nature geoscience

Article https://doi.org/10.1038/s41561-023-01341-w

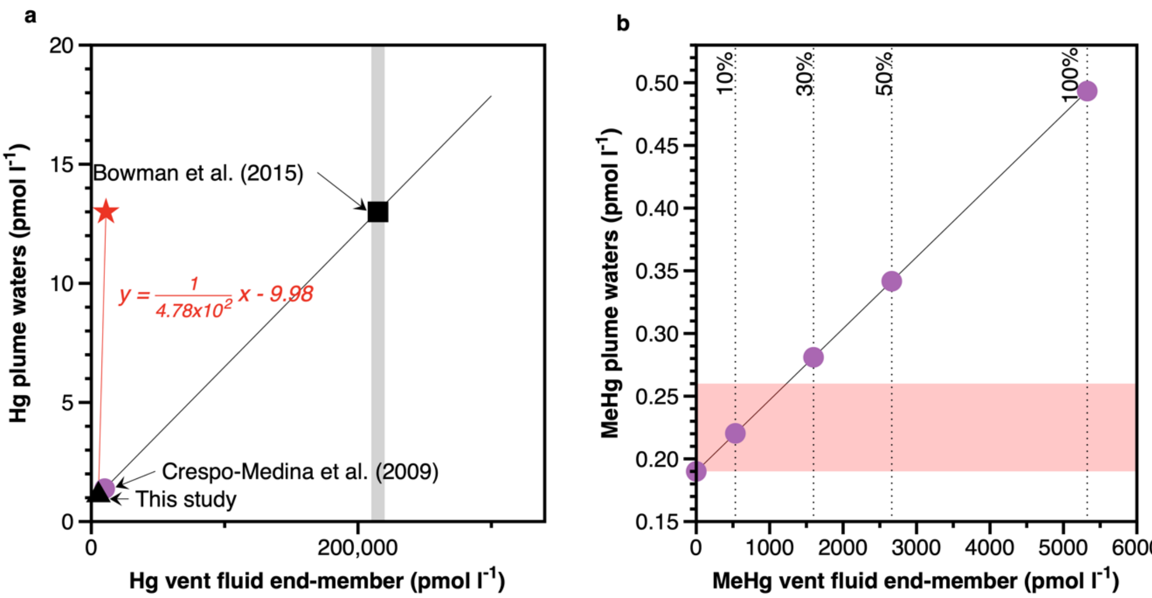
Mercury fluxes from hydrothermal venting at mid-ocean ridges constrained by measurements

In the format provided by the authors and unedited

SUPPLEMENTARY INFORMATION

SUPPLEMENTARY INFORMATION 1: ADDITIONAL DISCUSSIONS

One cruise crossing the Mid-Atlantic ridge reported one high tHg value of 13 pmol l^{-1} at the non-buoyant plume above the TAG site [1]. The highest value that we found in the non-buoyant plume at the TAG station was 1.29 pmol l^{-1}. There are two possibilities to reach higher concentrations in the plume waters. If the dilution factor from the vent to the non-buoyant plume stays the same ($2.68x10^4$, **Extended data Fig. 3**) then a higher tHg concentration of the vent fluid is needed. To reach 13 pmol l^{-1} in the plume, a vent fluid end-member between 210,000 - 220,000 pmol l^{-1} would be needed (grey shading in **Supplementary information Fig. S1**). This needed vent fluid end-member tHg concentration is one to five orders of magnitude higher than reported vent fluids from other sites (purple circle in **Supplementary information Fig. S1**) [2–5] and two orders of magnitude higher than the vent fluid concentration measured in the present study (black triangle in **Supplementary information Fig. S1**). Another possibility to reach higher tHg concentrations in the plume is to reduce the dilution factor (**Eq. 2**). To reach 13 pmol l^{-1} in the plume, the dilution factor must be reduced two orders of magnitude to around $5x10^2$ (red in **Supplementary information Fig. S1**). However, typical dilution factor values of the non-buoyant plumes are in the range of 10^4 [6]. A previous study has reported hydrothermal fluids composed almost entirely (close to 100%) of MeHg (up to 16.4 ± 3 pmol l^{-1}) [4]. We calculated the expected MeHg concentration of the plume waters at the TAG site for a vent fluid with varied percentages of MeHg from 0 - 100% of the tHg. The better fit with the concentrations measured in the plume occurs for MeHg concentrations between 0 - 27% of the tHg (**Supplementary information Fig. S1**). However, future studies should focus on measuring all Hg species to better constrain MeHg percentages.



Supplementary information Fig. S1. Estimation of vent fluid end-member tHg concentration for getting higher tHg concentrations in the plume waters and estimation of the percentage of MeHg in the vent fluid. a, the black line shows the relationship between the vent fluid tHg concentration and the resultant tHg concentration in the plume waters. The grey shading (210,000-220,000 pmol l^{-1}) indicates the range of the vent fluid tHg concentration needed to reach 13 pmol l^{-1} (black square) in the plume waters. The red line shows how much the dilution factor must decrease so that the slope increases to reach 13 pmol l l^{-1} (red star) with the vent fluid tHg concentration found in this study (black triangle). **b**, the purple dots and black line show the MeHg concentrations that the plume would have with varied vent fluid end-member MeHg percentages from the tHg. The red shading shows the measured MeHg concentration in the plume.

References

1. Bowman, K. L., Hammerschmidt, C. R., Lamborg, C. H. & Swarr, G. Mercury in the North Atlantic Ocean: The U.S. GEOTRACES zonal and meridional sections. *Deep Sea Res Part Ii Top Stud Oceanogr* **116**, 251–261 (2015).

2. Crespo-Medina, M. *et al.* Adaptation of chemosynthetic microorganisms to elevated mercury concentrations in deep-sea hydrothermal vents. *Limnol Oceanogr* **54**, 41–49 (2009).

3. Lee, S. *et al.* Mercury accumulation in hydrothermal vent mollusks from the southern Tonga Arc, southwestern Pacific Ocean. *Chemosphere* **127**, 246–253 (2015).

4. Lamborg, C. H., Damm, K. L. V., Fitzgerald, W. F., Hammerschmidt, C. R. & Zierenberg, R. Mercury and monomethylmercury in fluids from Sea Cliff submarine hydrothermal field, Gorda Ridge. *Geophys Res Lett* **33**, (2006).

5. Sherman, L. S. *et al.* Mercury isotopic composition of hydrothermal systems in the Yellowstone Plateau volcanic field and Guaymas Basin sea-floor rift. *Earth Planet Sc Lett* **279**, 86–96 (2009).

6. Feely, R. A. *et al.* Composition and sedimentation of hydrothermal plume particles from North Cleft segment, Juan de Fuca Ridge. *J Geophys Res Solid Earth* **99**, 4985–5006 (1994).

SUPPLEMENTARY INFORMATION 2: Uncertainty and error calculations

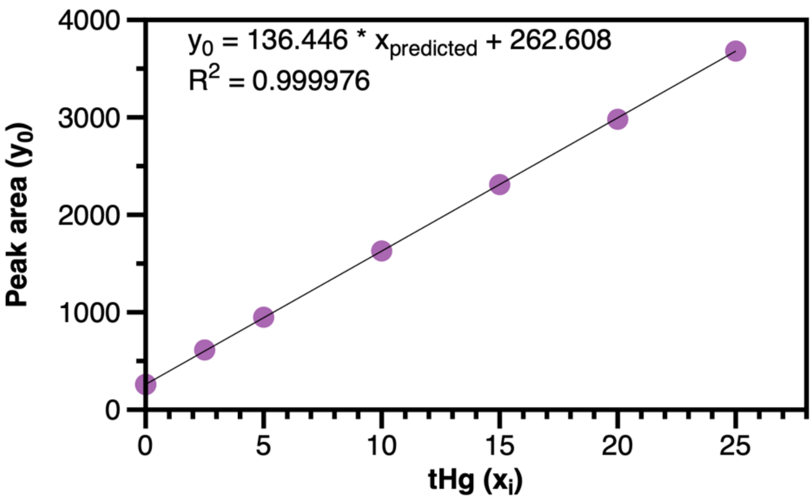
Total mercury in fluids, plume, and seawater

Uncertainty calculations of the total mercury (tHg) values reported in this study were done following the GUM/Eurachem guidelines. The method for sampling, handling, oxidation/reduction of Hg, and analysis by cold-vapor atomic fluorescence is described in the methods section. The analytical method is based on the use of NIST-3133 (National Institute of Standards and Technology) to construct a calibration curve from which the tHg concentration of the sample can be determined by regression analysis of the line.

$$y_0 = mx_{predicted} + c$$

Eq. S1

where $y_{(0)}$ is the measured fluorescence signal for the tHg concentration $x_{(predicted)}$ (in pg) of the unknown sample and c the cutoff of the Y axis.



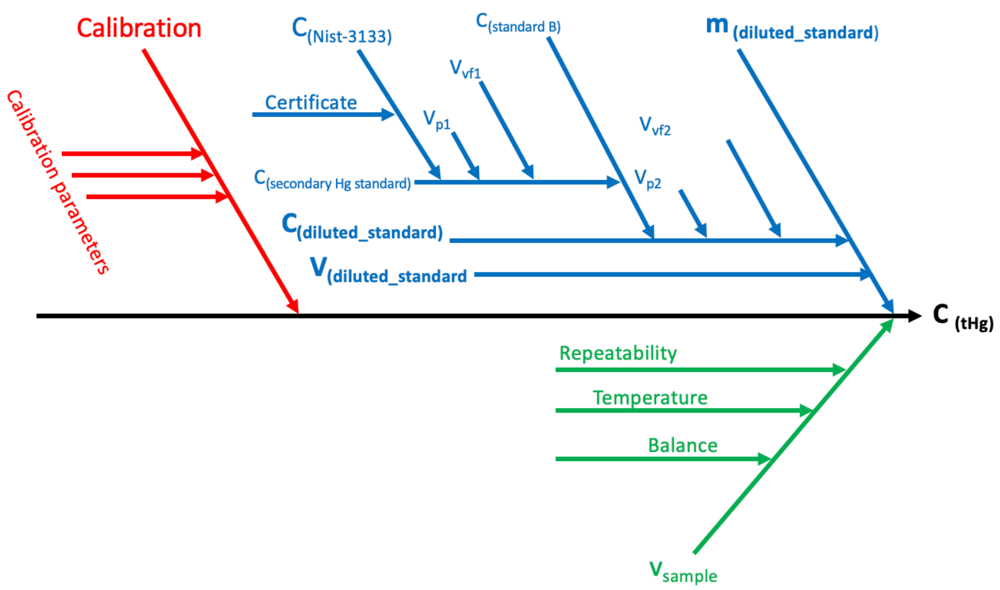
Supplementary information Fig. S2. Calibration curve

Following the GUM/Eurachem guidelines46 the model equation is defined as

$$C_{tHg} = x_{predicted} = \frac{y_0 - c}{m} * \frac{1}{R} * F_{rep}$$

Eq. S2

where 1/R is the uncertainty due to recovery that is ≤ 1 by definition but that it has uncertainty, and F_{rep} is the uncertainty due to reproducibility that is 1 by definition but that it has uncertainty. A fishbone diagram was constructed to identify sources of uncertainty based on the model equation (**Eq. S2**) and the analytical method described in the methods section. The diagram includes uncertainties related to the construction of the calibration curve (red), the certified reference material NIST-3133 (blue), and the volume of the sample analyzed (green).



Supplementary information Fig. S3. Fishbone diagram for identification of the uncertainty sources.

When identifying the contributions of each one of the uncertainties sources expanded relative standard deviation at k=2 is 11.1% for tHg in the seawater and plume waters, 6.2% for tHg in fluids of more than 4,000 pmol l^{-1}, 11.1% for fluids between 2,000 and 4,000 pmol l^{-1}, and 4.9% for fluids between 100 and 2,000 pmol l^{-1}.

Vent fluid end-member

The magnesium (Mg) free tHg vent fluid end member was calculated by linear regression of magnesium (Mg) as the independent variable and tHg. Used seawater Mg concentration was 53 mmol l^{-1} [7] and seawater tHg concentration 0.80 pmol l-1 (taken from the median of the entire Atlantic Ocean concentration reported in the literature, **Extended data Fig. 2**, **Extended data Tab. 1**). The linear regression displays a coefficient of determination R^2 = 0.91, a root mean squared error (RMSE) = 758, a 90% confidence interval of 1,635 and a standard deviation calculated from the confidence interval of 497.14. The end member tHg concentration is reported in the main text as ± the standard deviation.

Dilution factor

A Monte-Carlo simulation was done to account for the error propagation of the calculation of the dilution factor. Input assumptions for the Monte-Carlo simulation were as follows: tMn vent fluid end member concentration of 0.43 ± 0.0639 mmol l^{-1} (with the ± calculated from 95% confidence interval of the regression line reported in Findlay et al., 2015), dMn in the deep North Atlantic Ocean of 0.15 nmol l^{-1} [8], and dMn in the plume waters as reported in Gonzalez-Santana et al.,2020 [9]. The used standard deviation of the dMn in seawater and plume waters was 0.02 nmol l^{-1} taken from the value reported in Gonzalez-Santana et al.,2020. The final standard deviation of the Monte-Carlo simulation was 1,402. The error at a 95% confidence interval is 2,744. The dilution factor is reported in the main text as ± the standard deviation.

References

7. Damm, K. L. V. *et al.* Chemistry of submarine hydrothermal solutions at 21 °N, East Pacific Rise. *Geochim Cosmochim Ac* **49**, 2197–2220 (1985).

8. Hatta, M. *et al.* An overview of dissolved Fe and Mn distributions during the 2010–2011 U.S. GEOTRACES north Atlantic cruises: GEOTRACES GA03. *Deep Sea Res Part Ii Top Stud Oceanogr* **116**, 117–129 (2015).

9. González-Santana, D. *et al.* Processes Driving Iron and Manganese Dispersal From the TAG Hydrothermal Plume (Mid-Atlantic Ridge): Results From a GEOTRACES Process Study. *Frontiers Mar Sci* **7**, 568 (2020).