

Silver isotopes: A tool to trace anthropogenic contamination

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Little is known about the stable isotopes of silver (Ag) in the environment, its fate and geochemical behavior. Here, we report the concentration and isotopic data of Ag in a variety of ore and metallurgical samples and forest soils contaminated by Ag-Pb smelter emissions. Similar to Ag concentrations, we identified a wide range of $\delta^{109}\text{Ag}$ values (from -0.8 to +2.4‰), a ~3‰ spread, within the primary and secondary materials (i.e., galena, fly ash, slag, and matte). This phenomenon is apparently unrelated to Ag isotopic fractionation during the smelting process, but it reflects the initial $^{109}\text{Ag}/^{107}\text{Ag}$ signal in the ore mineral(s) and/or the specific type of ore genesis. The two studied soil profiles differed in Ag isotopic composition, but on the other hand they consistently showed significantly lighter Ag ($\leq +0.8\text{‰}$) of metallurgical origin in the upper horizons compared to the lower horizons and bedrock, with low amounts of Ag depleted of ^{107}Ag ($\leq +2.9\text{‰}$). This isotopic pattern can be attributed to a ternary mixing relationship involving two major anthropogenic Ag components and a minor contribution of geogenic Ag. Accordingly, we did not observe post-depositional isotopic fractionation in our soils, because Ag was geochemically stable and was not subjected to leaching. In conclusion, Ag isotopes have the potential to track changes in anthropogenic phases, monitor specific geochemical processes, and are clearly applicable as anthropogenic Ag source/load proxies [1].

[1] Vaněk, A., Vaňková, M., Mihaljevič, M., Ettler, V., Drahot, P., Vondrovicová, L., Vokurková, P., Galušková, I., Zádorová, T., Mathur, R. (2023), *Environmental Pollution* 337, 122557. DOI: 10.1016/j.envpol.2023.122557.