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Mercury in paleoarchives as a proxy of environmental and climate changes

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ABSTRACT. The paper presents a case study of mercury in two types of paleoarchives: ice cores and prehistoric animal hair, to assess the potential of Hg using as a proxy for environmental and climate changes. Belukha ice core is well-suitable for reconstruction short-term and long-term Hg deposition, recording global and regional, natural and anthropogenic emissions as well as regional climate changes during 320 years. Hg concentrations in hair of mammoth fauna mammals reflect the variation in Hg level in the environment during period from 45 to 10 ka yr BP. Hg concentrations changes following climatic changes are in a good agreement with other paleoarchive data (Hg fluxes of the EPICA Dome C ice core and Lake Baikal sediments).

Keywords: mercury, paleoarchives, ice cores, animal hair, climate changes, proxy

1. Introduction

Proxy Data represent preserved physical characteristics of the environment that can be used for direct measurements. Proxy data from natural archives such as ice cores and ice caps, lake, marine and ocean sediments, peat bogs, tree rings, caves, and corals record information about climate variability and environmental changes. There are 3 main criteria for the suitability of an archive for paleoreconstructions: 1) Correlation between climatic and ecological changes in the environment and the concentration of marker in the corresponding layers (samples) of the natural archive; 2) Stability (or controlled change in concentration) of substances-markers throughout the lifetime of the archive; 3) Possibility to separate and identify layers (samples) with ensuring their reliable dating. Layers or rings store information about the climate and the state of the environment at the time of their formation, differing in temporal resolution (it can be a decade, a year, or growing season). Each type of archive has its own advantage and disadvantage. Ice cores from high altitude glacier are well-suited for studying anthropogenic influence and rapid climate changes, since they provide continuous records having high temporal resolution, but have rather short time interval. The oldest continuous ice core records date back 123,000 years in Greenland and 800,000 years in Antarctica. Antarctic ice cores are used to reconstruct past climate changes, while Greenland ice-core records are ideal for studying fast climate variations in the North Atlantic region (Steffensen et al., 2008) due to their well-constrained chronologies. The main limitations for ice cores are their location in remote sites (at high latitudes or high elevation hard to reach), the complexity of the work (cold and high mountain condition, climbing skills, expensive expedition), and special requirements for storage and analysis (ultra-clean protocol, low temperatures (bellow -20°C), expensive equipment, well-trained staff). Lake and marine sediments having a wide time interval are widely used to reconstruct past trends of climate and anthropogenic pollution, although there is delay of response and multifactor influence on it. Lake sediments accumulate Hg deposited directly on the lake surface itself and exported from the watershed to the lake. This is confirmed by the Hg isotopes analysis demonstrated that lake sediments contain a mix of both precipitation-derived Hg and vegetation-bound Hg (Chen et al., 2016). So small remote lakes with little watershed can reveal variability in the global atmospheric Hg cycle, while lakes located near industrial, or urban centers, mining, etc. will record local Hg emissions and its change through time. Most of marine sediments' researches are based on the sampling of surface sediments in bays and estuaries, identified Hg contamination from plants, waste discharges, shipyard activity, etc. Complexation by organic matter, binding to Fe-Mn oxides, hydrothermal emissions, river discharge, point pollution sources, competition with sulfides and methylation may play a significant role

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on the accumulation of Hg (Cooke et al., 2020). Peat bogs are the most widely used archive for researches of atmospheric Hg deposition, since in comparison with other environmental archives peatlands cover a broader spatial distribution (from the tropics to the high latitudes), have relatively high time-resolution and record atmospheric input (both dry and wet deposition). Although there are some problems such as fires influence, mobility/release of mercury after deposition, peat decomposition, and mire vegetation. Biester et al. (2007) stated that the lower background mercury accumulation rates in peat as compared to lake sediments is the result of nonquantitative retention and loss of mercury during peat diagenesis. Tree rings are active samplers of atmospheric Hg recording regional gradients in GEM concentrations; also they contain annual records of climate for centuries to millennia. Temporal consistency may vary within a geographic location due to differing biotic and abiotic factors influencing ring growth (Peckham et al., 2019). It should be noted that in addition to continuous natural archives, there are such “keepers of history” as hair which help to assess the level of environmental pollution by its impact on the body (Thompson et al., 2014). Hair presents the cumulative average exposure, so museum samples of animal and human hair, bird feathers were used for assessment environmental Hg pollution and anthropogenic impact on the environment. Thus, all considered environmental archives make it possible to reconstruct spatial and temporal patterns in atmospheric Hg deposition at different timescales, but their using requires an understanding of how each archive accumulates and retains Hg (Cooke et al., 2020).

2. Materials and methods

Whereas for the ice core analysis ultra-clean conditions and ultra-sensitive method of determination are decisive, for the hair analysis the most important points are optimization of pretreatment and digestion.

2.1. Ice core

In July 2001 a 139 m ice core was recovered at the Belukha glacier (49°48’26’’N, 86°34’43’’E, 4062 m a.s.l.), the highest mountain in the Altai region. Ice-core sections were transported frozen to the Paul Scherrer Institute (PSI, Switzerland) for glaciochemical analyses. 671 samples of ice and firn were prepared for Hg analyses in the cold room of the PSI at -20°C. Details of ice core cutting and decontamination procedure were described in the paper (Eyrikh et al., 2017). All field and analytical works were carried out in accordance with the “ultra-clean protocol”. Possible contamination of an ice core samples during sample preparation was tested using radial experiments using both artificial and real ice. Total Hg concentrations were determined by Mercur Duo Plus Analyzer (Analytik Jena, Germany) in accordance with the US EPA 1631 method. A certified reference material (ORMS-2, Natural Research Council Canada) and standard addition method were used to prove analytical accuracy. The recovery was 98-102% and the reproducibility 1-6%. The average limit of detection (LoD) was 0.04 ng/L.

2.2. Mammoth fauna mammals hear

Mercury was determined in seven specimens of mammoth fauna mammals: 4 woolly mammoths, 2 steppe bisons and 1 woolly rhino. Hair samples were obtained from the Geological Museum of DPMGI (Yakutsk). All the studied fossil mammals inhabited in Yakutia region in the period from 45 to 10 ka yr BP. Detailed description of fossil mammals (location and time of the discovery, estimation of the geological age by radiocarbon dating, calibrated age, sex and physiological age of the animal) and method of Hg analysis were presented in the paper (Eyrikh et al., 2020). It was necessary to select the optimal parameters at which there are no losses of volatile components and complete decomposition is achieved. Procedure of sample preparation (washing, cutting and microwave digestion) and Hg determination were developed and tested using hair samples of modern yak and Certified Reference Material of human hair (Hair DC 73347, China). Total Hg concentrations were determined by Mercur Duo Plus Analyzer (Analytik Jena, Germany). Method Detection Limit was 0.003 μg/g. The average uncertainty on duplicate sample analysis did not exceed 5%.

3. Results and discussion

3.1. Hg in the Belukha ice core

A high resolution paleoreconstruction from the Belukha ice core reflected the history of atmospheric deposition of Hg over a 320-year period. The concentration profile represents both prolonged mercury emission and short-term events (such as volcanic eruptions, dust storms, and anthropogenic accidents). The obtained results showed that the part of the core related to the period 1700-1900 mainly reflected the history of the regional mining and metallurgical industry of Rudny Altai in the 18-19 centuries (Fig. 1). Hg concentrations increased from 1740 to 1850 due to the contribution of the regional component, then from 1850 the regional contribution decreased and the global one increased, and after 1880 mercury concentrations mainly reflect the global atmospheric background. In the 20th century, trends in Hg concentrations and deposition fluxes are in a good agreement with other glaciers in the world, with the exception of the last 10 years, when an increase in Hg concentrations in the Belukha core revealed growing mercury emissions from Asian countries due to coal burning and small-scale gold mining (Eyrikh et al., 2017). Regional climate response following the Little Ice Age (LIA) is amplified as compared to the Northern Hemisphere average, most probably caused by the strong continentality of the Siberian Altai region (Henderson et al., 2006). Thus, the ice core reflects both regional and global environmental changes, as well as regional climate changes.

3.2. Hg in hairs of prehistorical animals

Such archives as wool and hair give a screening assessment in a certain period of time recording the cumulative mid- to long-term average exposure (depending on the length of the hair sample). The hair of mammoth fauna mammals is a screening material reflecting the environmental situation in the last year of their life, since the animal's hair is replaced by new one across 1-1.5 year. All prehistoric animals have low Hg level in their hair below concentrations associated with toxicity in wildlife and do not exceed background levels of mercury in hair of non-seafood consumers (0.5 μg/g). Most of Hg concentrations were within the reference range for modern cattle (Eyrikh et al., 2020). Hg concentrations in hair reflect the variation in Hg level in the environment following climatic changes. Increase of Hg concentration in hair during the coldest climatic stages (such as LGM) coincided rise of Hg deposition on the surface associated the highest atmospheric dust loads. Also mercury can release to the atmosphere because of permafrost thawing during interstadial warming, highest Hg concentration belongs to Karginian interstadial of the Late Pleistocene, the period when maximum insolation and warming was observed. Hg concentrations in mammoth fauna mammals related to different climatic periods are in a good agreement with Hg fluxes recorded in the EPICA Dome C ice core (Fig. 2A) and bottom sediments from Baikal (Fig. 2B) demonstrated the response of Hg cycle on the climate oscillates between cold and warm periods.

4. Conclusions

Mercury record from the Belukha ice core reflected both short-term and long-term Hg deposition preserved both global and regional impacts which contributions have varied considerably over time. Short-term climatic changes also were recorded in the studied ice core. Hg in hairs of prehistorical animals is new and promising proxy of environmental and climatic changes. It is prehistoric animals that can be the key to understanding the relationship of Hg level changes associated with climate changes. This is a big deal, especially since the extent of climate fluctuations across the Earth and regional differences in climate shifts are still unclear. At this point, there are a lot of Hg records recovered from natural archives for many regions of the world (such as Canada, USA, Europe), but for such huge regions as Russia more data are needed. Russia has a great potential for research of almost all kinds of natural archives. Reconstructed data on wide spatial-temporal scale will allow assessing past trends in atmospheric Hg deposition and distribution, identifying natural and anthropogenic sources involved in Hg cycling. Joint consideration of different records taking into account the strengths and weaknesses of each archive is a way to get better understanding of the processes and patterns influencing on Hg cycling and the response of Hg cycling on environmental and climate changes.

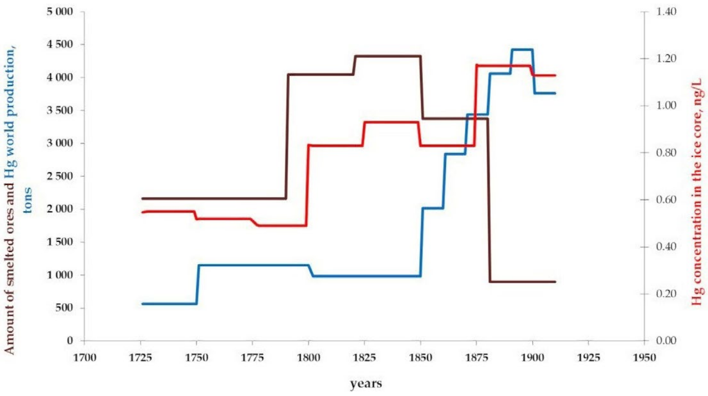

Fig.1. The amount of smelted ore (tons*10) in Altai mining district, world mercury production and average 25-year Hg concentrations record in the Belukha ice core.

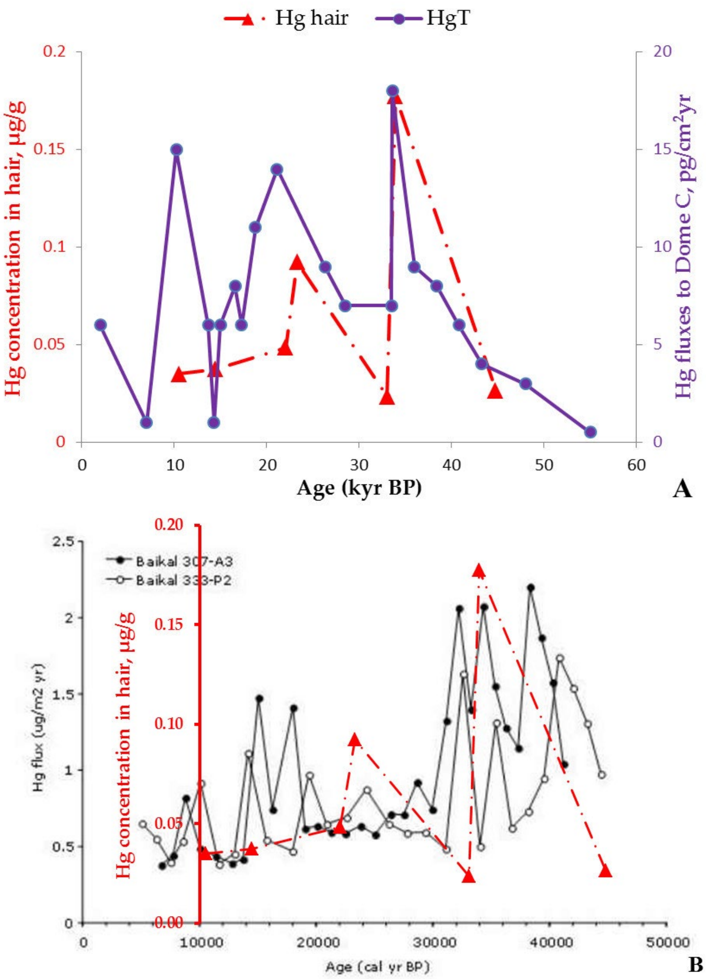

Fig.2. Total Hg concentrations in mammoth fauna mammals' hair and fluxes of total mercury (HgT) in the EPICA Dome C ice core (A) (data taken from Jitaru, 2009_SI) and Hg accumulation in Lake Baikal (B) (Lamborg, 2011).

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Conflict of interest

The authors declare no conflict of interest.

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