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# Effects of mercury and thallium concentrations on high precision determination of mercury isotopic composition by Neptune Plus multiple collector inductively coupled plasma mass spectrometry†

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Thallium (Tl) has been widely used as an internal standard for mass bias correction during high precision mercury (Hg) isotope ratio measurements using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). However, a recent study by Georg and Newman indicated the potential for Hg hydride formation ( $\text{HgH}_x$ ,  $x = 1, 2$ ) during Hg isotope measurements using an X skimmer cone with a Neptune Plus MC-ICP-MS. Mercury hydride formation could result in an artificial change in  $^{205}\text{Tl}/^{203}\text{Tl}$ . Due to this observation, the applicability of using Tl as an internal standard for instrumental mass bias correction during high precision Hg isotope measurements has been questioned. In this study, using an adapted gas/liquid phase separator for Hg introduction and the NIST SRM 997 Tl standard for mass bias correction, mercury isotope measurements were performed using a Neptune Plus MC-ICP-MS. While we confirm Georg and Newman's observations, we show that Hg hydride formation is less important when Hg isotope measurements are conducted with high Tl and low Hg concentrations. With careful sample-standard bracketing (with Hg concentration matching within 10%), we demonstrate that measuring 20 to 50  $\text{ng mL}^{-1}$  of Tl and 0.5 to 3.0  $\text{ng mL}^{-1}$  of Hg, high precision Hg isotope ratio measurements are achievable. We caution researchers using other Hg inlet systems to recognize the importance of Hg and Tl concentrations and encourage the optimization of these values during their Hg isotope measurements.

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## 1. Introduction

Multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has enabled simultaneous determination of Hg's seven natural stable isotopes (196, 198, 199, 200, 201, 202 and 204).<sup>1–9</sup> Both mass dependent fractionation (MDF, reported as  $\delta$  values) and mass independent fractionation (MIF, reported as  $\Delta$  values) have been observed during a variety of chemical, physical, and biological processes. Large variations of  $\delta^{202}\text{Hg}$  ( $\sim 10\text{‰}$ ),  $\Delta^{199}\text{Hg}$  ( $\sim 10\text{‰}$ ) and  $\Delta^{200}\text{Hg}$  ( $\sim 1\text{‰}$ ) have been reported

in environmental samples.<sup>10–12</sup> Stable mercury isotopes have been successfully used as tracers to understand the sources and fates of Hg in the environment.<sup>10–12</sup>

Mercury isotope measurements have been performed by using two commercial MC-ICP-MS systems, Nu-Plasma<sup>3,7</sup> and Thermo Finnigan Neptune.<sup>1,2,4,5,8,9</sup> To enhance the ion sampling efficiency and overall sensitivity, the new generation Neptune Plus MC-ICP-MS has combined modified skimmer and sample cone geometries with an enhanced interface pumping configuration.<sup>13</sup> Compared to the H cone geometry, the X skimmer cone has been shown to result in a seven-fold increase in sensitivity for Tl, and a 10–20% increase in sensitivity for Hg.<sup>1</sup> Thus, the sample quantity needed for isotope ratio measurements can be significantly reduced. However, concerns have been recently raised by the observation of Hg hydride formation ( $\text{HgH}_x$ ) when using high-sensitivity X skimmer cones with a Neptune MC-ICP-MS equipped with the Plus upgrade.<sup>1</sup> Hg hydride formation has shown to result in increased  $^{203}\text{Tl}$  beam intensities. Due to its close isotopic mass to Hg, Tl has been widely used as an internal standard for instrumental mass bias correction of Hg isotopes<sup>1–9</sup> using the Russell equation to determine the instrumental mass bias factor ( $\beta$ ):

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$$\beta = \ln[(^{205}\text{Tl}/^{203}\text{Tl})_{\text{true}}/(^{205}\text{Tl}/^{203}\text{Tl})_{\text{measured}}]/\ln(m^{205}/m^{203}) \quad (1)$$

where  $^{205}\text{Tl}/^{203}\text{Tl}_{\text{true}}$  and  $^{205}\text{Tl}/^{203}\text{Tl}_{\text{measured}}$  are the true (mass bias corrected) ratio (2.38714) and the measured ratio of  $^{205}\text{Tl}/^{203}\text{Tl}$  for the NIST SRM 997 Tl standard, respectively; and  $m^{205}$  and  $m^{203}$  are the masses of  $^{205}\text{Tl}$  and  $^{203}\text{Tl}$ , respectively. The estimated  $\beta$  is applied to the mass bias correction of Hg isotope ratios (eqn (2)):

$$^{xxx}\text{Hg}/^{198}\text{Hg}_{\text{true}} = ^{xxx}\text{Hg}/^{198}\text{Hg}_{\text{measured}} \times (m^{xxx}/m^{198})^{\beta} \quad (2)$$

where  $^{xxx}\text{Hg}/^{198}\text{Hg}_{\text{true}}$  and  $^{xxx}\text{Hg}/^{198}\text{Hg}_{\text{measured}}$  are the true and the measured ratio of  $^{xxx}\text{Hg}/^{198}\text{Hg}$ , respectively;  $m^{xxx}$  and  $m^{198}$  are the masses of  $^{xxx}\text{Hg}$  and  $^{198}\text{Hg}$ , respectively; and xxx values are 199–204 amu. According to Georg and Newman,<sup>1</sup> the increase of  $^{203}\text{Tl}$  beam intensity due to Hg hydride formation could result in decreased  $^{205}\text{Tl}/^{203}\text{Tl}_{\text{measured}}$ , which would unavoidably cause artificial effects on the  $\beta$  (according to eqn (1)) and Hg isotope ratios (according to eqn (2)). As a result, mercury hydride formation has raised significant concerns not only to users of Neptune Plus MC-ICP-MS, but also to others using Tl for mass bias correction for Hg isotope measurements.<sup>1</sup>

In order to confirm whether the concerns of Hg hydride formation were directly applicable to our analyses, we performed a series of independent tests based on well known Hg standard solutions. It is worth noting that measurements by Georg and Newman<sup>1</sup> were mainly based on high Hg concentrations (e.g., 5, 10 and 25 ng mL<sup>-1</sup>). To our knowledge, most Hg isotope data reported to date were mainly measured at low Hg concentrations (0.5 to 5 ng mL<sup>-1</sup>).<sup>1–9</sup> Theoretically, the effects of Hg hydride formation may be reduced by measuring low Hg concentrations. To test this speculation, we performed Hg isotope analysis at much lower Hg concentrations (0.3 to

3.0 ng mL<sup>-1</sup>). We acknowledge the potential for discrepancies between the system of Georg and Newman<sup>1</sup> and our own system due to inlet system differences. A Cetac HGX-200 cold vapor system was used by Georg and Newman<sup>1</sup> and others;<sup>1,2,4,5,8,9</sup> however, we used an adapted gas–liquid phase separator (Fig. 1) which was initially developed at the Department of Earth Sciences laboratory, University of Toronto. Our study, however, was designed to investigate the potential for artifact formation using conditions typical of our laboratory's protocol for geological and environmental samples.

## 2. Experimental methods

### 2.1 Instrumentation and mercury isotope determination

Mercury isotope measurements were conducted on a Neptune Plus MC-ICP-MS housed at the University of Wisconsin-Madison's State Laboratory of Hygiene. The instrument was equipped with a gas–liquid phase separator (Fig. 1) and an Apex-Q nebulizer (Elemental Scientific Inc., USA) for Hg and Tl introduction, respectively. Briefly, stannous chloride (SnCl<sub>2</sub>) was continually pumped along with Hg(II) solutions and allowed to mix prior to being introduced into a frosted glass phase separator, producing gaseous elemental Hg(0). The Hg(0) was then mixed with a dry Tl aerosol generated by using the Apex-Q nebulizer before being introduced into the plasma. The Apex-Q nebulizer (free flow-mode) and the glass phase separator were flushed with the “sample” gas (Ar) and “additional” gas (Ar) of the MC-ICP-MS, respectively. The NIST SRM 997 Tl standard ( $^{205}\text{Tl}/^{203}\text{Tl} = 2.38714$ ) was used as an internal standard for simultaneous instrumental mass bias correction of Hg. Seven of the nine faraday cups were used to monitor the  $^{198}\text{Hg}$ ,  $^{199}\text{Hg}$ ,  $^{200}\text{Hg}$ ,  $^{201}\text{Hg}$ ,  $^{202}\text{Hg}$ ,  $^{203}\text{Tl}$  and  $^{205}\text{Tl}$  isotopes, respectively (Table 1). The nickel X skimmer cone was combined with a jet cone. Hg and Tl concentrations in solutions were monitored by using  $^{201}\text{Hg}$  and  $^{203}\text{Tl}$  signals. The signals for  $^{201}\text{Hg}$  and  $^{203}\text{Tl}$  were  $0.6 \times 10^{-2}$  and  $0.2 \times 10^{-2}$  V for acid blanks, respectively. Isobaric interferences of  $^{196}\text{Pt}$ ,  $^{198}\text{Pt}$  and  $^{204}\text{Pb}$  were evaluated by measuring the peak intensities of  $^{194}\text{Pt}$  and  $^{206}\text{Pb}$ , and no signals above the background were observed ( $<10^{-4}$  V).

The gains of the amplifier associated with each Faraday collector were calibrated for efficiency on a daily basis. Instrumental parameters (e.g., Ar gas flows, torch settings, and lens system) were tuned for a maximum ion intensity of Hg and Tl in standard solutions (Table 2). Data were acquired using 3 blocks each of 60 cycles, 2.097 seconds per cycle. An initial uptake of sample solution for 3 min ensured stable signals before isotope analyses were initiated. Between samples, the glass phase separator was rinsed using 3% (v/v) HNO<sub>3</sub> for 6 minutes until the signal intensity returned to the background level. A sample-standard bracketing (SSB) approach was used to compare

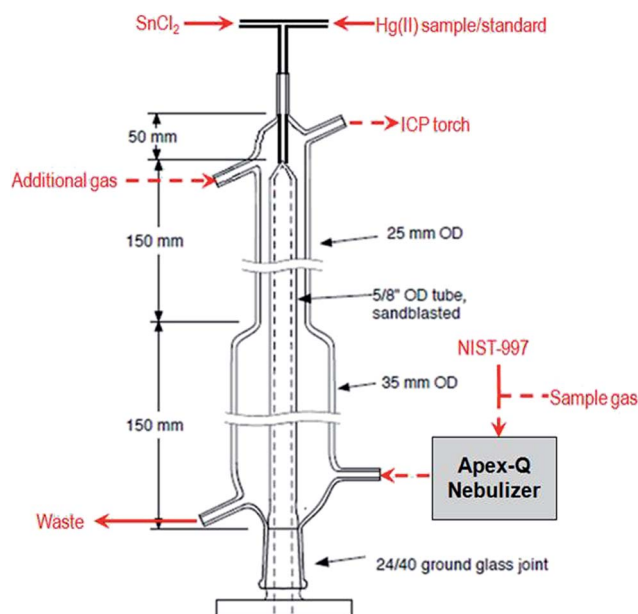


Fig. 1 Hg gas phase separator for Hg isotope measurements in this study.

Table 1 Faraday cup configuration for Hg isotope ratio measurements

Cups	L4	L3	L2	L1	C	H1	H2	H3	H4
Isotopes	$^{198}\text{Hg}$	$^{199}\text{Hg}$	$^{200}\text{Hg}$	$^{201}\text{Hg}$	$^{202}\text{Hg}$	$^{203}\text{Tl}$	$^{205}\text{Tl}$		

Table 2 Operating parameters during Hg isotope analysis

**MC-ICP-MS plasma parameters**

Sample gas	0.82–0.84 L min <sup>-1</sup>
Additional gas	0.23–0.25 L min <sup>-1</sup>
Cool gas	16.0 L min <sup>-1</sup>
Auxiliary gas	0.80 L min <sup>-1</sup>
RF power	1400 W

**Apex-Q**

Heater temperature	100 °C
Chiller temperature	2 °C
Nebulizer	PFA-50
TI solution uptake rate	0.05 mL min <sup>-1</sup>

**Peristaltic pump**

Hg solution uptake rate	0.65 mL min <sup>-1</sup>
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relative per mil (‰) deviation (using the  $\delta$  notation) of all our measurements to NIST SRM 3133, according to Blum and Bergquist:<sup>3</sup>

$$\delta^{xxx}\text{Hg} (\text{‰}) = \left\{ \frac{(^{xxx}\text{Hg}/^{198}\text{Hg})_{\text{sample}}}{(^{xxx}\text{Hg}/^{198}\text{Hg})_{\text{NIST SRM 3133}}} - 1 \right\} \times 1000 \quad (3)$$

where  $xxx$  values are 199, 200, 201 and 202 amu. Hg-MIF is reported in  $\Delta$  notation ( $\Delta^{xxx}\text{Hg}$ , deviation from mass dependency in units of permil, ‰) and is the difference between the measured  $\Delta^{xxx}\text{Hg}$  and the theoretically predicted  $\Delta^{xxx}\text{Hg}$  value following equations by Blum and Bergquist:<sup>3</sup>

$$\Delta^{199}\text{Hg} \approx \delta^{199}\text{Hg} - \delta^{202}\text{Hg} \times 0.2520 \quad (4)$$

$$\Delta^{200}\text{Hg} \approx \delta^{200}\text{Hg} - \delta^{202}\text{Hg} \times 0.5024 \quad (5)$$

$$\Delta^{201}\text{Hg} \approx \delta^{201}\text{Hg} - \delta^{202}\text{Hg} \times 0.7520 \quad (6)$$

**2.2 Reagents**

SnCl<sub>2</sub> (3%, w/w) was prepared in 10% (v/v) HCl. In Sections 2.3 and 2.4, all Hg solutions were prepared by using 3% HCl. We observed that using HCl is necessary to prevent the volatilization of Hg from acidic solutions, whereas using 3% HNO<sub>3</sub> is insufficient. In Section 2.5, acid mixtures (HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>) were used to prepare different standard reference materials (SRMs). All acids used in this study were of ultrapure grade (certified ACS Plus, Fisher Scientific), and 18.2 M $\Omega$  cm water (ELGA LabWater) was used for the preparation of reagents and solutions.

**2.3 Measurements of varied Hg concentrations with constant TI concentrations**

Four sequences were conducted to evaluate the effect of Hg concentration on Hg isotope ratios. We prepared four different NIST SRM 997 standard solutions with variable TI concentrations (2, 20, 30 and 50 ng mL<sup>-1</sup>). For each sequence, the concentration of TI was held constant, whereas we measured UM-Almadén secondary standard Hg solutions containing 0.3, 0.5, 0.8, 1.2, 1.7, 2.3 and 3.0 ng mL<sup>-1</sup> of Hg. The bracketed NIST

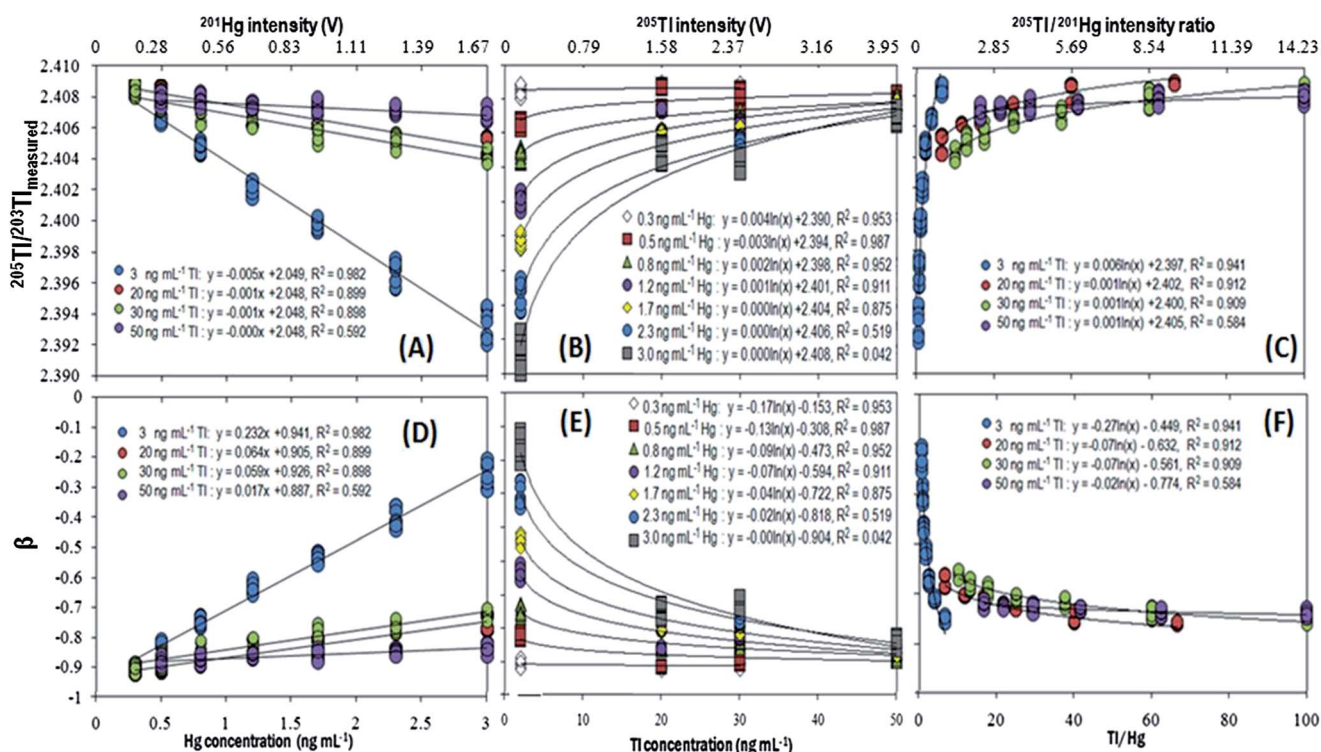


Fig. 2 Correlations between  $^{205}\text{Tl}/^{203}\text{Tl}_{\text{measured}}$  and Tl concentrations (A), Hg concentrations (B) and Hg/Tl ratios (C); correlations between the mass-bias correction factor ( $\beta$ ) and Tl concentrations (D), Hg concentrations (E) and Hg/Tl ratios (F).



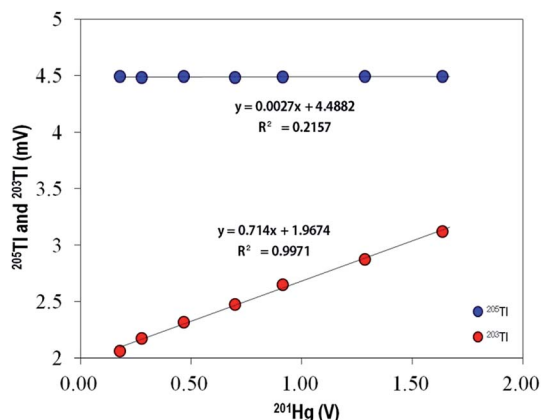


Fig. 3 Correlation between  $^{201}\text{Hg}$  and Tl ( $^{203}\text{Tl}$ : black circles;  $^{205}\text{Tl}$ : blue circles) beam intensities. Measurements were conducted by introducing 0.3 to 3.0  $\text{ng mL}^{-1}$  of Hg without Tl.

SRM 3133 Hg solutions were diluted to have the same Hg concentrations as the UM-Almadén standard solutions. With the SSB approach, replicate measurements of UM-Almadén ( $n = 4$ ) and NIST SRM 3133 ( $n = 5$ ) of each specific Hg concentration were measured, which enabled measurement reproducibility ( $n = 4$ ).

#### 2.4 Measurements of varied Tl concentrations with constant Hg concentrations

Two sequences were performed to evaluate the effect of Tl concentrations on Hg isotope ratios. We prepared two different NIST SRM 3133 Hg solutions with Hg concentrations of 0.5 and 1.0  $\text{ng mL}^{-1}$ . The concentrations of NIST SRM 3133 were held constant during each sequence however, instrumental mass bias correction was performed by measuring NIST SRM 997 with variable Tl concentrations (1, 2, 3, 4, 7, 15, 20, 30, 40, 50, 60, and 100  $\text{ng mL}^{-1}$ ). Replicate measurements ( $n = 4$ ) for a specific Tl concentration were conducted.

#### 2.5 Measurements of standard reference materials

For biological SRMs such as TORT-2 (Lobster), DORM-2 (Fish protein), DORM-3 (Fish protein) and DOLT-2 (dogfish liver), about 0.2 g of each SRM was weighed and digested at 95 °C for 3 h with a 4 mL acid mixture ( $\text{HNO}_3 : \text{H}_2\text{SO}_4 = 7 : 3$ , v/v) following the method reported by Pfeil and Stalvey.<sup>15</sup> BrCl (200  $\mu\text{L}$ ) was later added to each sample and kept for 12 h to allow the conversion of Hg to Hg(II). Hydroxylamine (400  $\mu\text{L}$ ) was added to the biological solutions prior to Hg isotope measurements. For other SRMs such as NIST SRM 2711 (Montana Soil II) and MESS-1 (marine sediment), about 0.2 g of the

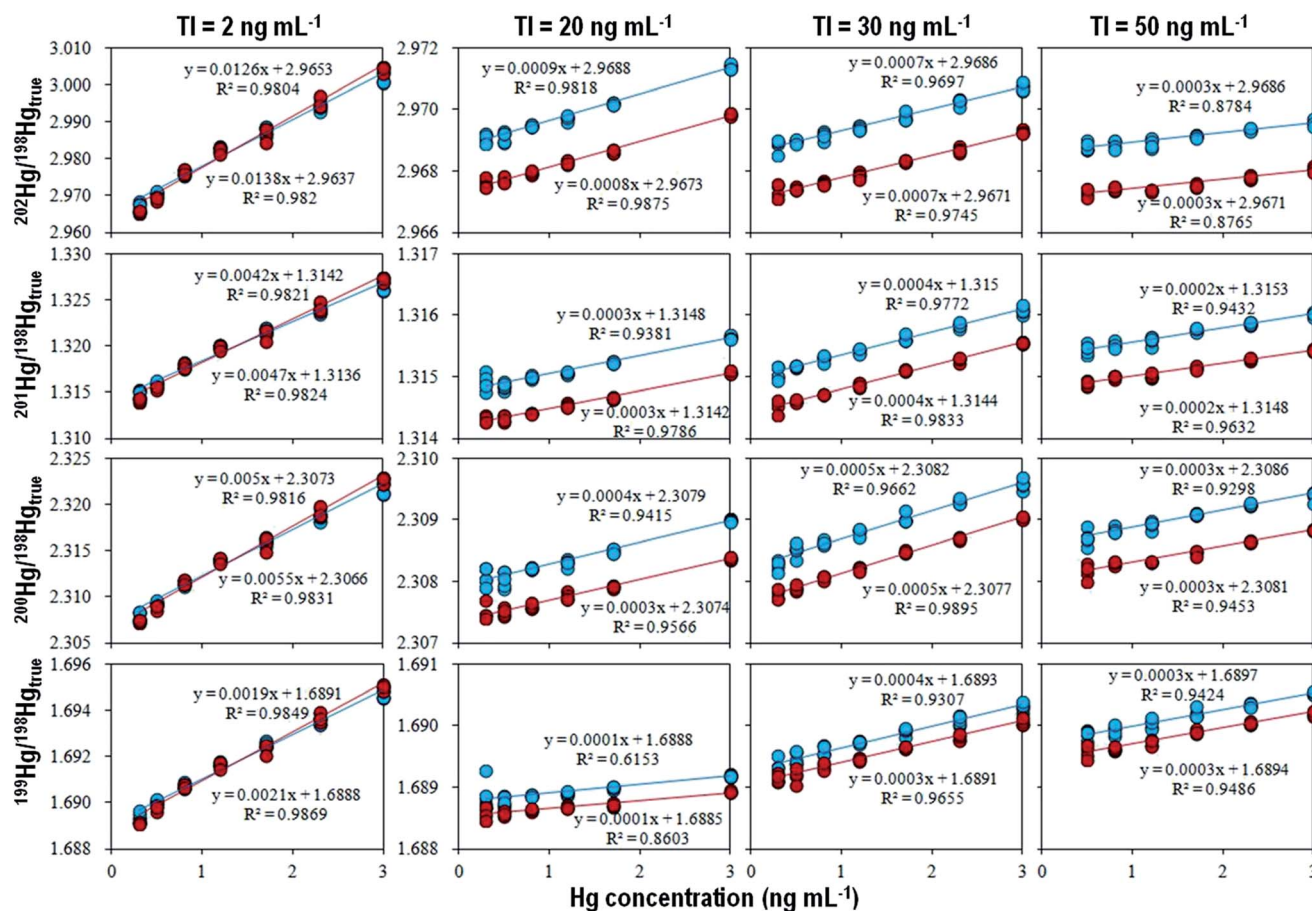


Fig. 4 Correlations between  $^{xxx}\text{Hg}/^{198}\text{Hg}_{\text{true}}$  ratios and Hg concentrations over varied Tl concentrations. Red circles represent UM-Almadén; blue circles represent NIST SRM 3133.

ground sample was digested (95 °C, 1 hour) in 2 mL aqua regia (HCl : HNO<sub>3</sub> = 3 : 1, v/v) according to Yin *et al.*<sup>16</sup> For each SRM, triplicate digests were prepared ( $n = 3$ ).

On the basis of the certified total Hg concentrations for SRMs, about 5 and 10 ng Hg were taken and diluted to 0.5 and 1.0 ng mL<sup>-1</sup> of Hg, respectively. The acid solution used for the dilution of biological SRMs was a 10% HNO<sub>3</sub> : H<sub>2</sub>SO<sub>4</sub> mixture (7 : 3, v/v), whereas that used for other SRMs was 10% HCl : HNO<sub>3</sub> (3 : 1, v/v). UM-Almadén and NIST SRM 3133 solutions containing 0.5 and 1.0 ng mL<sup>-1</sup> of Hg were also prepared by using 10% HNO<sub>3</sub> : H<sub>2</sub>SO<sub>4</sub> (7 : 3, v/v) and 10% HCl : HNO<sub>3</sub> (3 : 1, v/v) acid mixtures. During analysis, Hg concentrations and acid matrices of the NIST SRM 3133 solutions were matched to those of the bracketed samples. THg concentrations in the digest solutions were measured by using the <sup>201</sup>Hg intensities, which showed that the recoveries of Hg for the SRMs were 94 to 109%.

## 2.6 Reporting uncertainties

For the isotope ratios of Hg and Tl, uncertainties were reported using the theoretical statistical errors (SEs) of all cycles, which were automatically calculated by using online data acquisition software of the instrument. For  $\delta$  and  $\Delta$  values of UM-Almadén, uncertainties were reported using the standard deviation (SD) of

repeated measurements of the same solution; for  $\delta$  and  $\Delta$  values of SRMs, uncertainties were reported using the SD values of the duplicate sample digests.

## 3. Results and discussion

### 3.1 Hg and Tl sensitivities during Hg isotope analysis

Sample uptake rates for Hg and Tl solutions in this study were about 0.65 and 0.05 mL min<sup>-1</sup>, respectively. The intensities of Hg and Tl showed linear correlations with Hg and Tl concentrations as shown in Fig. S1 of the ESI.† The sensitivity of <sup>201</sup>Hg (~0.56 V per ng mL<sup>-1</sup> Hg) in our study is higher than that in previous studies.<sup>1,2,4,5,8,9</sup> Sensitivity differences can be caused by a variety of factors, such as the type of cones and the operating conditions of individual instruments, and the inlet system used for Hg introduction.<sup>1,2,4,5,8,9,14,17</sup>

### 3.2 Effects of Hg and Tl concentrations on Tl isotope ratios

Our data confirm that varied Tl and Hg concentrations have a large effect on <sup>205</sup>Tl/<sup>203</sup>Tl<sub>measured</sub> ratios (Fig. 2A–C). When Tl concentration was held constant, increased Hg concentration resulted in decreased <sup>205</sup>Tl/<sup>203</sup>Tl<sub>measured</sub> (Fig. 2A). When measuring Hg standards with similar Hg concentrations, the increase of Tl concentration resulted in increased

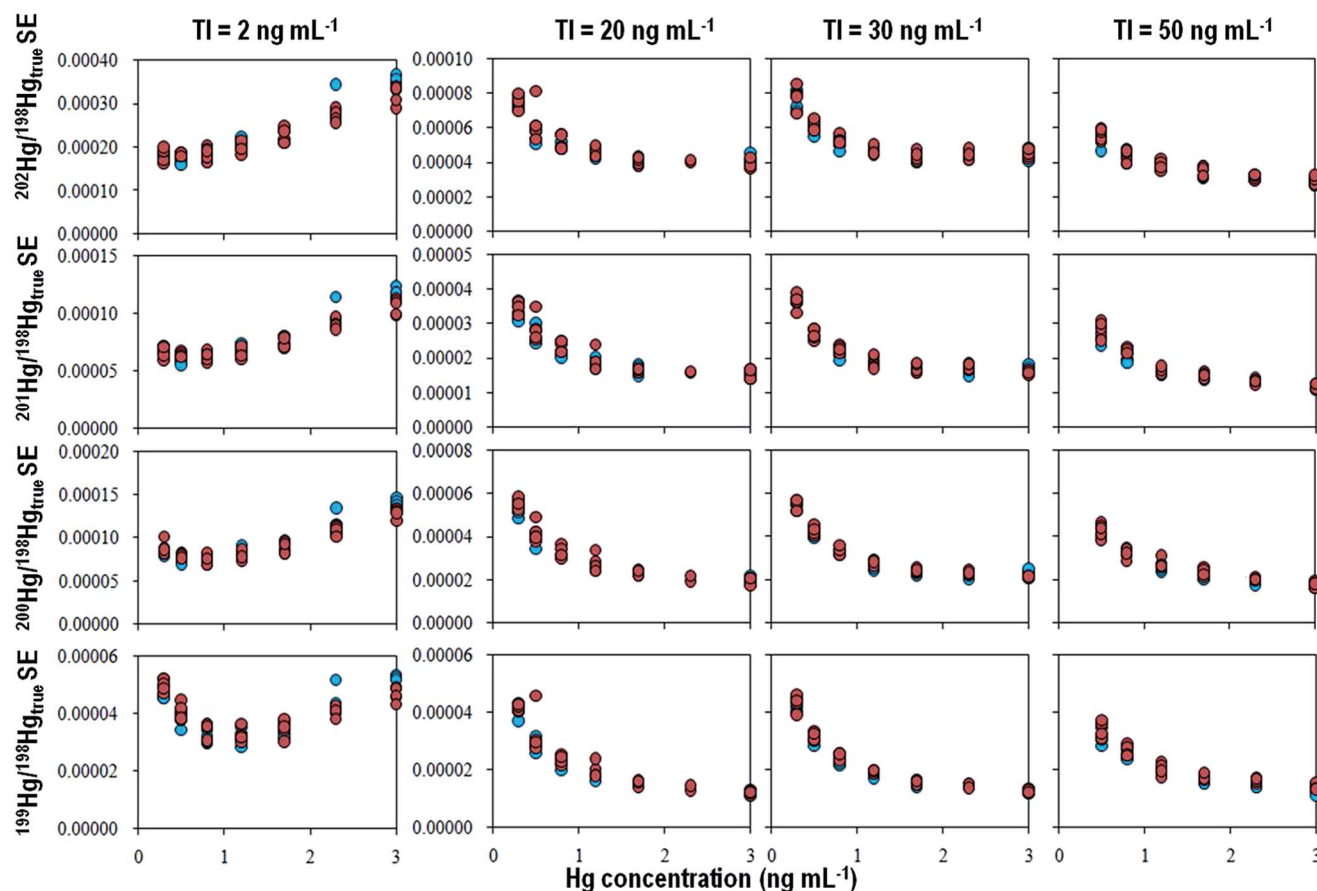


Fig. 5 Relationship between the standard error of <sup>xxx</sup>Hg/<sup>198</sup>Hg<sub>true</sub> ratios and Hg concentration over varied Tl concentrations. Red circles represent UM-Almadén; blue circles represent NIST SRM 3133.

$^{205}\text{Tl}/^{203}\text{Tl}_{\text{measured}}$ , but such an increase was smaller at higher Tl concentrations (Fig. 2B). The increase of  $^{205}\text{Tl}/^{203}\text{Tl}_{\text{measured}}$  was small at higher Tl/Hg ratios (Fig. 2C). These results are consistent with the observations by Georg and Newman,<sup>1</sup> which shows that the formation of Hg hydride could result in increased  $^{203}\text{Tl}$  intensities and decreased  $^{205}\text{Tl}/^{203}\text{Tl}$ , when using Neptune Plus MC-ICP-MS with an X skimmer cone. By measuring 0.3 to 3.0 ng mL<sup>-1</sup> of Hg and without Tl introduction (only 3% HNO<sub>3</sub>) by using the Apex-Q, we monitored the  $^{203}\text{Tl}$  and  $^{205}\text{Tl}$  intensities to evaluate the rate of Hg hydride formation. All our measurements showed increased  $^{203}\text{Tl}$  intensities but no increase for  $^{205}\text{Tl}$  (Fig. 3). This is consistent with the previous prediction that Hg hydrides are mainly formed in HgH<sub>2</sub><sup>+</sup> rather than in HgH<sup>+</sup> species.<sup>1</sup> A positive linear correlation was observed between  $^{201}\text{Hg}$  and  $^{203}\text{Tl}$  intensities, which indicated a rate of  $\sim 0.07\%$  for HgH<sub>2</sub><sup>+</sup> formation in our study (Fig. 3) and was comparable to that reported by Georg and Newman (0.1%).<sup>1</sup>

According to eqn (1), artificial changes of  $^{205}\text{Tl}/^{203}\text{Tl}_{\text{measured}}$  due to Hg hydride formation should cause the shift of  $\beta$  values. Our results showed that when Tl concentrations were held constant, increased Hg concentrations resulted in the increase of  $\beta$  (Fig. 2D). When measuring Hg standards with similar Hg concentrations, an increase in Tl concentration caused a negative shift of  $\beta$ , but the shift was small at high Tl concentrations (Fig. 2E). For instance, measurements of high Tl solutions (20 to 50 ng mL<sup>-1</sup>) resulted in small shifts of  $<0.3$  for  $\beta$  (Fig. 2E), whereas measuring low Tl solutions (2 ng mL<sup>-1</sup>) resulted in a large shift of  $\beta$  of  $\sim 1$  (Fig. 2D). The shift of  $\beta$  was much smaller at high Tl/Hg ratios (Fig. 2F).

### 3.3 Effects of Hg and Tl concentrations on Hg isotope ratios

The mass-bias corrected  $^{xxx}\text{Hg}/^{198}\text{Hg}_{\text{true}}$  ratios (e.g.  $^{199}\text{Hg}/^{198}\text{Hg}_{\text{true}}$ ,  $^{200}\text{Hg}/^{198}\text{Hg}_{\text{true}}$ ,  $^{201}\text{Hg}/^{198}\text{Hg}_{\text{true}}$  and  $^{202}\text{Hg}/^{198}\text{Hg}_{\text{true}}$ ) are summarized in Table S1 (ESI<sup>†</sup>) and Fig. 4. The mean ratios of NIST SRM 3133 measurements (Table S1, ESI<sup>†</sup>) are in the range of previous results.<sup>3,4,9,18</sup> The uncertainties of  $^{xxx}\text{Hg}/^{198}\text{Hg}_{\text{true}}$  ratios are of the same magnitude as those reported by Blum and Bergquist,<sup>3</sup> and Ridley and Stetson,<sup>18</sup> but smaller than those reported by Berni *et al.*<sup>9</sup> The larger uncertainties reported by Berni *et al.*<sup>9</sup> are representative of a very long period of time, accounting for variability within several measurement sessions (480 measurements). Yang and Sturgeon<sup>4</sup> also reported larger uncertainties of the  $^{xxx}\text{Hg}/^{198}\text{Hg}_{\text{true}}$  ratios, but their uncertainties were estimated as random error propagation, and uncertainty from the  $^{205}\text{Tl}/^{203}\text{Tl}$  ratio was included in their reported Hg ratios. According to eqn (2), artificial shifts of  $\beta$  could unavoidably cause changes in mass-bias corrected Hg isotope ratios. In our study, positive linear correlations between Hg concentrations and  $^{xxx}\text{Hg}/^{198}\text{Hg}_{\text{true}}$  ratios (e.g.  $^{199}\text{Hg}/^{198}\text{Hg}_{\text{true}}$ ,  $^{200}\text{Hg}/^{198}\text{Hg}_{\text{true}}$ ,  $^{201}\text{Hg}/^{198}\text{Hg}_{\text{true}}$  and  $^{202}\text{Hg}/^{198}\text{Hg}_{\text{true}}$ ) were observed (Fig. 4). When Tl concentration was constant, the rates of increase for mass-bias corrected Hg isotope ratios were similar for UM-Almadén and NIST SRM 3133. The slopes between  $^{xxx}\text{Hg}/^{198}\text{Hg}_{\text{true}}$  and Hg concentrations were much higher at lower Tl concentrations (Fig. 4), consistent with the observation that lower Tl concentrations

tend to result in more artificial shifts of  $\beta$  (Fig. 2D and E). This observation confirms that measuring lower Hg and higher Tl solutions is necessary for Hg isotope measurements and that the concentrations of Hg between samples and standards must be carefully matched, which is necessary for Hg isotope measurements.

### 3.4 Optimization of Hg and Tl concentrations for Hg isotope measurements

Changes in Hg and Tl concentrations also affect the SE values of  $^{xxx}\text{Hg}/^{198}\text{Hg}_{\text{true}}$  ratios (Fig. 5). Using a low Tl standard of 2 ng mL<sup>-1</sup>, the SE of  $^{xxx}\text{Hg}/^{198}\text{Hg}_{\text{true}}$  ratios is much higher than that of high Tl standards (20, 30, and 50 ng mL<sup>-1</sup>). The high SE of  $^{xxx}\text{Hg}/^{198}\text{Hg}_{\text{true}}$  ratios using the low Tl standard (2 ng mL<sup>-1</sup>) could be explained by the fact that the precision of  $^{205}\text{Tl}/^{203}\text{Tl}_{\text{measured}}$  is compromised at lower Tl concentrations (Fig. 6B). Using higher Tl standards (20, 30, and 50 ng mL<sup>-1</sup>),

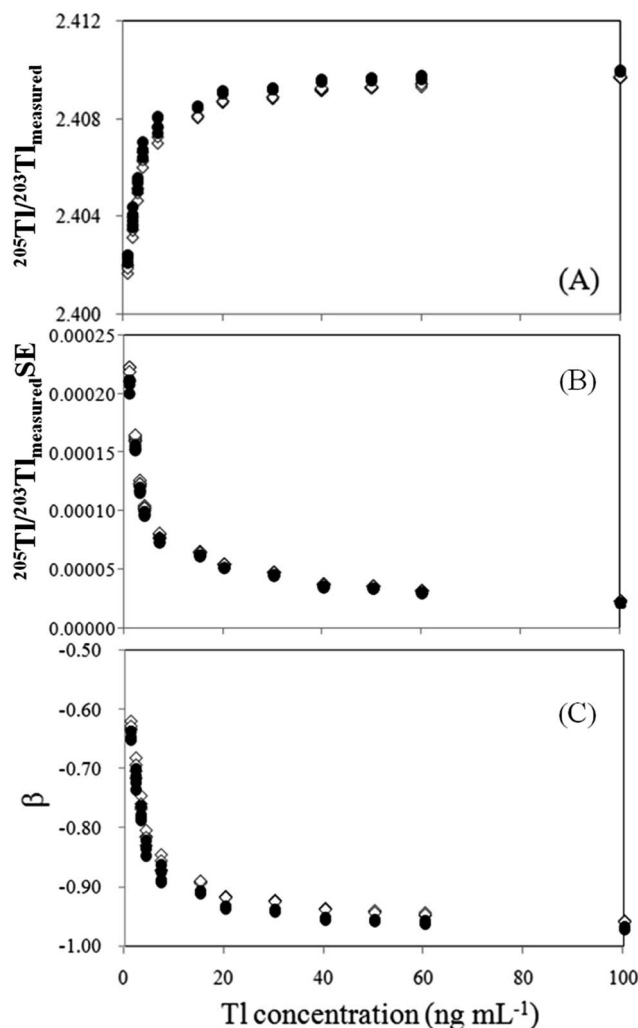


Fig. 6 Variations of  $^{205}\text{Tl}/^{203}\text{Tl}_{\text{measured}}$  (A), standard error of  $^{205}\text{Tl}/^{203}\text{Tl}_{\text{measured}}$  (B), and mass-bias correction factor  $\beta$  (C) over varied Tl concentrations. Dark circles represent the measurements based on NIST SRM 3133 of 0.5 ng mL<sup>-1</sup> Hg; tubular diamonds represent the measurements based on NIST-3133 of 1.0 ng mL<sup>-1</sup> Hg.

the SE of  $^{xxx}\text{Hg}/^{198}\text{Hg}_{\text{true}}$  ratios decreased as Hg concentration increased (Fig. 5), similar to previous observations by Foucher and Hintelmann.<sup>2</sup> The SE of  $^{202}\text{Hg}/^{198}\text{Hg}_{\text{true}}$  decreased from 0.00008 to 0.00004 as Hg concentrations increased from 0.3 to 3.0 ng mL<sup>-1</sup>, which is only equivalent to 0.02‰ to 0.03‰ changes for  $\delta^{202}\text{Hg}$ . No significant decreases of the SE for  $^{xxx}\text{Hg}/^{198}\text{Hg}_{\text{true}}$  were observed when Hg concentrations were above 0.5 ng mL<sup>-1</sup>, whereas increasing Hg concentrations would (1) increase the rinsing time and the risk of carry over between samples and (2) increase the sample quantities for measurements. We suggest that Hg concentrations of 0.5 to 1.0 ng mL<sup>-1</sup> should be the best compromise between the obtainable precision, rinsing time and analyte consumption.

Varied Tl concentrations (1, 2, 3, 4, 7, 15, 20, 30, 40, 50, 60, and 100 ng mL<sup>-1</sup>) were measured to evaluate the optimum concentrations of Tl when measurements were performed at specific Hg concentrations of 0.5 and 1.0 ng mL<sup>-1</sup>. We observed that the  $^{205}\text{Tl}/^{203}\text{Tl}_{\text{measured}}$  increased exponentially with increase of Tl concentrations, whereas the SE of  $^{205}\text{Tl}/^{203}\text{Tl}_{\text{measured}}$  and  $\beta$  decreased (Fig. 6). As shown in Fig. S2,<sup>†</sup> the SE of

$^{xxx}\text{Hg}/^{198}\text{Hg}_{\text{true}}$  is positively correlated with the SE of  $^{205}\text{Tl}/^{203}\text{Tl}_{\text{measured}}$ . Hg isotope ratios and their SE values decreased significantly with increase of Tl concentrations until the Tl concentrations were beyond 20 ng mL<sup>-1</sup> (Fig. 7). For our instrument therefore, we suggest that at least 20 ng mL<sup>-1</sup> of Tl should be used during high precision Hg isotope measurements.

### 3.5 Importance of matching Hg concentrations between Hg solutions and NIST SRM 3133

The SSB approach is a common practice to correct for mass bias of Hg isotope measurements with the assumption that samples and bracketing standards are subjected to similar mass bias.<sup>3</sup> However, our results showed that mass bias is in fact concentration dependent (Fig. 4), so the SSB requires a concentration match between the sample and standard. We evaluated the effect of mismatch in Hg concentrations between UM-Almadén and NIST SRM 3133 [termed as  $\text{THG}_{\text{UM-Almadén}}/\text{THG}_{\text{NIST SRM 3133}} - 1$  (%) ] on Hg isotopic compositions. The mean Hg isotope ratios of UM-Almadén and NIST SRM 3133 with the same Hg

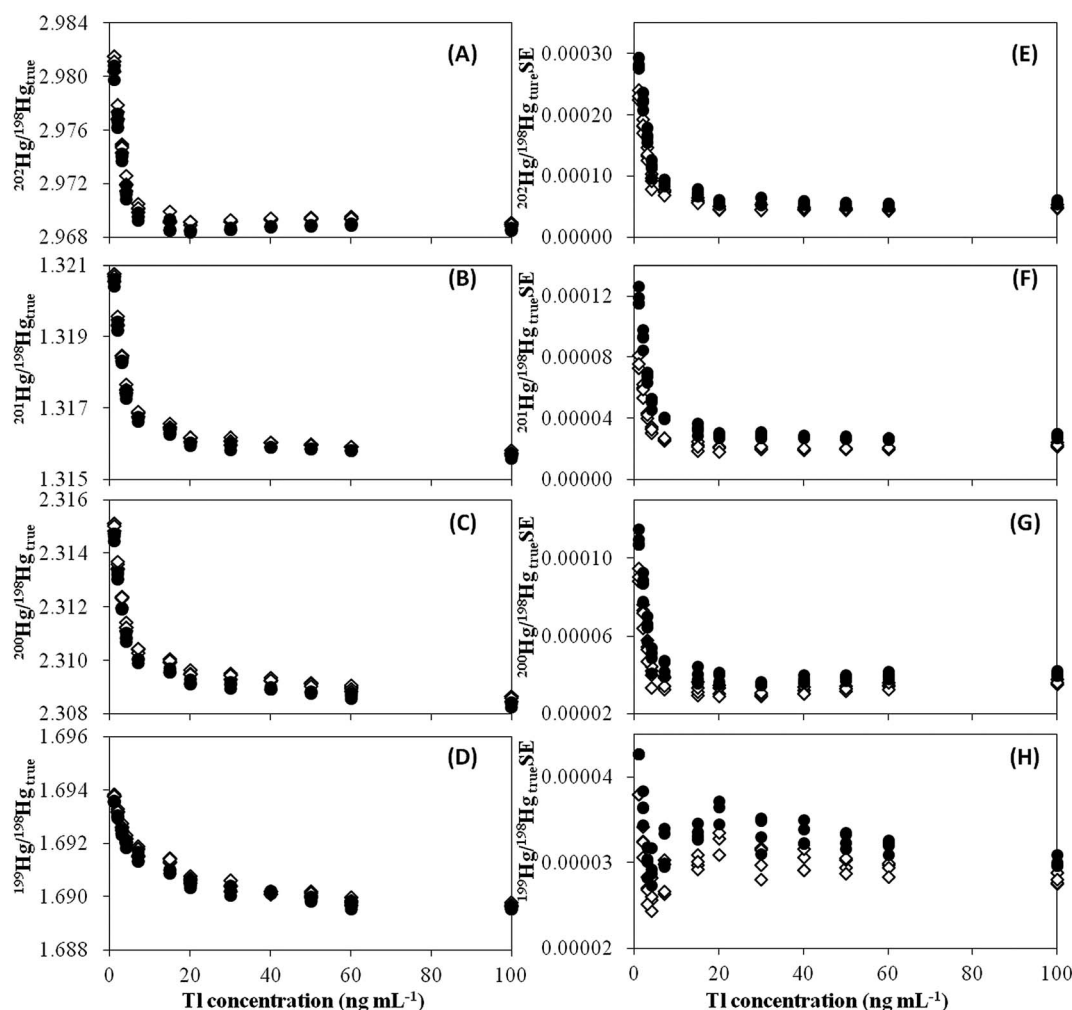


Fig. 7 Variations of  $^{xxx}\text{Hg}/^{198}\text{Hg}_{\text{true}}$  ratios and standard errors (SEs) over varied Tl concentrations. Dark circles represent the measurements based on NIST SRM 3133 of 0.5 ng mL<sup>-1</sup> Hg; tubular diamonds represent the measurements based on NIST SRM 3133 of 1.0 ng mL<sup>-1</sup> Hg.



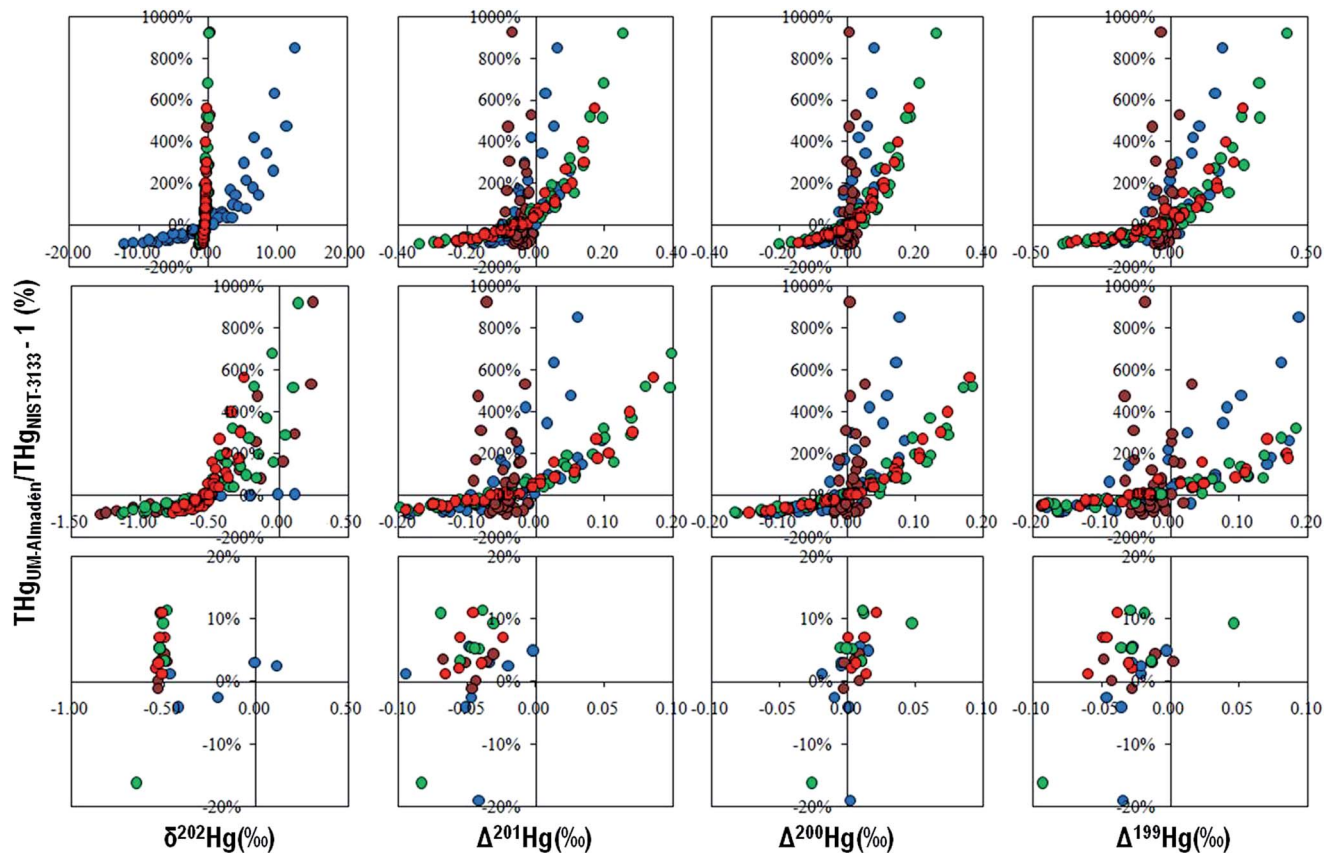


Fig. 8 Relationship between Hg isotopic compositions ( $\delta^{202}\text{Hg}$ ,  $\Delta^{199}\text{Hg}$  and  $\Delta^{200}\text{Hg}$ ) and relative Hg concentration differences between UM-Almadén and NIST SRM 3133 over varied Tl concentrations. Row 2 is an expansion of row 1. Row 3 is a more detailed expansion of row 2. (Blue circles:  $3 \text{ ng mL}^{-1}$  Tl; brown circles:  $20 \text{ ng mL}^{-1}$  Tl; green circles:  $30 \text{ ng mL}^{-1}$  Tl; red circles:  $50 \text{ ng mL}^{-1}$  Tl).

concentrations were calculated, and then the mean Hg isotope ratio of UM-Almadén with a certain Hg concentration was bracketed by that of NIST SRM 3133 with other Hg concentrations. As shown in Fig. 8, the isotopic composition of Hg for concentrations matched within 10% agreed with published values,<sup>3</sup> whereas the THg mismatched results show large deviations in both  $\delta^{202}\text{Hg}$  values and  $\Delta$  values (Fig. 8). It appears as though bracketing with higher NIST SRM 3133 concentrations results in more negative  $\delta^{202}\text{Hg}$ , whereas bracketing with lower NIST SRM 3133 concentrations results in  $\delta^{202}\text{Hg}$  that is larger than the reported number. This can be explained by positive linear correlations between Hg concentrations and measured  $^{202}\text{Hg}/^{198}\text{Hg}$  (Fig. 4). The calculated values for UM-Almadén (Fig. 8) highlight the importance of concentration matching while using the SSB method.

The  $\delta$  and  $\Delta$  values of UM-Almadén, based on Hg concentration matched NIST SRM 3133, were estimated (Table S2, ESI†). With the exception of the analysis using a  $2 \text{ ng mL}^{-1}$  Tl internal standard, all analyses showed consistent  $\delta$  and  $\Delta$  values which is in good agreement with previous results.<sup>3</sup> Our results suggest that high precision measurements of Hg isotopes should be performed based on higher Tl internal standards. Typically, for low Hg solutions ( $0.3$  to  $3.0 \text{ ng mL}^{-1}$ ) measured in our study, the results of  $\delta$  and  $\Delta$  values were consistent for internal standards containing  $\geq 20 \text{ ng mL}^{-1}$  of

Tl. Theoretically, accurate Hg isotope measurements for high Hg solutions may be also achieved by increasing the concentrations of Tl for mass bias correction. However, this is not necessary considering that higher Hg and Tl concentrations will result in a larger rinsing time and analyte consumption. In previous studies from our laboratory, most measurements are based on  $0.5$  to  $1 \text{ ng mL}^{-1}$  Hg and  $20 \text{ ng mL}^{-1}$  Tl solutions. A minimum of at least 4 to 8 ng of Hg per measurement (an initial uptake of 3 min for signal stabilization plus  $\sim 7$  min of acquisition, sample solution uptake:  $0.65 \text{ mL min}^{-1}$ ) is required to reach precise determination of  $\delta^{202}\text{Hg}$  (within  $\pm 0.10\%$ , 2 SD).

### 3.6 Mercury isotopic composition of standard reference materials

As mentioned in Section 2.5, SRMs were measured to test the potential isotope bias during measurements of different environmental matrices. All tests were performed with low Hg solutions containing  $0.5$  and  $1.0 \text{ ng mL}^{-1}$  of Hg and a high internal standard containing  $20 \text{ ng mL}^{-1}$  of Tl. Based on well-matched THg concentrations and acid matrices between samples and the bracketed NIST SRM 3133, the measured Hg isotope composition and uncertainties for SRMs (Table S3, ESI†) were in agreement with previous studies.<sup>6,16,19–22</sup>



## 4. Conclusion

While our study agrees with the results reported by Georg and Newman<sup>1</sup> that measuring Hg isotopes using a Neptune Plus MC-ICP-MS with high sensitivity X skimmer cones may result in interference with the <sup>205</sup>Tl/<sup>203</sup>Tl ratio and inaccurate mass bias determination due to Hg hydride formation. We confirm that these interferences can be minimized when higher Tl (20 to 50 ng mL<sup>-1</sup>) and lower Hg (0.5 to 3 ng mL<sup>-1</sup>) concentrations are introduced. Based on careful optimization of Tl and Hg concentrations, combined with carefully matched Hg concentration between samples and bracketing standards, we demonstrated that accurate Hg isotope measurements can be achieved. We acknowledge that our measurements were performed using an adapted inlet system, which may not directly apply to other introduction systems such as the Cetac HGX-200. Therefore, we advise other Neptune users to perform internal optimization steps to minimize potential matrix effects when measuring Hg isotopes.

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