea

C. M. Tseng,^{*a} C. H. Lamborg^b and W. F. Fitzgerald^c

Received 18th November 2009, Accepted 18th January 2010

First published as an Advance Article on the web 5th February 2010

DOI: 10.1039/b924184a

A simple and reliable gaseous elemental mercury analyzer (GEMA) was developed to investigate atmospheric gaseous elemental Hg (GEM) over the northern South China Sea (SCS). This on-line flow injection system couples the main sampling and analytical steps from sample introduction, Au amalgamation/pre-concentration to final detection/data acquisition. This approach provides ease of operation and high analytical performance and is suitable for shipboard use. The analyzer can be fully automated and also be modified to examine other atmospheric Hg species (*e.g.*, reactive gaseous, particulate and methyl-Hg). Here, we present the results of laboratory performance tests and comparison with a traditional manual method, which showed good agreement. The results demonstrate that this approach is accurate and precise. The GEMA allows the reliable GEM determination in ambient air samples (*i.e.* high recoveries of $107 \pm 6\%$, obtained from 6 spiked gas standards) with a low detection limit of 0.1 ng m^{-3} for a sample volume of 10 L and an excellent reproducibility (relative standard deviation $\leq 5\%$, $n = 6$). Representative field atmospheric GEM data from spring, summer, fall and winter 2003 over the northern SCS are also presented. Seasonal GEM variations with higher GEM ($6.9 \pm 1.0 \text{ ng m}^{-3}$) in winter and lower in late spring (2.2 ± 0.5) and summer (2.7 ± 0.8) were evident in relation to the East Asian monsoon cycles.

Introduction

Mercury (Hg), is a relatively volatile metal, which can be moved through Earth's biologically active reservoirs *via* the atmosphere. Gaseous elemental Hg (GEM) is the major atmospheric species ($\text{Hg}^0 > 95\%$ of total) and has an atmospheric residence time of $0.5 \sim 1$ years.^{1–6} Once emitted from anthropogenic and natural sources, Hg^0 can be transported intra- and inter-hemispherically and subsequently deposited even to remote marine environments.^{7–11} Human activity, especially fossil fuel combustion (*e.g.*, coal¹⁰) has increased emissions to and deposition from the atmosphere and presumably to the ecosystems receiving this additional load, and may pose a threat to human health *via* the consumption of fish and fish products.^{12,13}

Globally, Hg emissions have increased significantly as a result of human activities since the industrial revolution and anthropogenic Hg emissions represent about 60% of the total atmospheric emissions.^{3,6} About 54% of global anthropogenic emissions (2200 ton yr^{-1}) are estimated to come from Asia and this sector is expected to increase in dominance due to the rapidly expanding economies of East Asia and their use of high-sulfur and -mercury, domestic coal.^{14,15} In order to quantify atmospheric Hg concentrations and the scale of current and future anthropogenic perturbations within East Asia, its surrounding

marginal seas (*e.g.*, South China Sea (SCS)) and the rest of the world, a robust and reliable GEM monitoring method for the atmosphere is urgently needed.

The accurate determination of atmospheric GEM is challenging. First, as the concentration of GEM is extremely low (*ca.* $1\text{--}2 \text{ ng m}^{-3}$ of air), a highly sensitive technique involving pre-concentration is required.^{16–19} Second, problems such as Hg contamination and loss could occur during air sampling and storage making on-site measurements highly desirable.^{19,20} Third, the GEM distribution may vary diurnally and synoptically so that high frequency, *in situ* measurements are needed to resolve the physical factors affecting GEM concentrations.^{21,22} Commonly used methods make use of a sampling train consisting of a filter to retain particulate mercury followed by an adsorbent trap which retains GEM, and are manually operated and frequently require long-time air sampling, storage and further analysis performed back in laboratory.^{16,19,23,24} Since GEM sampling and analytical systems are generally not coupled, the analytical and field requirements cannot be completed in an efficient manner to get rapid and accurate measurements of GEM.

Our GEM analyzer (GEMA) is a simple, robust, on-line sampling and trap system combining flow-injection, and gold amalgamation preconcentration techniques together with cold vapor atomic fluorescence detection, and is well-suited for field or shipboard use. It has been successfully used in laboratory and field studies of GEM in Taipei, Taiwan and at the South-East Asian Time-series Study (SEATS) station in the northern SCS since 2003. Analytical operation is simple and manual handling of samples is minimized. Simultaneous operation of sampling and analysis should give high sample throughput. Each run

^aInstitute of Oceanography, National Taiwan University, P.O. Box 23-13, Taipei, 106, Taiwan, Republic of China. E-mail: cmtseng99@ntu.edu.tw; Fax: +886-2-23644049; Tel: +886-2-33669775

^bWoods Hole Oceanographic Institute, MS 51, Woods Hole, MA, 02543, USA

^cDepartment of Marine Sciences, University of Connecticut, 1080 Shennecossett Road, Groton, Connecticut, 06340, USA

analysis is separately calibrated for utmost accuracy. Furthermore, contamination from lab air is eliminated by establishing a closed circuit. Common interferences from aerosol samples by three stage Teflon filters and water vapor by a pre-drying Nafion® tube are readily eliminated. Below, we describe the GEMA, and its reliability/performance in laboratory and field tests with comparison to the manual approach. In addition, selected spring, summer, fall and winter GEM results from the northern SCS are presented, and these include seasonal distribution patterns, and potential source attribution.

Experimental

Sampling sites and strategies

Two sampling sites were included in this study: metropolitan Taipei and the SEATS site in the South China Sea (SCS), southwest of Taiwan (Fig. 1). The Taipei sampling site was located on the roof of the National Taiwan University Institute of Oceanography building (NTUIO), approximately 25 m above ground level. This site was used for analytical testing and represented the urban GEM signal as well. The sampling system consisted of an air intake (an open face 3-stage filtration holder protected by plastic housing), which was connected to the Hg trapping system *via* Teflon tubing (6.4 mm o.d., 30 m long), the GEMA analyzer (described below) and finally a vacuum pump (Cast). The GEMA was placed inside the laboratory of the NTUIO building.

The Taiwanese National Center for Ocean Research (NCOR) has been operating the SEATS program, featuring regular sampling at SEATS (18.2°N, 115.4°E) in the northern SCS since 1999.^{25,26} This location is far enough away from the land/continent (~400 km) so that the signals observed will be broadly integrative and not local. Hence, the temporal variation of the atmospheric Hg associated with regional atmospheric forcing could be directly examined and characterized.

The SEATS station was occupied with on-board atmospheric Hg sampling 4 times between May and December, 2003 in

approximately seasonal intervals aboard *R/V Ocean Research-I* (Cruise numbers 682, May 19–20; 690, August 3–10; 696, October 2–7; 705, December 14–20). During the cruise runs, uncontaminated marine air samples for the GEM measurements were collected underway from the front of the ship head *ca.* 15 m above the sea surface using a Teflon tube (40-m length, 6.4 mm o.d.) and additionally collected at the SEATS station while the ship was facing into the wind and moving slowly. The analysis of GEM was carried out in the on-board laboratory immediately after the sampling.

The SCS is the largest marginal sea (surface area: 3.5×10^6 km², Fig. 1) in the tropical-subtropical western North Pacific. The SCS and Taiwan are subjected to the forcing of alternating monsoons (southwest from May to early September and northeast from late September till April) and many tropical cyclones. There are also inter-monsoon periods in the late spring (April to May) and the early fall (September to October). During the winter, air pollutants and dusts from the northern China are transported southwardly to the SCS by the prevailing northeast winds^{27,28} and during the summer in the southern monsoon, oceanic and some biomass burning materials may be brought from Indochina Peninsula and Indian Ocean by southwest winds.

Reference methodology

Traditional manual procedures used in this study were mainly based on the approach developed by Fitzgerald and Gill.¹⁶ Generally, two separate systems were used for the GEM analyses: 1) the field sampling system for collecting the atmospheric GEM by the Au amalgamation, and 2) an analytical set-up for measuring GEM in the laboratory. Briefly, ambient air was sampled with a vacuum pump. Samples were collected in triplicate. Each sampling train had an open face Teflon filter holder, which Teflon filters (47 mm, 0.45 µm) were housed in to remove particles, and 3 Au-coated sand traps, which retained the GEM. The GEM was collected on the first “sample” trap, while the second sample trap acted as a blank and the third trap as a “protective” trap to prevent Hg return from the pump if/when the system is idle. The sampling traps were removed from the sampling train after complete of the sampling and then connected upstream of a calibrated “analytical” trap in the analytical set-up for Hg⁰ measurement. The analysis of GEM was then carried out by thermal desorption of the collected GEM from the sample trap, onto the analytical trap, and then from there into the detector following a second desorption. This “dual amalgamation” approach is also the basis for the US EPA Standard Method #1631 for analysis of Hg in water.

GEMA description

The on-line coupling system for GEM measurements combined four main components: a) an air sampling train including a vacuum pump, 2) manifold for the flow path of dual Au amalgamation, 3) AFS detection and, 4) data acquisition by a personal laptop. A flow diagram of the GEMA system was, shown in Fig. 2a,b, similar to the ones presented by Tseng *et al.*^{29,30} for the dissolved elemental mercury (DEM) measurements. The entire process, from air sampling through detection

Fig. 1 Sampling sites of Institute of Oceanography, National Taiwan University (NTUIO) in metropolitan Taipei (circle) and of the South-East Asian Time-series Study station (SEATS) in the northern South China Sea (SCS). The routine cruise tracks (arrow) in this study were between the Kaoshiung (kao) and the SEATS station (circle).

Fig. 2 Schematic of GEMA with (a) in series one-channel analysis and (b) two-channel analysis for GEM determination in natural airs. 1. sampling introduction device; 2. six-way injection valves (injection-V1, -V2, -V3); 3. atomic fluorescence spectrometer (AFS); 4. personal computer for data acquisition.

and data acquisition, was performed on-line within a closed circuit made of Teflon tubing. The main flow path of the manifold was constructed with Teflon tubing of 3.2 mm o.d., except for the tubing of 6.4 mm o.d. for gas sampling and the waste line.

Sample gas was pulled by an air vacuum pump (Cast) through Teflon sampling lines (PFA tubing of 6.4 mm o.d., 30 m long) with a Teflon filter holder, located at the mouth of the tubing, and pre-drying trap, located before the gold column, to the manifold of the GEMA, followed by a “protective” trap and then mass flow meter and finally vented out (Fig. 2a,b). The outlet from the manifold to vacuum pump was made of the same PFA tubing diameter (6.4 mm o.d., 2 m long). An open face 3-stage Teflon filter holder with three Teflon filters was placed at inlets of the GEMA sampling lines to remove particles and to some extent water vapor. The pre-drying Nafion® tube (Perma Pure MD-110-12 Teflon tubing, 3.2 mm i.d., 6.4 mm o.d., 14” length), was used to remove water vapor. The “protective” trap is placed prior to the mass flow meter to prevent backward diffusion of Hg from the pump. The gas flow rate could be adjusted from 0.2 to 1.5 L min⁻¹ depending on the required analysis frequency and monitored with Sierra mass flow meters. In this study, the gas flow rate of 1.0 L min⁻¹ was used throughout all experiments.

Methods for sampling and measurements of GEM

The manifolds can be flexibly modified according to sampling strategies and experimental needs. The GEMA can be operated in two separate ways. For application in low frequency sampling strategy (long-time sampling), the two sample traps (ST1 and ST2) are linked in series (Fig. 2a). This one-channel method can also be used to test trap efficiency, capacity and recovery. The alternate method, used for measurement at high temporal frequency, makes use of the two sample traps simultaneously, namely while one trap is sampling ambient air, the other is being analyzed (Fig. 2b). The principles of operation in two different ways are respectively described in the following.

In-series one-channel analysis. During the sampling, the sample gas loaded onto in-series connected sample traps, *i.e.*, the first and second “sample” traps in two separate six-way injection valves, V1 and V2 (Rheodyne 5020), were looped together (Fig. 2a). The Hg⁰ in the sample gas was primarily amalgamated on the Au-sand (*ca.* 0.1 g, 60~80 mesh) in the first sample trap (ST1, quartz tubing, 13 cm length, 3.2 mm i.d.), while the Hg-free sample gas then passed through the second sample trap (ST2). The ST2 thus acted as a blank. Meanwhile, V3 was positioned so that the analytical Au-sand trap (AT3) was isolated from Ar flow, being the background trap as a reference for blank.

After completion of sampling, V2 and V1 were turned together from the “trap” position (amalgamating GEM in the sample trap) to the “desorption” position (ready to desorb Hg onto the analytical trap) and V3 was turned from the isolating “stand-by” position to the “trap/desorb” position. Hg⁰ trapped on each trap will be respectively desorbed by heating to ~600 °C by powering a nichrome heating coil wrapped around the trap for 2 min. The running sequences of analyses were from AT3 firstly, then to ST2, finally to ST1. The Ar stream (30 mL min⁻¹) then carried the Hg to the AFS detector (Tekran 2500). Detection of Hg took place through observation of cold vapor atomic fluorescence at 253.7 nm. The analytical process, from desorption, detection to data acquisition, took 2 min for one trap run and was fully controlled by a programmable timer/controller (ChronTrol).

Two-channel analysis. The alternative method is more efficient for that sampling and analysis shall be operated simultaneously. While one trap (ST2) is sampling *i.e.*, the sample gas loaded onto ST2, the other (ST1) is being analyzed (Fig. 2b). The running sequence of analysis is firstly for ST1 and then for ST2. The AT3 acted as a background trap for blank. The analytical process takes 4 min for one channel run. The operations and conditions of valves regarding the sampling and Au trapping, thermal desorption-amalgamation and detection by AFS are similar to those mentioned above.

Blank and calibration

Low blanks for ultra-trace GEM analysis in natural air are established by Au-sand trap cleaning and conditioning. Newly packed lab-made Au traps are heated to ~600 °C for one hour in an Ar carrier flow of 30 mL min⁻¹ to remove Hg from the column. The sampling train inlets (tubing and filter holder) are cleaned before each field trip using dilute (5% v/v) HCl (36% w/w)

and HNO₃ (70% w/w), and are thoroughly rinsed with reagent-grade water. For trap conditioning, before starting each analysis session, the Au traps were blanked initially by heating at 600 °C to bring their blanks down to an acceptable level (≤ 1 pg). Once the blank is low and stable, analysis of real samples may begin. Generally, blanks are determined once every sample of each run analyzed. Further details on conditioning of Au traps and cleaning the labware can be found in Tseng *et al.*³⁰

Calibration was performed before and during sample analysis by injecting a known mass of Hg⁰ vapor (aliquot of headspace over a droplet of pure liquid Hg, sampled with a Hamilton gas-tight syringe³⁰). The concentration of Hg-saturated vapor (Y) injected was calculated by the fitting relationship as a function of temperature ($T/^{\circ}\text{C}$): $Y = 1.5747 \times 10^{-7} \times T^5 - 1.5532 \times 10^{-7} \times T^4 + 3.7825 \times 10^{-4} \times T^3 + 8.9195 \times 10^{-3} \times T^2 + 2.3213 \times 10^{-1} \times T + 2.3806$ ($r^2 = 1$), which is an empirical fit to the data of Huber *et al.* (2006).³¹ The Hg was injected into the Ar carrier stream through a Teflon injection tee (containing a Teflon-faced silicone septum) just upstream of the sample or analytical traps. When the injections were made upstream of the Au sand traps, excellent calibration ($r^2 > 0.995$) and high precision (relative standard deviation (r.s.d.) $< 5\%$, $N = 10$) were obtained. When trap recoveries fell below 85%, the old columns were repacked with new material and reconditioned as above. Sample trap recovery tests were conducted with injections in the carrier stream once per sample.

Intercomparison test in NTUIO-Laboratory study site

Intercomparison experiments of the GEMA with the manual method were performed by analyzing the urban air at the site of NTUIO, Taipei. These experiments were performed during three days (June 11–13, 2003) and included twelve runs where both the manual and GEMA systems were operated side-by-side. Initially, both methods sampled air from the roof top of the NTUIO building, (*ca.* 25 m above the ground surface). The manual method employed Teflon tubing to the Au-sand traps to deliver the ambient air by a vacuum pump. Time interval between runs for exchanging Au traps in the manual sampling train and analyzing in triplicate was within one hour. The GEMA method employed in-line Teflon sampling lines (6.4 mm o.d., 30 m long) to deliver the air sample to the GEMA system. The GEMA operated continuously and simultaneously during the study. The GEM was collected by Au-sand traps and then analyzed by the GEMA every 30 min. The sampling gas flow rate was constantly set on 1 L min⁻¹ for the both methods and monitored with Sierra mass flow meters.

Results and discussion

Optimization of the GEMA

The on-line GEM analyzer was originally made so that its performance and optimization could be performed before using in the field. Optimization experiments were conducted in the following areas: trap efficiencies and capacity and evaluation of analytical performance (blank, recoveries, precision and accuracy).

Trap efficiencies. The Au-coated sand trap was examined for the Hg adsorbing properties in an air stream of an in-series dual

amalgamation gas train (Fig. 2a) at a constant flow of 1 L min⁻¹ under the following experimental conditions: (1) without spike of standard gas Hg⁰ for replication ($n = 6$) at the constant sampling time (*ca.* 1 h) and (2) with a spike of *ca.* 390 pg Hg⁰ under 6 different sampling intervals from 10 min to 4 h.

In the first experiment, we performed the replicate experiments to have consecutive measurements from 9 am to 5 pm on May 14 2003. The data showed that sample air Hg⁰ was trapped completely in only the first trap, ST1, ($99.5 \pm 0.3\%$ for 6 consecutive measurements) and less than 1 percent of Hg was on the second trap ST2. Furthermore, the ST2 signal was similar to the Hg blank in analytical trap and represents the trap blank. The results showed the Au-coated sand (*ca.* 0.1 g) had complete trapping efficiencies at a constant flow of 1 L min⁻¹ under the sampling time of 1 h. Sample Hg⁰ in Taipei airs ranged from 4.4 to 5.6 ng m⁻³ ($n = 6$) measured in May 14 2003 through these experiments.

The spiking experiments were performed from May 15 to 16, 2003. For this experiment, the recovery was calculated as the ratio of measured to spiked Hg, with the measured Hg corrected for ambient air concentration from a simultaneous unspiked sample. The results show that high trap recovery (Averaged: $107 \pm 6\%$ during 6 different measurements) was obtained for sampling intervals from 10 min to 4 h ($n = 6$) at air flow rate of 1 L min⁻¹ (Fig. 3a). Additionally, an excellent correlation of found sample Hg mass to the sampling time was observed with a linear relationship as Hg mass (pg) = $4.53 (\pm 0.04) \times$ sampling time (min) ($r^2 = 0.999$, $n = 6$, Fig. 3b). The tests confirmed that Au-coated sand traps Hg⁰ well in this application with accurate determination of GEM. The GEM concentrations measured during those experiments of May 15–16 2003 ranged from 3.9 to 6.3 ng m⁻³ ($n = 6$).

Collection efficiency. Collection efficiency of the Au-sand traps was examined for the different sampling intervals. The experiment for complete trapping of GEM was tested by analysis of the atmospheric ambient air, containing 4–7 ng m⁻³ of GEM. The sampling rate was about 1 L min⁻¹ with time intervals of 5 min, 30 min, 1 h, 2, 5, 10, 14, 22 h. The results, presented in Fig. 4, show that complete trapping of GEM was achieved when total integration time was less than 10 h at an air flow of 1 L min⁻¹. *i.e.*, $\sim 99\%$ of all Hg in the ambient air was trapped in the first sample trap, ST1. For the longest integration time of 22 h, only 86% was observed in the trapping of ST1. Thus, full trapping can be achieved with sample volumes < 600 L (*i.e.*, by multiplying sampling rate of 1 L min⁻¹ to sampling time of 10 h) with the air Hg⁰ concentration of ~ 5 ng m⁻³, suggesting a trapping of 3 ng Hg⁰ (~ 0.1 g Au sand). Therefore, the sampling strategy can be modified according to the trap capacity estimated.

Evaluation of analytical performance. The analytical performance of the GEMA under the optimum working conditions was evaluated in terms of blank, reproducibility, recoveries and detection limit. Low blank values were obtained from the second trap blank (ST2) of in-series one channel analysis and the reference blank (AT3) performed in laboratory and field trip (≤ 1 pg, $n = 50$). Excellent reproducibility (relative standard deviation (r.s.d.) $\leq 5\%$) was achieved during the analyses of spiked gas standard ($n = 50$) and real samples ($n = 6$). High recoveries of

Fig. 3 (a) Efficiency test of the Au-sand trap for the GEM analysis under the different sampling intervals from 10 min to 4 h ($n = 6$) at the constant air pumping flow (1 L min^{-1}); (b) A good correlation of found sample Hg mass to the sampling time was observed. Spiked Hg⁰ denotes the 20 μL of Hg⁰-saturated air at the constant temperature ca $24.5\sim 24.6^\circ\text{C}$ injected the ST1. Errors are $\pm 1 \text{ SD}$ ($N = 3$).

Fig. 4 Effects of sampling times on the collection efficiency for trap capacity test of GEMA at a constant air pumping flow (1 L min^{-1}) with the averaged air Hg⁰ concentration of $\sim 5 \text{ ng m}^{-3}$. All the data for ST1 and ST2 were presented net values which all were substituted the blank obtained from AT3, respectively.

GEM obtained from spiked gas standard were demonstrated in the discussion section on trap efficiencies. The results demonstrate that this method is accurate and precise.

Calibration of the GEMA was performed with a range of 5 duplicate injections of Hg⁰-saturated vapor from 10 to 500 pg, displaying a linear relationship (r^2 0.995–0.999). Good precision (r.s.d. $\leq 5\%$, $n = 50$) in the slopes of calibration curves was obtained during March to December 2003 for laboratory test and 4 SEATS cruises. The method detection limit, defined as three times the standard deviation of the procedural blank, was about 0.1 ng m^{-3} at a constant flow of 1 L min^{-1} for the sampling time of 10 min.

Validation of method. The proposed method was validated by analysis of the NTUIO atmospheric samples with different levels of GEM. Results, as shown in Fig. 5, for the GEMA were in good agreement with the traditional manual methods. Those traditional manual measurements were conducted with attention to the precautions described in the introduction. The excellent agreement of the GEM concentrations indicates that the GEMA is a robust device for reliable examining and monitoring of GEM in natural air samples.

Advantages of the GEMA. The analytical performance of the GEMA is briefly summarized in Table 1, being comparable to that of a commercial Tekran 2537A Mercury Vapor Analyzer (www.tekran.com) as a worldwide standard for ambient mercury measurement. The GEMA can therefore be considered as an excellent approach for determining GEM in ambient air. Specific characteristics of the GEMA with respect to the manifold design and functionality are further worth of mentioning. First, manifold design of the GEMA is versatile and can be modified according to environmental application. The GEMA can be extended from dual channel operations to three or more channels *via* the use of multiple injection valves. Second, the GEMA device could be expanded by adding additional sorbent traps as well. Through a combination of multiple traps and flow paths, the GEMA can be developed for detecting reactive gaseous, particulate and potential organo-Hg, in addition to GEM,

Fig. 5 Comparison of GEM measured by GEMA with those by manual sampling with a linear regression relationship. All the data were collected with the following operating conditions: 2–3 h sampling and 1 L min^{-1} of sample gas flow (1 : 1 dotted line plotted for reference). Errors are $\pm 1 \text{ SD}$ ($n = 3$).

Table 1 Figures of merit of the GEMA

Characteristic items	GEMA
Potential Hg speciation	Reactive gaseous, particulate and organo-Hg
Trap efficiency (%)	~100
Accuracy (%)	107 ± 6
Absolute detection limit (pg)	1
Method detection limit/ng m ⁻³	0.1 (10 L of sample)
Calibration range	Wide dynamic (pg to ng)
R. square (n = 5)	≥ 0.995
Reproducibility (%)	≤ 5
Flow rate/L min ⁻¹	0.2~1.5
Sample cycle time	5 min ~ 24 h
Memory effect at 3 ng Hg (°)	No
Interference from water vapor	No
Versatile/Practical Feasibility	Multi-trap applications, multifunctional Hg speciation analysis

together in one manifold. For example, the various species can be collected in series on different preconcentrating surfaces (“reactive” gaseous Hg on a KCl denuder, particulates on a quartz wool plug, and organo-Hg on Tenax), with each collected isolated from the rest by switching valves.¹⁹ Additionally, the GEMA, designed for multifunctional Hg speciation analysis, can be applied to the polluted areas such as high-intensity industries and landfills. The system could be readily portable for operation in the laboratory or field and is similar to the one proposed by Tseng *et al.*³² In short, additional multi-trap applications and specific practicability seem like the good choices for the GEMA as an alternative in Hg-species measurements in ambient air.

Fig. 6 Summary of (a) monthly wind field data in 2003 (thin arrow) provided by the ECMWF (European Centre for Medium-Range Weather Forecasts) and real-time averaged wind data collected during the cruises (wide arrow) and (b) averaged GEM data in spring (May), summer (August), Fall (October) and winter (December) 2003 over the northern SCS and selected data in Taipei urban airs. Errors are ± 1 SD.

Environmental: GEM distributions and sources

We have used the GEMA during several sampling campaigns as part of the SEATS program to examine atmospheric Hg cycling over the SCS. GEM data from May to December 2003 surveys with wind field data are presented here (Fig. 6a,b). Surface air samples between the northern SCS and the SEATS station were collected during the cruise track. The seasonal distributions of GEM varied significantly over the northern SCS. The concentrations in spring, summer, autumn and winter averaged 2.2 ± 0.5 (mean ± standard deviation, $n = 20$), 2.7 ± 0.8 ($n = 42$),

Fig. 7 Results of the HYSPLIT model 4-day backward trajectory analysis started at 0400UTC (1200LST), in (a) summer (August 7), and (b) winter (December 17) at altitudes of 100, 500, 1000 m at the SEATS station in northern SCS. The upper and lower panels in each plot display horizontal and vertical motion. Symbols denote the location of the air parcel every 6 h.

4.0 ± 1.0 ($n = 30$), and 6.9 ± 1.0 ($n = 38$) ng m^{-3} , respectively. The values in spring and summer are almost two times lower than those observed in Taipei urban air during the same season (Fig. 6b). The much more elevated GEM concentrations in Taipei urban air were presumably the result of locally human-induced Hg emissions. Seasonal GEM concentrations in the air of the northern SCS were higher than global background values ($1.5\sim 2 \text{ ng m}^{-3}$) at the same latitude in the Pacific Ocean.^{6,12,33} Distribution patterns show GEM maxima in winter (December) associated with northeast wind and lower in late spring (May) and summer (August) with southwest wind. These data suggest that the seasonal variation of GEM is related to the supply and source of GEM controlled by East Asian monsoons with the prevailing northeast wind in winter and southwest in summer.

In order to identify the GEM sources and examine the air transport paths, air mass backward trajectory analysis was performed by using the HYSPLIT model of NOAA.³⁴ Four-day backward air trajectories at three altitudes of 100, 500 and 1000 m starting at the SEATS station in summer and winter are given in Fig. 7a,b, respectively. The three-level trajectories on August 7 all came from the northeastern Indian Ocean (Fig. 7a). The GEM concentrations measured at SEATS from this trajectory tended to be lower than the average. This suggests lower concentrations associated with clean oceanic air, as well as little emissions from Indochina. In winter, the backward trajectory analysis shows the air parcels of December 17 came from northern China and then passed through northern Shanghai, both highly polluted areas in northeastern China (Fig. 7b). The GEM can be expected to be elevated as we observed in Fig. 6b. Thus, seasonal GEM changes over the northern SCS are apparently determined by the origin of the air masses and the sources of Hg within those regions, as governed by the East Asian monsoons.

Conclusions

A novel and robust gaseous elemental mercury analyzer (GEMA) has been developed to investigate atmospheric GEM in ambient airs. This approach provides ease of operation and high analytical performance and is suitable for field use. The GEMA allows the reliable GEM determination in ambient air samples with high recoveries of $107 \pm 6\%$ and a low detection limit of 0.1 ng m^{-3} . Besides, our studies of GEM in the northern SCS reveal the prominent role of GEM in examining the environmental Hg pollution in marginal seas of East Asia surrounding China. The elevated GEM could be caused *via* long range atmospheric transportation of Hg^0 , especially from anthropogenic emissions of China to the SCS. High frequency sampling and analysis is furthermore essential for future investigations into the dynamic distribution and source attribution of GEM in important ocean marginal regions. Future development of the GEMA can include computer-assisted automation to fulfil the field need of increasing spatial and temporal resolution of GEM patterns in natural airs.

Acknowledgements

We thank P.W. Chiang, and C.-S. Liu from Institute of Oceanography, National Taiwan University, and the officers and the

crew of the R/V Ocean Research I and also the Reviewers for their constructive and detailed suggestions. This work was supported by National Science Council, Taiwan through grants NSC 97-2745-M-002-001- and 98-2611-M-002-013- and from the Academia Sinica, Taiwan through a thematic research grant titled "Atmospheric Forcing on Ocean Biogeochemistry (AFOB)" and from the National Taiwan University through an Industrial-Academic Cooperation grant of the "Aim for Top University Project".

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