Riverine HFSE geochemistry and the Hf isotopic flux to the ocean: Two examples from Iceland and Germany

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Rivers are commonly assumed to be the major source of the particle-reactive elements Zr, Hf, Nb, and Ta to the oceans. However, only little data are available and sound knowledge about the net riverine fluxes of these elements from the continent into the ocean at different geological and environmental conditions is limited. The role of continental weathering and runoff in controlling the Hf isotopic composition of seawater (with its more radiogenic εHf for a given εNd relative to igneous rocks) is of specific interest. We here present high precision HFSE concentration and Hf (and Nd) isotope data for the particulate, dissolved (which includes nanoparticles/colloids <200 nm), and truly dissolved (<1KDa) fractions in the polar Markafljöt River, Iceland, which is dominated by inorganic nanoparticles derived from volcanic ash, and in the temperate Weser River, Germany, with its mix of organic and inorganic nanoparticles. For the first time these data provide detailed insight into the distribution of these elements between the different physical trace element pools. During estuarine mixing the colloidal and truly dissolved pools are differently affected, and the elemental and isotopic composition of the truly dissolved pool may play an important role in determining the riverine flux to the ocean.

The two rivers are characterized by very different HFSE signatures. Whereas in the Weser River, 10 - 20% of the HFSE are truly dissolved and 80 - 90% are bound to colloids/nanoparticles, almost 100% of HFSE in the Markafljöt River are bound to inorganic colloids >10 KDa. The subchondritic dissolved Zr/Hf (25.4) and subchondritic dissolved Nb/Ta ratio (17.6) in the Markafljöt River contrast with the slightly superchondritic dissolved Zr/Hf (42) and strongly subchondritic dissolved Nb/Ta ratio (1.7) in the Weser River. Compared to the dissolved pool (42), the Zr/Hf ratio of the truly dissolved pool (13) in the Weser River is significantly lower. The isotope composition of dissolved (<200 nm) Hf of the Markafljöt River is 12.1 , ε-units, which is similar to that of rocks in the catchment. In the Weser River, the dissolved εHf is 3.2, whereas the truly dissolved εHf is -4, i.e., considerably less radiogenic.