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Continuous Flow−Double Purge and Trap Method for Preconcentrating Mercury in Large Volumes of Seawater for Stable Isotope Analysis

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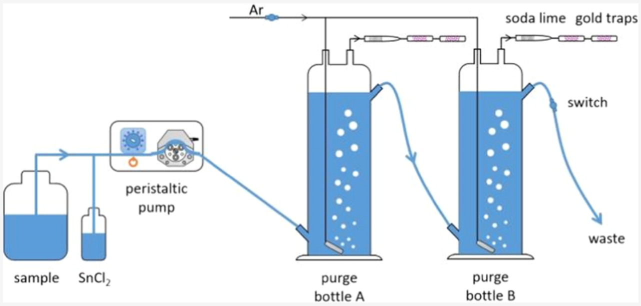

ABSTRACT: Mercury (Hg) isotopes provide a useful tool to understand Hg sources and processes in the environment. The Hg isotopic composition of seawater remains poorly constrained due to the lack of an efficient method to process large volumes of low-Hg-concentration seawater samples. Here, we develop a continuous flow−double purge and trap device for the in situ preconcentration of Hg in seawater. This method yielded a good Hg recovery of 91.7 ± 3.3% (n = 4, 1SD) for spiked seawater samples and gave reasonably similar Hg isotope ratios of NIST 8610, indicating a limited matrix effect and limited Hg isotope fractionation during processing of seawater. NIST 8610 δ^{202}Hg (−0.55 ± 0.09‰, n = 4, 1SD) and Δ^{199}Hg (0.07 ± 0.02‰, n = 4, 1SD) were similar to previously published data. The method was successfully applied to seawater collected from the Xiamen Bay and the South China Sea. The seawater samples showed a Hg recovery of 91.6 ± 5.4% (n = 12, 1SD). Seawater Δ^{199}Hg (−0.04 ± 0.05‰, n = 7, 1SD) in the Xiamen Bay was different from seawater Δ^{199}Hg (0.05 ± 0.07‰, n = 5, 1SD) in the South China Sea, which implies distinct Hg sources to coastal and open ocean areas and highlights the robustness of our method in understanding the Hg isotopic composition of seawater.

■ INTRODUCTION

Mercury (Hg) is a heavy metal pollutant that is highly toxic, strongly bioaccumulative, and highly volatile.[1] The ocean, as the largest Hg pool in the surface environment,[2] plays a critical role in the global Hg biogeochemical cycle. Natural stable isotopes of Hg (^{196}Hg, $^{198-202}$Hg, and ^{204}Hg) can provide important insights into the biogeochemical fate of Hg. Biogeochemical processes often trigger Hg isotope mass-dependent fractionation (MDF, reported as δ^{202}Hg).[3−5] Only a few specific reactions (e.g., photochemical demethylation,[6] abiotic Hg(II) photoreduction,[7] Hg(II) dark reduction,[8] liquid Hg(0) evaporation[9]) can induce mass-independent fractionation (MIF, reported as Δ^{199}Hg) of odd-mass Hg isotopes. Large variations of as much as ∼10‰ for both δ^{202}Hg and Δ^{199}Hg have been observed in environmental samples (e.g., soil, sediment, water, atmosphere, and biota),[3] making Hg isotopes a useful tool in tracing Hg sources and pathways in the environment. Gaseous Hg(0) photo-oxidation can induce MIF of even-mass Hg isotopes (reported as Δ^{200}Hg).[10−12] The pronounced Δ^{200}Hg signals were first observed in precipitation and atmospheric gaseous Hg.[13,14] Now, the anomalous isotope fractionation of even-mass Hg isotopes has mainly been observed in atmospheric-related samples.[15,16]

The Hg isotopic composition of seawater is still poorly constrained. Although recent studies documented a distinct Hg isotopic composition of particulate Hg in seawater in the North Pacific Ocean (δ^{202}Hg: −0.12 ± 0.26‰; Δ^{199}Hg: 0.16 ± 0.18‰; n = 12, 2SD),[17] the Atlantic Ocean (δ^{202}Hg: −0.61‰; Δ^{199}Hg: −0.21‰),[15] the Mediterranean Sea (δ^{202}Hg: −0.22‰; Δ^{199}Hg: −0.06‰),[15] and coastal areas in the East China Sea (δ^{202}Hg: −1.53‰ to −0.30‰; Δ^{199}Hg: −0.20‰ to −0.11‰),[18] the total Hg isotopic composition of seawater remains rarely studied.[15] The low Hg concentrations in seawater,[19−22] typically ranging from 10^{-2} to 10 ng/L, present a challenge to measuring the Hg isotopic composition directly. Time-intensive procedures are required for preconcentrating sufficient amounts of Hg (typically >0.5 ng/mL) from large volumes of seawater for Hg isotope analysis. High Hg recoveries (typically >90%) are also required during Hg

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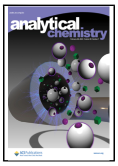

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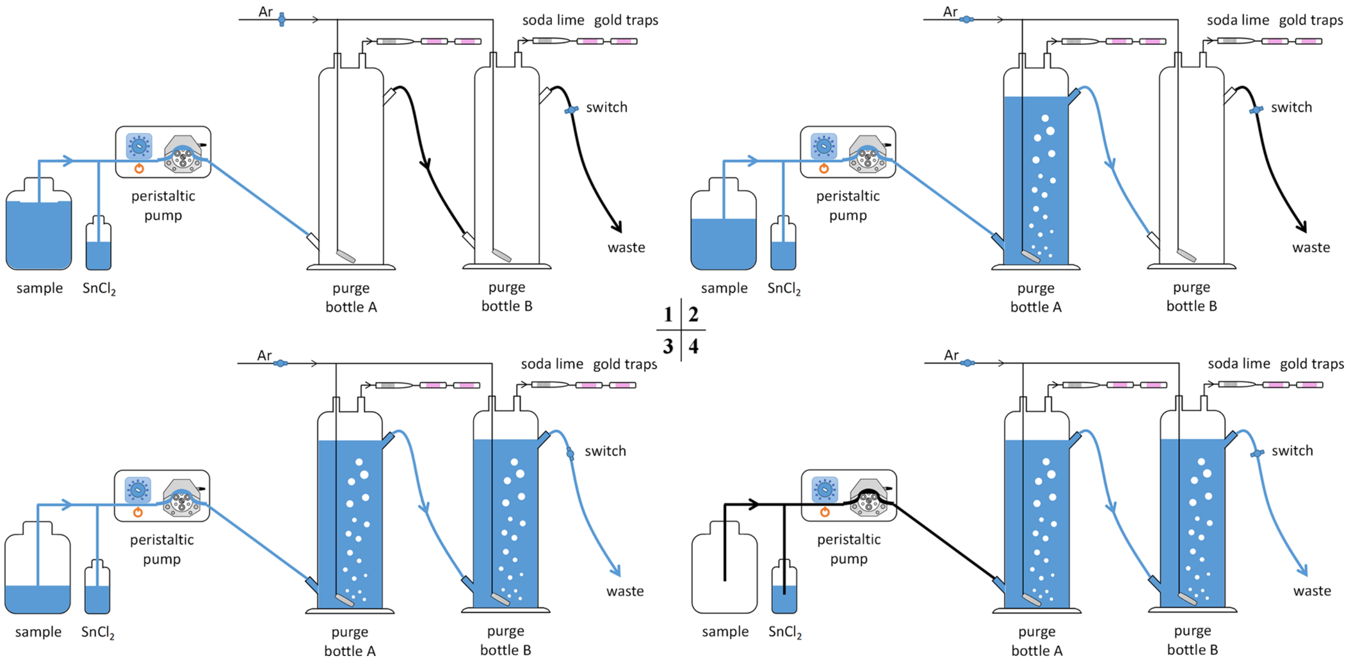

Figure 1. Schematic diagram and steps of the continuous flow–double purge and trap method.

preconcentration; however, this task is challenging for seawaters due to their low concentrations and complex matrices (e.g., high salinity and the presence of organic matter).

Three methods have been developed to preconcentrate seawater Hg for isotope analysis, including the chromatographic method,[23,24] the purge and trap method,[25] and the coprecipitation method.[26] The chromatographic method is largely affected by salinity; in particular, high iodine ion concentrations result in a lower efficiency of Hg preconcentration.[16] The coprecipitation method gained acceptable results in the laboratory but aimed at collecting Hg(II), so the method is unsuitable for preconcentration of dissolved gaseous Hg in seawater. Besides, in field applications, the pretreatment of coastal seawater using the coprecipitation method often gave recoveries of >110% (112–128%).[26] The purge and trap method yielded reasonable Hg isotope results, but it is inconvenient as it requires large bottles and sufficient time to collect enough seawater (typically several L) for subsequent laboratory pretreatment.[27,28] The traditional purge and trap method may be improved with the goal of time-saving by preconcentrating seawater Hg in the field. To meet this goal, here, we developed the continuous flow–double purge and trap method to preconcentrate Hg from large volumes of seawater for Hg isotope analysis.

■ EXPERIMENTAL METHODS

Materials and Reagents. All solutions and reagents were prepared with ultrapure water (UPW, 18.2 MΩ·cm). Ultrapure acids (HCl and HNO_3) were used in all experiments. Glass bottles, quartz tubes, and Teflon vessels were soaked in 20% (v/v) HCl overnight and rinsed three times with UPW, then filled with 5% (v/v) HCl for 6–8 h in 120 °C followed by three times rinse with UPW. The 20 L fluorinated polyethylene (FLPE) carboys, used for the collection and storage of seawater samples, were cleaned following a standard procedure.[29] Briefly, the FLPE carboys were rinsed three times with UPW, filled with Citranox solution for 6 d followed by three times rinse with UPW, filled with 10% (v/v) HCl for 6 days followed by three times rinse with UPW, and filled with 0.5% (v/v) BrCl followed by three times rinse with 0.1% (v/v) HCl and three times rinse with UPW. BrCl, $NH_2OH{\cdot}HCl$, and $SnCl_2$ solutions were prepared following the USEPA Method 1631. NIST 3133 and NIST 8610 Hg standard solutions were employed for method establishment. The trapping solution used for Hg preconcentration contained 25% (v/v) acid mixture (HCl/BrCl = 1:2, v/v).

Continuous Flow–Double Purge and Trap Method. Seawater collected from the West Pacific Ocean was filtered using PTFE membranes (0.22 μm), prior to being used for method establishment. Five liters of this filtered seawater, which has a Hg concentration of ~0.10 ng/L, was spiked with NIST 8610 at a Hg mass of 16–20 ng. The Hg-spiked seawater was oxidized with 0.5% (v/v) BrCl for at least 12 h, neutralized by approximately 10–12 mL of 30% (w/v) $NH_2OH{\cdot}HCl$ for 5 min until the yellow color disappeared,[30] and prepared using the continuous flow–double purge and trap method for Hg preconcentration. The schematic diagram of the method is illustrated in Figure 1. The purge bottles were made of quartz glass (height: 45 cm, diameter: 10 cm) and could hold a practical liquid volume of approximately 2 L. Argon gas, with varying flow rates for purge bottles A (400–1000 mL/min) and B (300–400 mL/min), was used to purge Hg from seawater. The continuous flow–double purge and trap method consisted of four steps. Briefly, (1) the seawater (125–385 mL/min) was continually pumped along with $SnCl_2$ solutions (0.3–1.0 mL/min) at varying rates, allowing well mixing prior to being delivered into purge bottles A and B, which were linked together to ensure a sufficient reduction of Hg from seawater. (2) Argon gas started purging solutions in purge bottle A since the solutions were pumped into purge bottle A. The switch was kept closed in case the gas flowed out from the waste outlet. (3) The switch was turned on when purge bottle B was full of seawater to ensure a continuous flow of solutions and to allow the extra seawater to be drained out to waste. (4) The switch was turned off and the solutions were purged for

Table 1. Information of Seawater Samples in the Xiamen Bay and the South China Sea

sample ID	location	date	long. (N)	lat. (E)	volume (L)	Hg (ng/L)	recovery (%)	δ^{202}Hg (‰)	Δ^{199}Hg (‰)	Δ^{200}Hg (‰)	Δ^{201}Hg (‰)
XB01	Xiamen Bay	19/05/21	24.573	118.133	14	0.71	91.1	−0.37	−0.03	0.03	−0.01
XB02	Xiamen Bay	19/05/21	24.516	118.220	15	0.84	85.7	−0.37	−0.07	0.01	−0.06
XB03	Xiamen Bay	19/05/21	24.519	118.294	10	1.34	89.0	−0.59	0.02	−0.02	0.03
XB04	Xiamen Bay	19/05/21	24.466	118.213	11	0.91	89.9	−0.44	−0.04	0.00	−0.07
XB05	Xiamen Bay	19/05/21	24.432	118.171	10	1.95	90.1	−0.62	−0.11	0.02	−0.02
D-XB03	Xiamen Bay	19/05/21	24.519	118.294	9	1.23	91.6	−0.70	0.01	0.01	0.01
D-XB05	Xiamen Bay	19/05/21	24.432	118.171	7	1.40	100.9	−0.72	−0.09	0.01	−0.08
SCS01	South China Sea	28/07/21	18.000	112.000	25	0.12	81.3	−0.76	0.13	0.04	0.09
SCS02	South China Sea	14/08/21	14.000	116.000	15	0.39	90.1	−0.77	0.06	0.07	−0.01
SCS03	South China Sea	08/08/21	12.000	112.000	20	0.19	97.4	−0.55	−0.05	−0.01	−0.06
SCS04	South China Sea	30/07/21	18.000	116.000	20	0.11	97.3	−1.05	0.10	−0.05	0.12
SCS05	South China Sea	23/08/21	18.000	119.000	20	0.21	95.2	−0.39	0.02	0.01	−0.01

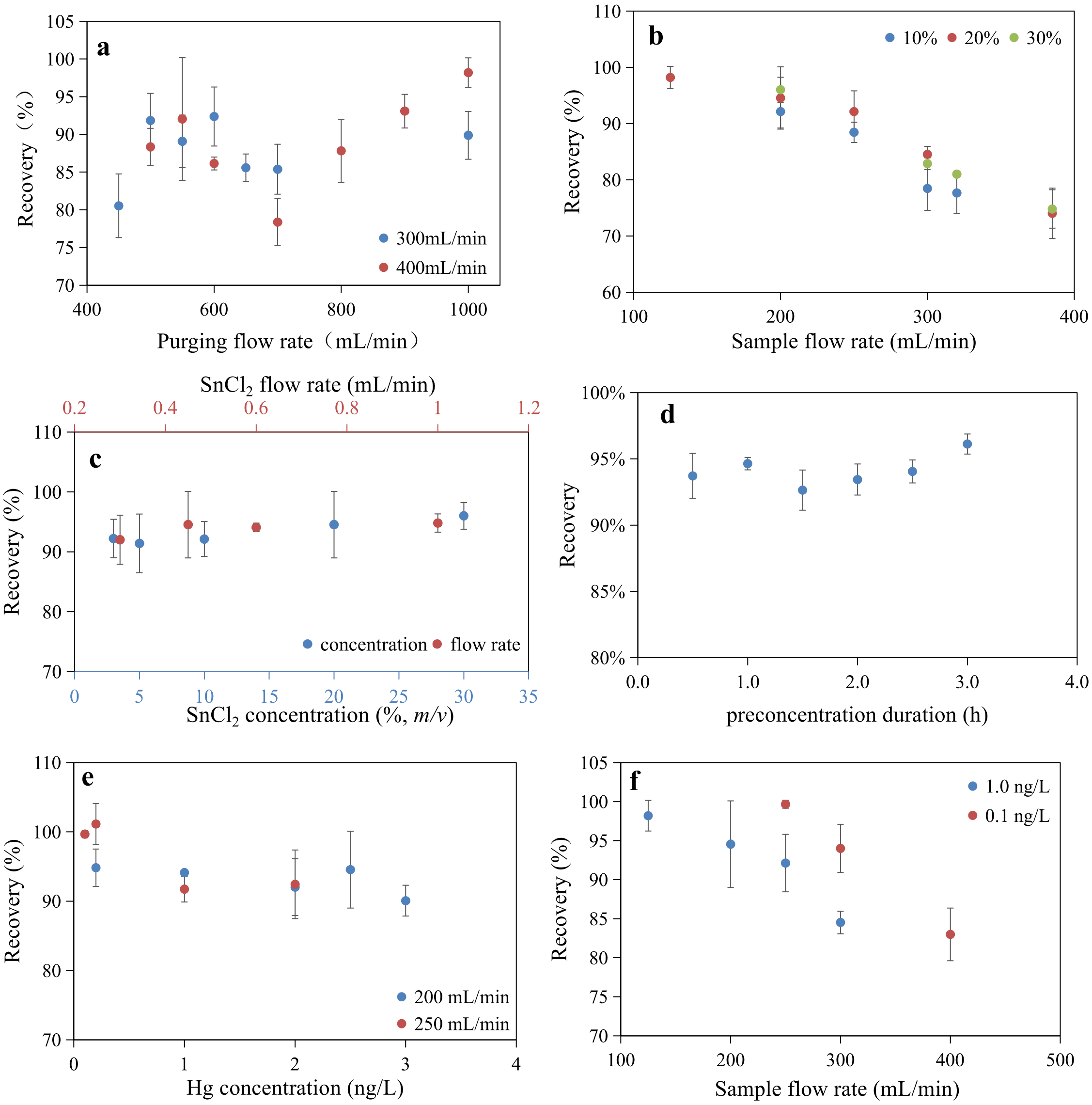

Figure 2. Results of parameter optimization. (a) Hg recoveries in different purging flow rates (the *X*-axis shows the purging flow rates of purge bottle A and the legend shows the purging flow rates of purge bottle B). (b) Hg recoveries in different sample flow rates (the legend shows the SnCl$_2$ concentrations). (c) Hg recoveries in different SnCl$_2$ concentrations and SnCl$_2$ flow rates. (d) Hg recoveries during the process of preconcentration of 40 L samples. (e) Hg recoveries in different Hg concentrations (the legend shows the sample flow rates). (f) Hg recoveries of samples with 0.1 and 1.0 ng/L in different sample flow rates. The error bars represent 1SD and $n \geq 3$.

another 20 min once all of the sample was pumped into the purge bottles. Gold traps, in connection with soda lime tubes in their front, were used to collect the released Hg from the seawater. The soda lime tubes were replaced every 1 to 2 h to avoid being fouled by aerosols laden with saline moisture. The gold traps were then prepared by thermal desorption at 450–500 °C, which transferred the trapped Hg into 5 mL of 25% (v/v) acid mixture (HCl/BrCl = 1:2, v/v) by purified argon carrier gas (25 mL/min).[25] The trapping solutions were kept in a refrigerator (4 °C) in the dark until analysis.

Sample Collection and Pretreatment. To test the effectiveness of our method, seawater samples were collected from the Xiamen Bay, China and the South China Sea, using the precleaned 20 L FLPE carboys. The sampling information is given in Table 1. The collected samples were pretreated in a class-100 clean room. The pretreatment includes filtration (0.22 μm, PTFE membrane/0.2 μm, PES capsule filter), BrCl oxidation, and Hg preconcentration using our method.

Hg Concentration and Isotopic Composition Analysis. Hg concentrations of all solutions were measured following the USEPA Method 1631, using cold-vapor atomic fluorescence spectroscopy (Model III, Brooks Rand Lab). The preconcentration efficiency was evaluated by Hg recovery, based on Hg concentrations before and after preconcentration. The standard curve range was 10–1000 pg and yielded a regression line of $r^2 > 0.999$. The long-term precision of Hg concentrations was estimated by calculating the relative standard deviation (RSD) of 200 pg, and the average RSD value was 6.6% (n = 26). The method detection limit was 5.9 pg. The procedure blank of the developed method was obtained by using 5 L of UPW instead of sample solution; it was done before and after sample preconcentration. The procedure blank gave an average value of 20.5 ± 1.2 pg/mL (n = 12, 1SD) and is lower than 3% of that in the trapping solutions.

Hg isotope ratios were determined using the Neptune Plus multicollector inductively coupled plasma mass spectrometer (Thermo Finnigan, Germany) at the Institute of Geochemistry, Chinese Academy of Sciences, following previous methods.[25,31,32] Following the convention recommended by Blum and Bergquist,[33] Hg isotopic compositions are reported in δ and Δ in units of per mil to represent MDF and MIF, respectively:

$$\delta^{xxx}\mathrm{Hg}_{\mathrm{sample}} = \left[\frac{({}^{xxx}\mathrm{Hg}_{\mathrm{sample}}/{}^{198}\mathrm{Hg}_{\mathrm{sample}})}{({}^{xxx}\mathrm{Hg}_{\mathrm{NIST3133}}/{}^{198}\mathrm{Hg}_{\mathrm{NIST3133}})} - 1\right] \times 1000 \tag{1}$$

$$\Delta^{xxx}\mathrm{Hg} = \delta^{xxx}\mathrm{Hg} - \beta \times \delta^{202}\mathrm{Hg} \tag{2}$$

where xxx = 199, 200, 201, and 202. The mass-dependent scaling factor β for ^{199}Hg, ^{200}Hg, and ^{201}Hg is 0.2520, 0.5024, and 0.7520, respectively. NIST 3177 was repeatedly measured, which yielded values of −0.51 ± 0.14‰ and −0.02 ± 0.05‰ (n = 20, 2SD) for δ^{202}Hg and Δ^{199}Hg, respectively, in agreement with reported results.[26,34,35] The uncertainty of the Hg isotopic composition of samples was reported as 2SD of NIST 3177.

■ RESULTS AND DISCUSSION

Method Optimization. The available purge and trap method for Hg concentration analysis suggests that the purging flow rate should not be more than 1000 mL/min, and an optimal rate of 150–500 mL/min was commonly used.[36] By setting the sample flow rate at 125 mL/min and the $SnCl_2$ (20%, v/v) flow rate at 0.45 mL/min, varying argon purging flow rates (400 to 1000 mL/min) for bottles A and B were tested in this study. We found that to ensure a consistent introduction of the samples, the purge gas flow rate for purge bottle B should be lower than that for purge bottle A. The system produced inconsistent recoveries for the lower purging flow rate (<700 mL/min) in purge bottle A, and the Hg recovery increased from 78.4 to 98.2% with the increasing purging flow rate (700–1000 mL/min) in purge bottle A (Figure 2a). The Hg recovery reached the highest (104.9%) when the purging flow rate was 400 mL/min for purge bottle B. Thus, in our method, the optimal purging flow rates were set to 1000 and 400 mL/min for purge bottles A and B, respectively, and the recovery was 98.2 ± 2.0% (n = 3, 1SD). Overall, bottle A released twice as much Hg as bottle B, and both were stable throughout the process.

A higher sample flow rate can save time for the pretreatment of samples but may cause a low preconcentration efficiency due to the insufficient mix of the sample and $SnCl_2$ and a short purging time. That is to say, purging time varies with the sample flow rate. For example, at a sample flow rate of 250 mL/min for 5 L seawater, seawater samples are effectively purged for 16 min during the flow-through process, and then the last ∼4 L is retained within the purge bottles and purged for an additional 20 min. By setting the purging flow rates to optimal values (1000 and 400 mL/min for bottles A and B, respectively) and the $SnCl_2$ flow rate (20%, v/v) at 0.45 mL/min, we tested the preconcentration efficiency at varying sample flow rates (125, 200, 250, 300, 320, and 385 mL/min). We obtained Hg recoveries (94.2 ± 4.7%, n = 17, 1SD) at sample flow rates ranging from 125 to 250 mL/min but poor Hg recoveries at sample flow rates higher than 250 mL/min (Figure 2b). Although even lower sample flow rates (<125 mL/min) could potentially provide more consistent and reliable recoveries, it makes no sense as the objective of this method was to preconcentrate Hg in larger volume samples in a shorter time. Therefore, in our method, we set 250 mL/min as the sample flow rate, as this still provided acceptable Hg recoveries (92.1 ± 3.7%, n = 7, 1SD) and will obtain a sample preparation time that is 2–6 times shorter than that obtained by the traditional purge and trap method[27,28] and the chromatographic method[23,24] (Table 2).

We also conducted a series of orthogonal experiments with varying $SnCl_2$ concentrations (10, 20, 30%) and sample flow rates (200 to 400 mL/min) to figure out the reason for the low preconcentration efficiency for the sample flow rates higher than 250 mL/min. As seen in Figure 2b, no significant difference in recoveries was observed between 20 and 30% (v/v) $SnCl_2$ concentration at the same sample flow rate, indicating that a short purging time, instead of the insufficient mix of the sample and $SnCl_2$, was the primary cause of the low efficiency for the sample flow rates higher than 250 mL/min.

The lower consumption of reagents could decrease the method blank. By setting the purging flow rates (1000 and 400 mL/min for bottles A and B, respectively) and sample flow rates (200 mL/min) to optimal values, experiments were performed to optimize the flow rates of $SnCl_2$ (20%, v/v). The Hg recoveries varied in the range of 94.1–94.8% at a $SnCl_2$ flow rate higher than 0.45 mL/min (Figure 2c), and no significant difference was observed ($p > 0.05$, one-way ANOVA). Thus, the optimal $SnCl_2$ flow rate was set to 0.45

mL/min. Obviously, both the dosage of $SnCl_2$ and the consumption of argon carrier gas was less than previously reported in the traditional purge and trap method (Table 2).

Preconcentration Efficiency. Based on the optimal parameters established above, 40 L of water containing Hg spiked to 1.0 ng/L was conducted for Hg preconcentration using our method. The instantaneous Hg recovery was obtained by measuring Hg in the wastewater every 30 min. As shown in Figure 2d, this Hg-spiked sample was successfully preconcentrated within 3 h and the instantaneous Hg recovery was 94.1 ± 1.2% ($n = 5$, 1SD) during preconcentration. The preconcentration efficiency of our method was tested by measuring Hg in the trapping solution and wastewater. The results showed that only minor Hg was left in the wastewater (0.39 ± 0.14 ng, $n = 30$, 1SD), whereas Hg in the trapping solution reached 37.4 ± 0.9 ng ($n = 5$, 1SD). Therefore, on an average, <1% of Hg was lost with wastewater, and the overall trapping efficiency was >93% ($n = 6$) for this Hg-spiked sample. We also tested the preconcentration efficiency for low-Hg seawater samples. As shown in Figure 2e, testing of seawaters with Hg concentrations lower to 0.1–0.2 ng/L yielded a higher average Hg recovery (98.4 ± 3.7%, $n = 11$, 1SD) in the trapping solution. Even at a sample flow rate of 250–300 mL/min, preconcentration of a seawater sample containing 0.1 ng/L Hg yielded good Hg recoveries of 90.8–100.1% (Figure 2f). However, the Hg recovery sharply decreased to 83.0 ± 3.4% ($n = 3$, 1SD) when the sample flow rate increased to 400 mL/min. Thus, this method has a higher preconcentration efficiency and a relatively shorter preconcentration duration for samples with lower Hg concentrations, implying the potential use of the method onboard during long-term ocean cruises.

Limited Matrix Effect. The matrix spike experiment was carried out by preparing 5 L of seawater (which has a background Hg concentration of 0.1 ng/L) spiked with 20 ng of Hg derived from the NIST 8610 Hg standard solution, using our method at a sample flow rate of 250 mL/min. As shown in Table 3, measurement of Hg-preconcentrated solutions yielded a Hg recovery of 91.7 ± 3.3%, δ^{202}Hg of −0.55 ± 0.09‰, Δ^{199}Hg of 0.07 ± 0.02‰, Δ^{200}Hg of 0.00 ± 0.04‰, and Δ^{201}Hg of 0.01 ± 0.07‰ ($n = 4$, 1SD), mostly consistent with the reference values of NIST 8610.[33]

Hg Isotopic Composition of Natural Seawater Samples. Our method was applied to the pretreatment of seawater samples collected from the Xiamen Bay and the South China Sea. The Hg concentrations are 0.71 to 2.00 ng/L ($n = 7$) for seawaters collected from the Xiamen Bay and 0.11 to 0.39 ng/L ($n = 5$) for those collected from the South China Sea. Processing of these seawaters yielded a Hg recovery of 91.6 ± 5.4% ($n = 12$, 1SD) at a sample flow rate of 250 mL/min. It should be noted that one sample yielded a relatively lower recovery (81.3%) compared to the optimization experiments. We suggest that the sample flow rate could be set lower to improve results. The Hg isotopic compositions of seawaters studied are illustrated in Figure 3. Specifically, seawaters from the Xiamen Bay show δ^{202}Hg and Δ^{199}Hg values of −0.54 ± 0.15‰ and −0.04 ± 0.05‰ ($n = 7$, 1SD), respectively, whereas those from the South China Sea show δ^{202}Hg and Δ^{199}Hg values of −0.70 ± 0.25‰ and 0.05 ± 0.07‰ ($n = 5$, 1SD), respectively. Seawaters from both areas show near-zero Δ^{200}Hg values of 0.01 ± 0.04‰. Overall, results of this study are within previous results on seawaters,[15] further validating the usefulness of our method. The distinct

Table 2. Comparisons of Different Hg Preconcentration Methods for Seawater

methods	procedure	trapping solutions	sample volume	reagent dosage	gas flow rate	method blank	preconcentration duration	Hg forms	refs
chromatographic method	a. purging to remove iodine; b. oxidized by BrCl and neutralized with $NH_2OH{\cdot}HCl$; c. preconcentration through the anion exchange column; d. elution with L-cysteine and sodium citrate dihydrate	0.05% L-cysteine and 0.5% BrCl solution	1–22 L	20 mL 0.05% L-cysteine	–	20 ± 11 pg Hg in 0.50 L sample	8 h purging +1 h for 2.5 L sample	THg, DHg	23, 24
traditional purge and trap method	a. oxidized by BrCl and neutralized with $NH_2OH{\cdot}HCl$; b. reduced with $SnCl_2$ and purging; c. trapped by gold traps and thermally desorbed; d. preconcentrated in trapping solutions	$KMnO_4$ solution	2 L	15 mL 3% (m/v) $SnCl_2$	0.3 L/min	–	75 min for 2 L sample	THg, DHg	25
		40% reverse aqua regia (2HNO_3/1HCl, v/v)	2.5 L	25 mL 20% (m/v) $SnCl_2$	1.6 L/min	125 pg Hg for 0.5% BrCl in 2.5 L sample	1 h for 2.5 L sample	THg	28
			10 L	30 mL 20% (m/v) $SnCl_2$	4.0 L/min	350 ± 50 pg Hg for 40 L sample	2 h for 10 L sample	RHg, DGM	27
coprecipitation method	a. oxidized by BrCl; b. bufferred with $CuSO_4$; c. coprecipitated with Na_2S and $CuSO_4$; d. filtration and digestion	Lefort aqua regia (3HNO_3/1HCl, *v*/*v*)	10 L	1.5 mL 0.5 M $CuSO_4$ and 1.0 mL 0.5 M Na_2S	–	103 pg Hg for 10 L sample	20 min for 10 L sample + filtration	DHg	26
continuous flow–double purge and trap method	a. oxidized by BrCl and neutralized with $NH_2OH{\cdot}HCl$; b. continuous flow, reduced with $SnCl_2$ and double purging; c. trapped by gold traps and thermally desorbed; d. preconcentrated in trapping solutions	25% HCl/BrCl (1:2, v/v)	5–40 L	0.45 mL/min 20% (m/v) $SnCl_2$ (18 mL for 10 L sample)	1.4 L/min	102 ± 6.0 pg Hg for 10 L sample	20–160 min for 5–40 L at a sample flow rate of 250 mL/min + 20 min final purge	THg, DHg	this study

Table 3. Results of Matrix Spike Experiments and Certified Values for NIST 8610

sample ID	seawater Hg concentration (ng/L)	seawater volume (L)	Hg addition (ng)	recovery (%)	δ^{202}Hg (‰)	Δ^{199}Hg (‰)	Δ^{200}Hg (‰)	Δ^{201}Hg (‰)
SW-1	0.10	5	16	92.1	−0.57	0.04	−0.03	−0.01
SW-2	0.10	5	20	88.5	−0.59	0.08	0.02	0.10
SW-3	0.10	5	20	96.1	−0.62	0.09	−0.04	−0.06
SW-4	0.10	5	20	90.0	−0.41	0.07	0.03	0.02
mean ± SD				91.7 ± 3.3	−0.55 ± 0.09	0.07 ± 0.02	0.00 ± 0.04	0.01 ± 0.07
NIST 8610 mean ± SD					−0.56 ± 0.03	−0.03 ± 0.02	0.00 ± 0.01	−0.04 ± 0.01

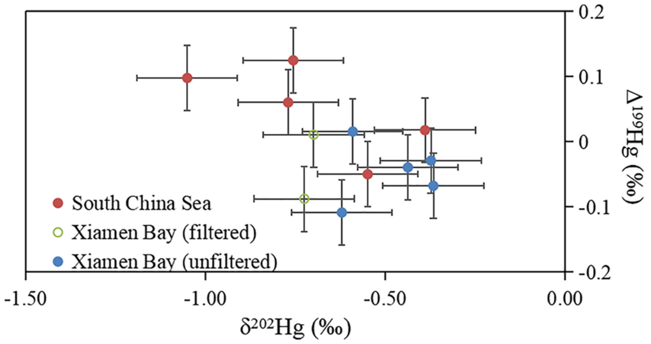

Figure 3. Hg isotopic compositions of seawater in the Xiamen Bay and the South China Sea reparation. The error bars represent 2SD.

Δ^{199}Hg values in seawaters from the study areas may be explained by different Hg sources from coastal and open ocean areas. Coastal regions receive a substantial amount of Hg from terrestrial runoff, which may explain the slightly negative Δ^{199}Hg values in the Xiamen Bay, given that terrestrial soil has negative Δ^{199}Hg values.[37,38] Open oceans receive Hg mainly through Hg(II) wet deposition, which could explain the slightly positive Δ^{199}Hg values in the South China Sea, as precipitation containing mainly Hg(II) species mainly show positive values.[39,40]

■ CONCLUSIONS

We developed a continuous flow−double purge and trap method to preconcentrate Hg from seawater for Hg isotope analysis. The method gives a good Hg recovery, limited matrix effect, and limited Hg isotope fractionation during processing of seawater with low Hg concentrations, with advantages of time-saving compared to previous methods. This method opens the possibility of measuring the Hg isotopic composition of seawater, which is of use for our further understanding of the marine Hg biogeochemical cycle. It is worth mentioning that the success of this rapid method for preconcentration of Hg at pg/L levels suggests that this method could potentially be further developed for preconcentrating dissolved gaseous Hg, which is important for understanding the air−sea exchange of volatile Hg in the open ocean. Application of our method to seawaters collected from the Xiamen Bay and the South China Sea yielded a distinct Hg isotopic composition between the two areas, which implies distinct Hg sources to coastal and open ocean areas and highlights the robustness of our method in understanding the Hg isotopic composition of seawater.

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Notes

The authors declare no competing financial interest.

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