

# Atmospheric gaseous elemental mercury and its sea-air evasion fluxes from the Sea of Okhotsk to the South China Sea: results of cruise studies in 2019

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**ABSTRACT.** At present, the behavior of mercury in the sea-atmosphere system in the north western Pacific Ocean is poorly understood. From September to December 2019, continuous measurements of atmospheric gaseous elemental mercury (Hg(0)) and point measurements of Hg(0) evasion fluxes from the sea to the atmosphere were carried out during two adjacent cruises from the South China Sea to the Sea of Okhotsk. The median concentration of Hg(0) (1.1 ng/m<sup>3</sup>) was below both the background of the Northern Hemisphere and the average values previously recorded in these areas. There was a trend of increasing Hg(0) concentration with decreasing latitude. The Yellow Sea with adjacent territories and northeast China were the Hg(0) source area for the Sea of Japan and the Sea of Okhotsk. The Kuril sector of the Pacific Ocean was identified as a source of Hg(0) for the Sea of Okhotsk. East China, Southeast China and Indochina were sources of Hg(0) for the East China and South China seas. A winter increase in Hg(0) concentrations was observed in the Sea of Japan and the East China Sea. Our data showed significant relationships between Hg(0) fluxes, latitude, and water temperature.

**Keywords:** mercury, atmosphere, fluxes, marginal seas of the Pacific Ocean

## 1. Introduction

East and Southeast Asia, mainly China, is the largest exporter of anthropogenic mercury in the atmosphere (AMAP/UN Environment, 2019). Atmospheric transport of Hg(0) from China was previously observed in the South China Sea, East China Sea, Yellow Sea, and Sea of Japan (Wang Y. et al., 2017; Wang C. et al., 2016; Kalinchuk et al., 2021). Transport of Hg(0) from East Asia by westerly winds was recorded in North America (Jaffe et al., 2005). Apparently, mercury from East Asia can be transported by air masses into the atmosphere over the Sea of Okhotsk and, possibly, further north, but experimental confirmation of this phenomenon has not yet been obtained.

To identify the source regions that affect the concentrations of Hg(0) in the atmosphere over the marginal seas of the northwestern Pacific Ocean, we conducted a study covering the water area from the South China Sea to the Sea of Okhotsk during two adjacent cruises on board the R/V Akademik M.A. Lavrentev.

## 2. Materials and methods

Hg(0) concentrations in the atmosphere at a height of about 2 m above the sea surface were continuously measured using a RA915M analyzer (Lumex Ltd, St. Petersburg, Russia) with a detection limit of 0.1–0.2 ng/m<sup>3</sup> at a 30-minute averaging (Mashyanov et al., 2021). Ambient air was supplied to the analyzer through a 20 m Teflon hose. The air intake was installed in the bow of the vessel in such a way as to take air that had not yet come into contact with the vessel. For analysis, all data were combined into 1-hour values.

Additionally, continuous current data on meteorological and hydrological parameters were obtained using a Davis Vantage Pro weather station (Davis Instruments Corp., USA), SBE45 MicroTSG thermosalinograph (Sea-Bird Scientific, USA), and 10-AU-005-CE fluorimeter (Turner Designs, USA).

Hg(0) emission fluxes were measured using a mercury analyzer in combination with a dynamic flux chamber. Briefly, the standard method is based on the difference between the Hg(0) concentrations in the

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ambient air entering the chamber and the air leaving the chamber (Qureshi et al., 2012). We modified this method by using mercury-free air instead of ambient air entering the chamber (Kalinchuk et al., 2021). This approach is explained by the fact that the ship is a source of Hg(0) to the ambient air, which can distort the flux measurements.

To study the effect of air mass movement of Hg(0) concentrations at the measurement points and to identify areas potentially influenced by atmospheric Hg(0) concentrations in the studied seas, we used backward trajectory analysis and the concentration weighted trajectory (CWT) analysis, respectively.

The backward trajectories of air mass movement were calculated on the READY website using the model of a hybrid single-particle Lagrangian integrated trajectory (HYSPLIT) (Stein et al., 2015). CWT analysis was performed based on the formula presented by Cheng et al. (2015).

### 3. Results and discussion

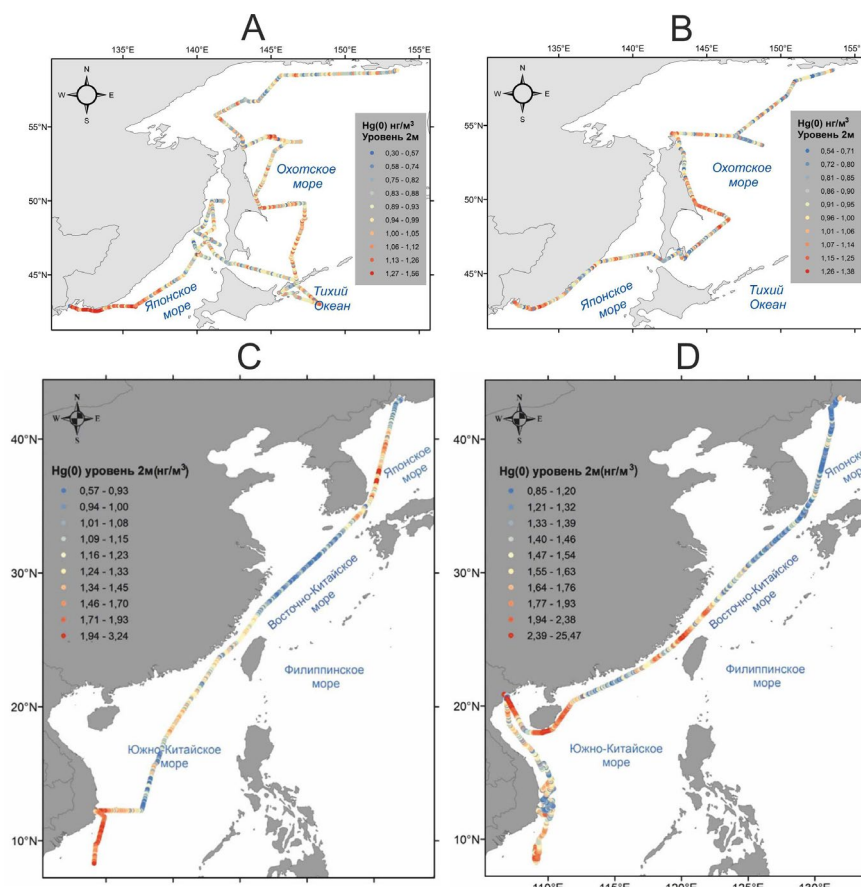
During the two expeditions, Hg(0) concentrations ranged from 0.5 to 2.98 ng/m<sup>3</sup> (N=1916) with mean ( $\pm$ SD) and median values of 1.23 ( $\pm$ 0.38) ng/m<sup>3</sup> and 1.09 ng/m<sup>3</sup>, respectively. As seen in Fig. 1, atmospheric Hg(0) concentrations over the marginal seas of the western Pacific decreased with increasing latitude. The highest concentrations were recorded in the South China Sea, and the lowest – in all water areas surveyed during the northern cruise. The decrease in Hg(0)

concentrations ranged from 5 to 12%, with an average of 8% for every 5 degrees from 10 to 55 degrees north latitude.

During the northern cruise, elevated CWT values were detected over northeastern China, southern Primorsky Krai (Russia), the Kuril sector of the Pacific Ocean, and the Sea of Okhotsk (Fig. 2). Atmospheric transport of Hg(0) from northeast China was repeatedly observed in the Sea of Japan and was likely associated with anthropogenic emissions (Kalinchuk et al., 2021). Elevated concentrations of Hg(0) were previously recorded over the Kuril sector of the Pacific Ocean, which were presumably caused either by volcanic emissions (Kalinchuk et al., 2019) or an increased flux of Hg(0) emissions from sea water in this region (Kalinchuk et al., 2021).

During the southern cruise, elevated CWT values were detected over the Korean Peninsula in the northwestern and southeastern parts. Higher CWT values were found above Pohang, a major industrial center in South Korea. The area extending from the southwestern coast of the Yellow Sea to southern Indochina was identified as the largest potential source region. Elevated CWT values over the South China Sea were likely caused by the spread of Hg(0) from continental sources. The release of Hg(0) from the sea into the atmosphere could be an additional impact.

Lower CWT values were identified over the Philippine Sea, the Yellow Sea, and northeast China. Although the latter, according to the northern cruise, was characterized by increased CWT values. This



**Fig.1.** Spatial distribution of Hg(0) concentrations in the atmosphere measured from September to December 2019. Letters A and B show the stages of the northern voyage from Vladivostok to the Sea of Okhotsk and back. Letters C and D designate the stages of the southern voyage from Vladivostok to the South China Sea and back.

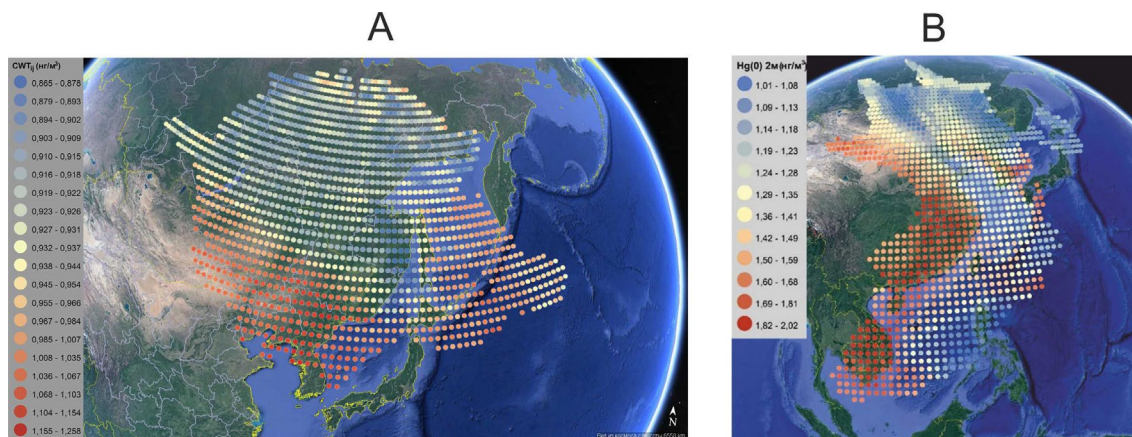


Fig.2. Distribution of the CWT values according to the data obtained in: A – northern cruise; B - southern cruise.

indicates that northeast China is a significant source region for areas north of it, but for more southerly areas it is a minor source.

During the two expeditions, Hg(0) fluxes varied from 0.6 to 2.5 ng/m<sup>2</sup>/h with an average value of 1.7 ± 0.6 ng/m<sup>2</sup>/h and a median of 1.6 ng/m<sup>2</sup>/h (Fig. 3). Lower values with a mean value of 1.2 ± 0.4 ng/m<sup>2</sup>/h and a median value of 1.3 ng/m<sup>2</sup>/h were observed during the northern cruise. The South China Sea was characterized by fluxes with mean and median values of 2.0 ± 0.5 ng/m<sup>2</sup>/h and 2.1 ng/m<sup>2</sup>/h, respectively. The highest positive correlation was found between Hg(0) flux and latitude (R<sup>2</sup>=0.46) and the highest negative correlation – between flux and water temperature (R<sup>2</sup>=0.48).

#### 4. Conclusions

In the Sea of Japan, Hg(0) concentrations increased with the arrival of air masses from northeast China and the Korean Peninsula. For the Sea of Okhotsk, the source area was the Kuril region and northeastern China with the Korean Peninsula. Northeast China and the Korean Peninsula were an important source of Hg(0) for the Sea of Japan and the Sea of Okhotsk, while they were a minor source for the East China and South China Seas. For these two seas, the most significant potential source area was the vast area from the southwestern coast of the Yellow Sea to southern Indochina. In the

marginal seas of the northwestern part of the Pacific Ocean, there was a trend towards a decrease in Hg(0) concentrations from south to north.

Hg(0) emission fluxes showed a similar trend. The fluxes had a positive relationship with the water temperature and a negative relationship with the latitude. Presumably, such relationships could be due to the combined action of two factors: i) the effect of water temperature on the formation of dissolved Hg(0) and the rate of its diffusion; ii) an increase in anthropogenic mercury emission in southern latitudes, followed by the precipitation of elevated concentrations of oxidized mercury from the atmosphere and its transformation into dissolved Hg(0) in seawater.

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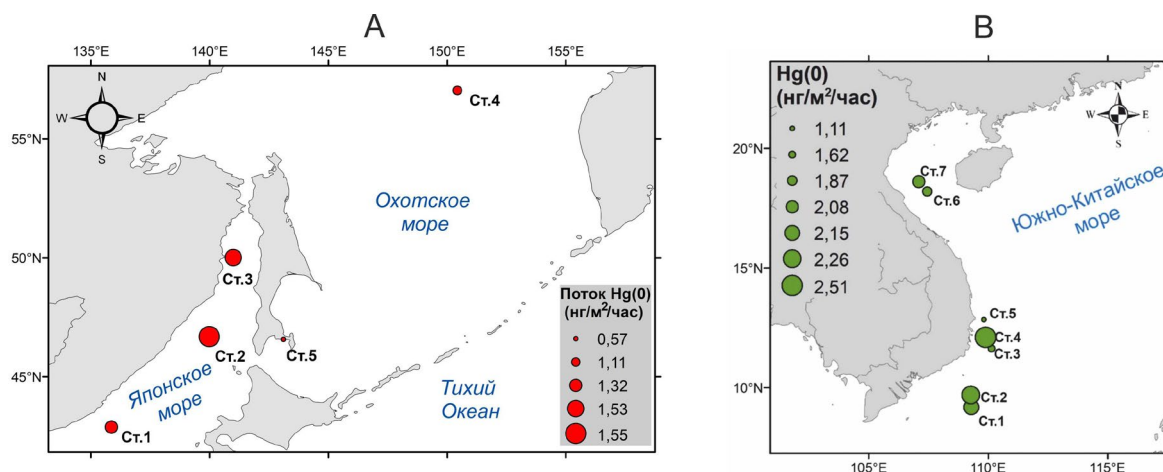


Fig.3. Hg(0) emission fluxes measured in September to December 2019.

## Conflict of interest

The authors declare no conflict of interest.

## References

AMAP/UN Environment. 2019. Technical Background Report for the Global Mercury Assessment 2018. Arctic Monitoring and Assessment Programme, Oslo, Norway/UN Environment Programme, Chemicals and Health Branch, Geneva, Switzerland.

Cheng I., Xu X., Zhang L. 2015. Overview of receptor-based source apportionment studies for speciated atmospheric mercury. *Atmospheric Chemistry and Physics* 15: 7877-7895. DOI: [10.5194/acp-15-7877-2015](https://doi.org/10.5194/acp-15-7877-2015)

Jaffe D., Prestbo E., Swartzendruber P. et al. 2005. Export of atmospheric mercury from Asia. *Atmospheric Environment* 39: 3029-3038. DOI: [10.1016/J.ATMOSENV.2005.01.030](https://doi.org/10.1016/J.ATMOSENV.2005.01.030)

Kalinchuk V., Aksentov K., Karnaukh V. 2019. Gaseous elemental mercury (Hg(0)) in the surface air over the Sea of Japan, the Sea of Okhotsk and the Kuril-Kamchatka sector of the Pacific Ocean in August - September 2017. *Chemosphere* 224: 668-679. DOI: [10.1016/j.chemosphere.2019.02.185](https://doi.org/10.1016/j.chemosphere.2019.02.185)

Kalinchuk V.V., Lopatnikov E.A., Astakhov A.S. et al. 2021. Distribution of atmospheric gaseous elemental mercury (Hg(0)) from the Sea of Japan to the Arctic, and Hg(0) evasion

fluxes in the Eastern Arctic Seas : results from a joint Russian-Chinese cruise in fall 2018. *Science of the Total Environment* 753: 142003. DOI: [10.1016/j.scitotenv.2020.142003](https://doi.org/10.1016/j.scitotenv.2020.142003)

Mashyanov N., Obolkin V., Pogarev S. et al. 2021. Air mercury monitoring at the Baikal area. *Atmosphere* 12: 807. DOI: [10.3390/atmos12070807](https://doi.org/10.3390/atmos12070807)

Qureshi A., Macleod M., Sunderland E. 2012. Exchange of elemental mercury between the oceans and the atmosphere. In: Liu G., Cai Y., O'Driscoll N. (Eds.), *Environmental chemistry and toxicology of mercury*. New York: Wiley, pp. 389-421. DOI: [10.1002/9781118146644.ch12](https://doi.org/10.1002/9781118146644.ch12)

Stein A.F., Draxler R.R., Rolph G.D. et al. 2015. NOAA's HYSPLIT atmospheric transport and dispersion modeling system. *Bulletin of the American Meteorological Society* 96: 2059-2077. DOI: [10.1175/BAMS-D-14-00110.1](https://doi.org/10.1175/BAMS-D-14-00110.1)

Wang C., Wang Z., Ci Z. et al. 2016. Spatial-temporal distributions of gaseous element mercury and particulate mercury in the Asian marine boundary layer. *Atmospheric Environment* 126: 107-116. DOI: [10.1016/J.ATMOSENV.2015.11.036](https://doi.org/10.1016/J.ATMOSENV.2015.11.036)

Wang Y., Liu R., Li Y. et al. 2017. GEM in the marine atmosphere and air-sea exchange of Hg during late autumn and winter cruise campaigns over the marginal seas of China. *Atmospheric Research* 191: 84-93. DOI: [10.1016/J.ATMOSRES.2017.03.004](https://doi.org/10.1016/J.ATMOSRES.2017.03.004)