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Natural and anthropogenic rare earth elements in Lago de Paranoá, Brasilia, Brazil

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Rare earth elements (REE) belong to the group of particle reactive elements and occur at ultratrace levels in natural waters. They are exclusively trivalent, but Ce and Eu can also be tetravalent and divalent, respectively, depending on the redox-level, the pH and the temperature of the fluid. Due to these redox changes, normalized REE patterns may show Ce and/or Eu anomalies. Recently, these high-tech metals raised significant public attention, as they are of great economic importance and consumption and hence release into the environment increased sharply.
The most prominent example of a REE contamination is anthropogenic Gd, which is derived from Gd-based contrast agents used in magnetic resonance imaging. Due to their high stabilities, these compounds are not readily removed by commonly applied waste water treatment technologies and, therefore, are released from treatment plants into surface and ground waters. Hence, this anthropogenic Gd can be used as a tracer for the presence of waste water-derived substances such as pharmaceuticals and personal care products in river, lake, ground and tap waters.
Lago de Paranoá is an artificial reservoir lake in the city of Brasilia, Brazil, and is currently considered a potential freshwater resource. The city's two waste water treatment plants are located on its shore and their effluents are discharged into the lake. To investigate the level of contamination, we took water samples at 11 stations in the lake and compared the REE concentrations in unfiltered and filtered (<200 nm) lake water. The unfiltered water samples show light REE enrichment (LaSN/YbSN: 1.37-1.98) and high REE concentrations (Sum REE: 192 – 476 ng/L), while the unfiltered water samples are heavy REE enriched (LaSN/YbSN: 0.15-0.61) at lower concentrations (Sum REE: 50 – 85 ng/L). This is due to the fact that light REE are preferentially bound to particle surfaces, while the heavy REE are preferentially complexed with ligands in solution.
In marked contrast to the filtered samples, REE patterns of the unfiltered waters show a positive anomaly of redox-sensitive Ce. This reveals oxidative scavenging of Ce onto particles in the lake water. As lithic particles, such as atmospheric dust, do not show positive Ce anomalies, the particles responsible for Ce oxidation are either inorganic Mn or Fe (oxyhydr-) oxides or organic particulates, which are known to oxidatively scavenge Ce.
All samples show pronounced positive Gd anomalies, revealing the presence of waste water-derived anthropogenic Gd in the lake waters. Because the anthropogenic Gd is bound to a very stable water-soluble chemical complex, it does not react with particles. Hence, both the filtered and unfiltered samples show REE patterns with a similar-sized positive Gd anomaly. The presence of anthropogenic Gd indicates that other waste water-derived substances of potentially high (eco-) toxicity may also be present in the lake water. This needs to be further investigated and monitored before using the lake water as a drinking water resource.