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Mercury in geological materials from Bulgaria: Significance, applications, new analytical capabilities, and initial results

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Живакът в геоложки материали от България: значение, приложения, нови аналитични уреди и първи резултати

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Abstract. The chemical properties of mercury (Hg) such as volatility, organic affinity, multiple oxidation states and extreme biotoxicity, determine its various industrial applications, but also health hazard concerns. Mercury data on geologic materials are important for characterizing the main sources and sinks of Hg, for tracking volcanic activity in the geology past, for refining regional and global stratigraphic correlations, and for minimizing anthropogenic mercury emissions. Newly obtained Hg and CHNS analyzers available at the Geological Institute at the Bulgarian Academy of Sciences, facilitate new geologic and environmental research in Bulgaria. Here we show initial results for the accuracy and precision of our Hg analyses based on repeated measurements of certified reference material NIST 2702 and identify avenues for further analytical improvements. The encouraging results allow for the initiation of diverse geological and ecological studies that are needed, but currently lacking in Bulgaria.

Keywords: mercury, geochemistry, geologic materials, applications.

Mercury in the environment

Mercury [Hg] is a chemical element with a complex geochemical and biogeochemical cycle (e.g., Fitzgerald, Lamborg, 2014). It is a silvery liquid at room temperatures, readily binds to sulfur into sulfide minerals, particularly cinnabar and sphalerite, and has affinity to organic matter. Mercury has numerous industrial applications in the chemical, pharmaceutical, mining and cement industries, dentistry, production of light bulbs, and others. However, mercury species, particularly the methylated ones are extremely toxic and harmful to all life. For example, exposure to volatile Hg leads to erethism, a serious neurological condition known in the past as “mad hatter disease”. Continuous release of methylated Hg species from industrial activity caused the infamous “Minamata disease” and numerous deaths in a Japanese community, prompting major international efforts for limiting Hg exposure to humans – the Minamata convention of 2013 (adopted by Bulgaria in 2017). The significance of Hg pollution is exacerbated by two intrinsic (bio)geochemical properties of mercury. First, volatility of reduced Hg species leads to release of Hg from a variety of natural and anthropogenic sources into the atmosphere and then into the oceans. Second, the organophilic nature of Hg and its multiple oxidation states (H^0, Hg^+ and Hg^{2+}) lead to biotic and abiotic methylation of Hg and accumulation of the neurotoxic methylmercury species in living tissues. Thus, Hg is enriched up the food web (biomagnification) and leads to harmful concentrations of Hg particularly in predator fish used for human consumption.

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Geologic and anthropogenic sources of Hg

Mercury is emitted to the atmosphere from natural sources including volcanism (the primary source of exogenic Hg emissions to the environment in pre-anthropogenic times), the oceans, biomass burning (wildfires), rock weathering, soil erosion, and from anthropogenic activities, which contribute significantly to present-day atmospheric and oceanic Hg budgets (Fitzgerald, Lamborg, 2014). Fossil fuel burning (primarily coal but also oil and others), cement manufacturing and waste incineration dominate anthropogenic Hg inputs (e.g., Pacyna et al., 2010).

Selected applications of Hg data

Elevated Hg content of sediments deposited during major volcanic eruptions represent one of the few chemical markers for volcanism in the geologic history. Because of Hg affiliation to sedimentary organic matter (e.g., Park et al., 2022), Hg anomalies are more informative when matched by concomitant peaks of Hg/TOC (total organic carbon) ratios. For example, uppermost Permian sedimentary successions deposited during the emplacement of the Permian–Triassic Siberian Traps contain distinct stratigraphic intervals of markedly elevated Hg contents (e.g., Georgiev et al., 2020). In another example, Hg enrichments in Toarcian sections from NW Bulgaria likely reflect the increased global Hg supply from the Karoo-Ferrar large igneous province (Metodiev et al., 2019). Because volcanic Hg is emitted to the atmosphere and is globally distributed, these Hg and Hg/TOC peaks are observed in most of the coeval sedimentary successions regardless of their proximity to the volcanic center, water depths, and depositional conditions. Therefore, Hg and Hg/TOC peaks in sedimentary rocks are increasingly used not only as markers for volcanic activity and its magnitude and duration, but also for regional and global correlations.

Apart from direct volcanic input of Hg, mercury enrichment also results from increased continental runoff associated with changing climatic conditions, either related (e.g., Them et al., 2019) or unrelated to volcanic eruptions and their CO_2 contribution. Therefore, trough changes in weathering rates, sedimentary Hg variations are broadly related to short- and long-term climate changes, hence Hg studies can be beneficial for understanding major environmental disruptions including glaciation/deglaciation cycles, mass extinctions and oceanic anoxic event.

The geochemical affinity of Hg to sulfur and the volatility of reduced Hg species allow the practical use of Hg data in soils and surface sediments as a geochemical exploration tool for geothermal prospects (e.g., van Kooten, 1987) and for base and precious metal ore bodies (e.g., Lentz, 2005). Similar approach uses the Hg concentration in living plants as a biogeochemical exploration tool for mineral deposits (e.g., Kovalevskii, 1986).

Efficient reduction of Hg emissions requires characterization of Hg contents in a variety of geologic materials, fuel, water, and soil. However, this characterization is incomplete and heterogeneously distributed with regards to sources of Hg (e.g., there are scarce global data on oils or biomass compared with coal). On a national level, several studies characterize Hg contents in selected Bulgarian coals and fly ashes (e.g., Kostova et al., 2016; Yossifova, Dimitrova, 2017; see also summary in Vassilev, Vassileva, 2023), but no data exists on crude oils, gasoline, or biofuels. At the same time, fossil fuel consumption dominates energy production in Bulgaria at present including coal (predominantly locally sourced; 27%), oil (25%), and natural gas (13%); biofuels contribute another 10% (source: International Energy Agency). Therefore, studies on Hg contents of these materials will provide a better understanding of local and regional Hg emissions. In addition, the knowledge on the sources and levels of natural Hg in the environment can be supplemented by geochemical (incl. Hg contents) results tracking the association and the re-distribution of anthropogenic Hg around potential Hg emitters from industrial activity.

New analytical capabilities and initial results

As part of a Hg-focused initiative, the Geological Institute at the Bulgarian Academy of Sciences obtained in 2023 two analytical instruments – a Dual-cell Double beam DMA-80 evo direct mercury analyzer (Milestone Inc) and a Flash*Smart* CHNS/O elemental analyzer (Thermo Scientific).

The DMA-80 evo is capable of directly analyzing mercury in solid, liquid, and gaseous samples without the need for chemical pretreatment of samples. The instrument is based on the principles of thermal decomposition, amalgamation, and atomic absorption detection. The accuracy and reproducibility of Hg analyses was evaluated through multiple measurements of certified reference material NIST 2702, marine sediment rich in organic matter (3.27 wt. % TOC) collected at the mouth of the Baltimore Harbor, USA. Our current results, using the factory calibration curve for quantifying Hg contents, average 459.6±27.8 ppb (n = 50; uncertainties reported as 1 SD), which overlaps the certified mean value and its range of 447.4±6.9 ppb (Fig. 1). These results are consistent both chronologically (Fig. 1a) and

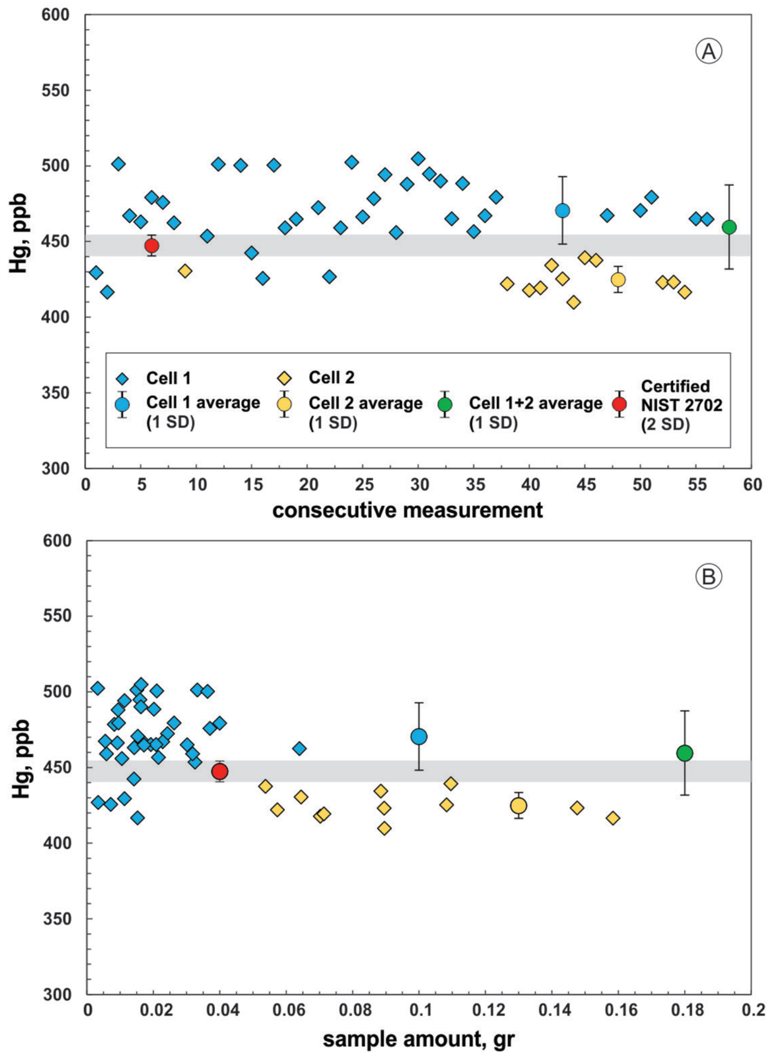

Fig. 1. Mercury contents in NIST 2702 measured by DMA-80 evo, factory calibration. Panel A shows results for consecutive measurements; Panel B shows measured mercury content versus the amount of analyzed powder (which defines the total amount of measured Hg per sample). SD is standard deviation.

across a range of sample weights and corresponding Hg loads (Fig. 1b). We observe consistently lower than certified values for Cell 2 (425±8.6 ppb) that is calibrated up to 1000 ng, while higher than certified values for Cell 1 (470.6±22.3 ppb) that is calibrated up to 15 ng. The results from Cell 2 show less scatter than Cell 1, although this could be attributed to fewer measurements for Cell 2. The better populated results from Cell 1 seem to stabilize with time: the last 5 analyses, which were measured in the same time interval as most of the Cell 2 analyses, produce more precise results (Fig. 1a). Custom-made calibrations for both cells, currently in progress, can further improve the accuracy/precision of the results.

In addition to quantifying Hg contents, understanding Hg mobility in the environment requires characterization of the geochemical affinity of Hg in the studied samples. This can partly be achieved through analyses of solid and liquid samples using the CHNS/O Flash*Smart* Elemental Analyzer (Thermo Scientific) that is based on the modified Dumas method for nitrogen, carbon, hydrogen, and sulfur determination (and oxygen determination by pyrolysis). This new equipment is currently being installed at GI-BAS.

Conclusions

In this contribution we highlight successful application of mercury data in geological and ecological studies. New analytical capabilities at the Geological Institute at the Bulgarian Academy of Sciences include a Hg analyzer and a CHNS analyzer, both capable of measuring the elemental contents in liquid and solid samples; Hg contents can be analyzed in gaseous samples as well. The initial test of the Hg analyzer using an organic-rich sediment reference standard NIST 2702 show encouraging results for precision and accuracy, with further avenues for improvements enroute.

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