Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
www.limnolfwbiol.com

Geochronology of mercury distribution in the bottom sediments of Inkerman Bay (Sevastopol Bay)

Stetsiuk A.P.

A.O. Kovalevsky Institute of Biology of the Southern Seas of RAS, Sevastopol, Nakhimov Ave, 2, 299011, Russia

ABSTRACT. Geochronological reconstruction revealed the mercury pollution in the water area of Inkerman Bay between 2002 to 2021. Mercury concentrations in the profile of bottom sediments in this water area ranged from 99.0 to 264.1 μg·kg^{-1}. The studies indicated that the largest mercury influx occurred in 2016 and 2017. The sorption saturation limit of the water area was not exceeded and amounted to 9.6% relative to the maximum value. The mercury deposition flux into the bottom sediments, which was calculated based on the geochronology of mercury distribution, was 0.6 kg·year^{-1}.

Keywords: mercury, bottom sediments, Inkerman Bay, Sevastopol Bay, Black Sea

1. Introduction

Inkerman Bay was artificially created in 1955 to 1961 and is currently the apex of Sevastopol Bay at the confluence of the Chyornaya River (Boltachyov et al., 2010). Inkerman Bay was formed as an estuary with special hydrodynamic conditions and an ecotone. As the sea current removes the silt brought by the river, the bottom sediments in this water area mainly consist of soft ooze (Kostova and Ivanov, 2009). Various hydrodynamic, physicochemical and biological phenomena occur at the river-sea hydrological barrier: slowdown of the flow of river waters, their dilution and saturation with sea salts, sedimentation of large fractions of suspended matter, coagulation of fine clay particles, physicochemical interaction of substances, which is not reduced to simple dilution (flocculation of organic matter and metals, sorption-desorption), and rapid development of production processes (Lisitsyn et al., 1983). The water of the Chyornaya River that inflows to the apex of the Sevastopol Bay near Inkerman carries an additional amount of nutrients and pollutants. The river-sea boundary plays the role of an important geochemical barrier, at which the bulk of suspended matter and diluted material is deposited, and chemical elements transform (Gordeev, 1983). In particular, most of the produced monomethylmercury is ultimately removed by deposition (Mason, 1993).

Inkerman Bay is well protected from the waves of the Black Sea, due to which it serves as a depot for various pollutants. Biogeochemical activity of the river-sea barrier zone is largely associated with the accumulation of living and non-living organic matter, mineral components and related trace elements there. At the same time, natural and anthropogenic metals can serve as specific indicators of anthropogenic pollution as well as convenient markers of natural biogeochemical processes. The layer-by-layer study of the core of bottom sediments can provide the chronology of the mercury influx as well as an assessment of the ability of the waters to self-clean.

The study of the mercury distribution in water is due to the high spatiotemporal variability of mercury concentration, depending on the seasonal changes in the river runoff and the development of phytoplankton communities. Therefore, to study the long-term dynamics of mercury accumulation processes in bottom sediments, geochronological methods are the most convenient to use.

The aim of this study was to geochronologically reconstruct mercury deposition in the bottom sediments of Inkerman Bay as well as to calculate mercury fluxes into the bottom sediments. In this regard, the following tasks were solved: determining the vertical distribution of mercury concentrations in the bottom sediments and calculating the fluxes of mercury deposition into the bottom sediments as criteria for estimating water quality in relation to mercury in Sevastopol Bay.

2. Materials and methods

Bottom sediments were sampled in May 2021 from Inkerman Bay. The cores of the bottom sediments were dissected into horizontal 1 cm thick layers under laboratory conditions using a piston extruder. The

*Corresponding author.
E-mail address: alex-ra-777@mail.ru (A.P. Stetsiuk)

Received: June 17, 2022; ***Accepted:*** June 21, 2022;
Available online: July 31, 2022

preparation of the bottom sediment samples for the Hg determination was carried out according to GOST 26927-86. Hg concentration was determined by cold vapor atomic absorption spectroscopy on a Hiranuma-1 analyzer. The accuracy of the analysis results was controlled using state standard reference samples of the composition of the sod-podzolic sandy loam soil (SDPS-1). To determine the age of the layers of the bottom sediments, the average sedimentation rate of 7094 $g \cdot m^{-2} \cdot year^{-1}$ was used, which was calculated by S.B. Gulin with ^{137}Cs based on gamma ray spectrometry analysis. The average sedimentation rate was 9.3 $mm \cdot year^{-1}$ (Egorov et al., 2018).

3. Results and discussion

The distribution of mercury concentrations in the column of the bottom sediments was heterogeneous. The highest concentration was detected in the 4-5 cm layer and amounted to 264.1 $\mu g \cdot kg^{-1}$ (hereinafter on a dry basis). According to the geochronology, the layer corresponded to 2016 and 2017 (Fig. 1).

Subsequently, the mercury concentration, in general, decreased monotonously from 199.3 $\mu g \cdot kg^{-1}$ in the 5-6 cm layer (2015-2016) to 164.0 $\mu g \cdot kg^{-1}$ in the 13-14 cm layer (2007-2008) and down to the minimum value of 99.0 $\mu g \cdot kg^{-1}$ at a depth of 17-18 cm (2002-2003) (Fig. 1).

According to the literature, the natural concentration of total mercury in marine shelf bottom sediments is 100 $\mu g \cdot kg^{-1}$ (Prokofiev and Stepanchenko, 1981). The NeueNiederlandischeListe standard is 300 $\mu g \cdot kg^{-1}$, which was not exceeded in this study (Neue Niederlandische Liste, 3/95). Also, mercury concentration can be estimated from the sorption saturation limit calculated for Sevastopol Bay and accounting for 2740 $\mu g \cdot kg^{-1}$ (Kostova et al., 2001), which is a more adequate estimate for high mercury concentrations. With the maximum mercury concentration of 264.1 $\mu g \cdot kg^{-1}$ the sorption saturation limit was 9.6%. Compared to other water areas of Sevastopol Bay, this value was not critical as well as in the bottom sediments from the Gollandiya, Ravelin and Inkerman stations where, with the maximum mercury concentrations in the profile of the bottom sediments, the sorption saturation limits were 48.0, 34.6 and 8.9%, respectively. At the same time, in the water area of Pavlovsky Cape, the sorption saturation value, with the mercury concentration of 3179.1 $ng \cdot g^{-1}$ in 2002, exceeded the previously detected limit (Stetsiuk, 2021). Therefore, the degree of reaching sorption saturation limit can serve as an indicator of water pollution, as confirmed by the previous research conducted near Pavlovsky Cape that was designated as a critical zone (Kostova and Ivanov, 2009). Lower mercury concentrations in the bottom sediments of Inkerman Bay can be associated with a faster period of horizontal water exchange than in the central part of Sevastopol Bay (Egorov et al., 2018), leading to more significant effect of hydrological factor on self-cleaning of water in Inkerman Bay from mercury.

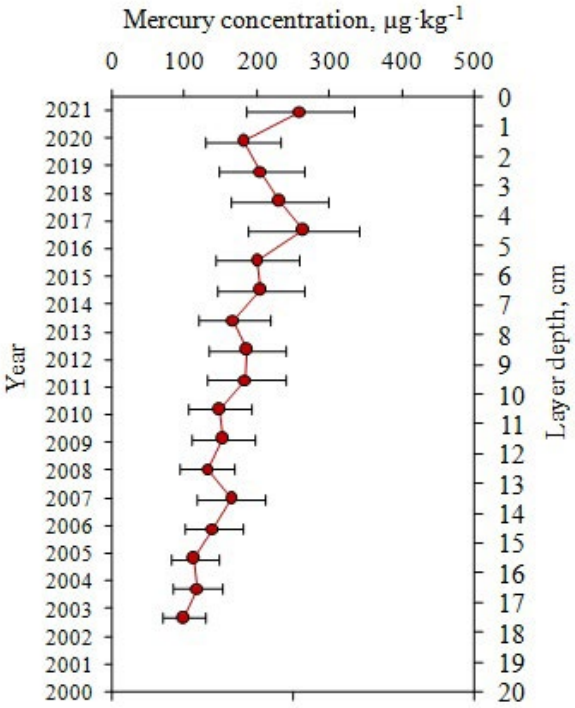

Fig.1. Profile of the mercury distribution in the bottom sediments of Inkerman Bay.

Water quality estimation in the water area can be based on mercury deposition fluxes into the bottom sediments (Egorov et al., 2018). Specific flux of pollutant deposition can be calculated by the following formula:

$$F_s = MAR \cdot C_{bs}, \quad (1)$$

where MAR (Mass Accumulation Rate) is the absolute mass of bottom sediments ($kg \cdot m^{-2} year^{-1}$), and C_{bs} is the pollutant concentration in the upper layer of the bottom sediments ($\mu g \cdot kg^{-1}$).

Hence, $F_{sHg} = 1836.6$ ($\mu g \cdot m^{-2} year^{-1}$).

Thereafter, the mercury flux in the entire Inkerman Bay was calculated by the following formula:

$$F_{Hg} = F_{sHg} \cdot S, \quad (2)$$

where S (m^2) is the water area = 322130 m^2 (Egorov et al., 2018).

Thus, the mercury deposition flux into the bottom sediments of Inkerman Bay was 0.6 $kg \cdot year^{-1}$, which was calculated for the upper layer corresponding to 2021. Variation of fluxes in 2002 to 2021 was 0.2 to 0.6 $kg \cdot year^{-1}$ (Fig. 2). This may indicate that during this period the water area of Inkerman Bay was self-cleaning from mercury with different intensities. The total mercury flux between 2002 and 2021 was 7.2 $kg \cdot year^{-1}$.

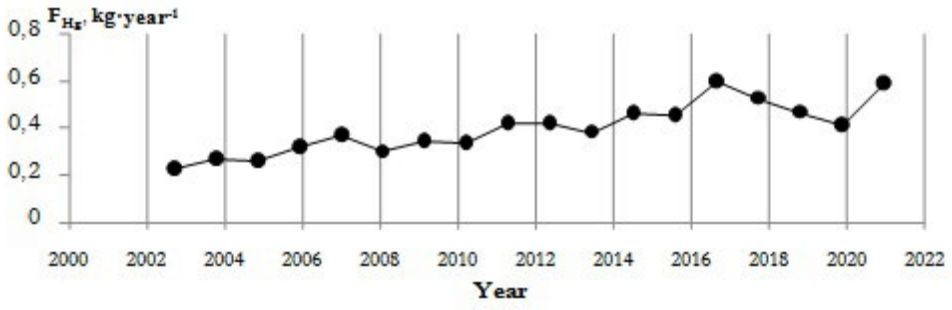

Fig.2. Mercury deposition fluxes (F_{Hg}) in the water area of Inkerman Bay

5. Conclusions

In summary, radiometric dating methods for the bottom sediments of Inkerman Bay allowed us to reconstruct in stages the chronology of mercury influx between 2002 and 2021. At the maximum mercury concentration of 264.1 μg·kg^{-1}, the sorption saturation limit in the studied water area was not reached, amounting to 9.6% with the deposition flux = 0.6 kg·year^{-1}.

Acknowledgements

The author thanks I.N. Moseichenko, lead engineer of the Department of Radiation and Chemical Biology at Institute of Biology of the Southern Seas of RAS, for sampling the cores of the bottom sediments.

This study was carried out within the framework of the State Project “Molismological and biogeochemical foundations of the homeostasis of marine ecosystems” (No. 121031500515-8).

Conflict of interest

The authors declare no conflict of interests.

References

Boltachyov A.R., Karpova E.P., Danilyuk O.N. 2010. Characteristics of thermohaline parameters and ichthyocene at the estuary of the Chyornaya River (Sevastopol Bay). Morskoy Ekologicheskiy Zhurnal [Marine Environmental Journal] 9(2): 23-36. (in Russian)

Gordeev V.V. 1983. Rechnoy stok v okean i cherty ego geokhimii [River runoff into the ocean and features of its geochemistry]. Moscow: Nauka. (in Russian)

Egorov V.N., Gulin S.B., Malakhova L.V. et al. 2018. Rating water quality in Sevastopol Bay by the fluxes of pollutant deposition in bottom sediments. Water Resources 45: 222-230. DOI: 10.1134/S0097807818020069

Prokofiev A.K., Stepanchenko T.V. 1981. In: Methods for the determination of toxic pollutants in sea water and bottom sediments. Collection of articles. Moscow: Gidrometeoizdat, pp. 34-42. (in Russian)

Kostova S.K., Ivanov V.E. 2009. Lithology and mercury contamination of bottom sediments in Sevastopol Bay (Black Sea). In: Geology, Geography and Ecology of the Ocean: International scientific conference dedicated to the 100th anniversary of D.G. Panov, p. 177. (in Russian)

Kostova S.K., Egorov V.N., Popovichev V.N. 2001. Long-term studies of mercury pollution in Sevastopol bays (Black Sea). Ekologiya Morya [Ecology of the Sea] 56: 99-103. (in Russian)

Lisitsyn A.P., Dyomina L.L., Gordeev V.V. 1983. Geokhimicheskiy barier reka-more i ego rol v osadochnom protsesse. Biogeokhimiya okeana [River-sea geochemical barrier and its role in the sedimentary process. Biogeochemistry of the ocean]. Moscow: Nauka, pp. 32-48. (in Russian)

Stetsiuk A.P. 2021. Use of the anthropogenic radionuclide, ^{137}Cs, for the geochronology of mercury distribution in the bottom sediments of Sevastopol bays. Study of aquatic and terrestrial ecosystems: history and modernity: abstracts of reports. In: International scientific conference dedicated to the 150th anniversary of Sevastopol Biological Station - A.O. Kovalevsky Institute of Biology of the Southern Seas and the 45th anniversary of the R/V “Professor Vodyanitsky”, pp. 556-557. (in Russian)

Mason R.P., Fitzgerald W.F., Hurley J. et al. 1993. Mercury biogeochemical cycling in a stratified estuary. Limnology and Oceanography. 38(6): 1227-1241. DOI: 10.4319/10.1993.38.6.1227

Neue Niederlandische Liste. Altlasten Spectrum 3/95.