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Distribution of geogenic and anthropogenic rare earth elements and yttrium in water and mussels from the Danube River System

KERAN ZHANG, ANNA-LENA ZOCHER, ADDIS KOKEB ALEMU, FRANZISKA KLIMPEL AND MICHAEL BAU

CritMET, School of Science, Constructor University Bremen gGmbH

Presenting Author: keranzh1995@gmail.com

Rare Earths and Yttrium (REY) are vital components of numerous high-technology products and are currently considered as “critical raw materials” due to supply risks and limited availability. However, their widespread use also results in increasing release into the environment. Thus, REY are now also considered as emerging contaminants in the hydrosphere. The quasi omnipresence of anthropogenic REY released from domestic or industrial effluents is well-documented. Despite recent investigations of the (eco)toxicity of REY and their compounds, their environmental fate and mechanisms of bioaccumulation remain unclear. Furthermore, a systematic overview on the distribution of both geogenic and anthropogenic REY in water and organisms from Danube River basin is still lacking. Thus, we studied water and organisms (mussels) from the Danube River and its major tributaries between its headwaters in southwestern Germany and downstream of Belgrade, Serbia. We focus on the concentration and distribution of REY in 0.2 µm-filtered water samples, in the shells of four different mussel species, and on the tissue and shells of *Anodonta anatina* mussels. All samples were matrix-separated and REY-preconcentrated prior to ICP-MS measurements. Analytical quality was monitored by analysing appropriate certified reference materials.

Except for pristine headwater samples close to the respective springs, filtered water samples display similar shale-normalized REY patterns that increase from the LREY to the HREY. As typically encountered for river water in countries with well-developed health care system, anthropogenic Gd is ubiquitous due to the presence of Gd-based MRI contrast agents, particularly in densely populated metropolitan areas. All biological samples are slightly MREY-enriched, but do not show any positive Gd anomaly, suggesting the biounavailability of the Gd-based contrast agents. Compared to the respective ambient water, REY concentrations are between three to five orders of magnitude higher in the biological samples, confirming significant bioaccumulation of REY. Preferential uptake of LREY relative to HREY is observed for tissue samples and the shells, possibly due to more stable complexation of HREY with dissolved ligands.