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Schweizerisches Zentrum für angewandte Ökotoxikologie
Centre Suisse d'écotoxicologie appliquée
Eawag-EPFL

Ecotoxicity of rare earth elements

Info Sheet

Rare earth elements (REEs) or rare earth metals is the common name given to 15 chemically similar periodic elements of the lanthanide family, scandium and yttrium[1] . The term is a misnomer arising from the rarity of the minerals from which they were originally isolated. Actually, most rare earth elements exist in the Earth's crust in higher concentrations than silver or mercury but there are few locations around the globe where they can be economically mined. Even though most people have never heard of rare earth elements, several of them govern mankind's modern lifestyle, being essential ingredients of electronic, clean energy, and military technological devices.

The REE's are grouped together as they display similar chemical properties, in particular the ability to readily discharge and accept electrons, making them indispensable and non-replaceable in many electronic, optical, magnetic and catalytic applications. So far, the ecotoxicological properties of these metals and their potential impacts when released into the environment are little known.

Use

The largest share of the REE market (mainly lanthanum and cerium) goes to catalysts used in oil refinery and in automotive converters that transform the primary pollutants in engine exhaust gases into non-toxic substances. REEs are also used in rechargeable batteries of hybrid cars and in wind turbines, and in numerous nuclear energy and defence technologies. In addition, REEs have many medical applications. For example, gadolinium is the most commonly used contrast agent in magnetic resonance imaging for tumour diagnosis. As phosphors, REEs are an important component of energy efficient light bulbs, and they are also used in optics, glass fibres, and lasers for cosmetics, dentistry, and surgical procedures.

In small quantities, REEs are used in a wide range of consumer products such as earphones, computer hard disks, screens, DVD drives, televisions and many other visual display devices. Phosphate fertilizers, if derived from apatite, also contain appreciable amounts of REEs. Lanthanum and cerium have been added as trace supplements to fertilizers for agriculture in China, where they have also been applied as food supplements in animal husbandry. In addition, many new technologies using REEs have been developed, including fuel cells, electromagnetic refrigeration, and new water treatment technologies both for drinking water and wastewater from mining or smelting industries.

Fate and exposure in ecosystems

REEs are primarily discharged into water and air during mining and subsequent refining processes, but also as a consequence of their use as catalysts in oil-fired power stations and vehicles. In addition, the application of fertilisers containing REEs or of manure from animals fed REE supplements may lead to their accumulation in agricultural soils.

So far, the most extensive anthropogenic release of REEs to the environment is that of gadolinium (Gd) into surface waters. Anthropogenic Gd mainly originates from contrast agents used in medical diagnosis and gets into surface waters through effluents from wastewater treatment plants. Since the anthropogenic enrichment of Gd in the Rhine river was first reported in the mid-1990s, Gd has been detected worldwide in rivers and estuaries, coastal seawaters, ground waters and tap water.

A recent study described significant contamination of lanthanum and samarium in the river Rhine, originating from a production plant of catalysts for petroleum refining near Worms (Germany). Both elements could be traced through the Middle and Lower Rhine to the Netherlands. Because some REE complexes such as carbonates, phosphates and fluorides are poorly soluble, REEs from surface waters tend to accumulate in sediments. So far, the environmental concentrations of REEs are regulated neither in the EU nor in Switzerland.

Ecotoxicological effects

Like other metals, anthropogenic REEs usually enter the environment in much more soluble and reactive forms than naturally occurring REEs, making them more bioavailable. Little is known, however, about the bioaccumulation and toxicity of REEs compared to heavy metals such as cadmium, copper, zinc or mercury. The ecotoxicological profile of REEs is similar to that of essential metals, which have stimulatory effects at low exposure concentrations and are increasingly toxic at higher concentrations. This phenomenon, observed in terrestrial and aquatic animals and plants, explains the growth-promoting effects of trace amounts of REEs. However, no essential role of REEs to humans, animals or plants has been attributed so far. At increasing exposure concentrations, REEs are mainly toxic because they disrupt biological processes by their displacement of calcium due to their similar size or by their high affinity for phosphate groups of biological macromolecules. This has been observed in a wide

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[1] Lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), scandium (Sc), and yttrium (Yt).

variety of organisms, suggesting that these mechanisms are not specific.

Because REEs are used in fertilizers, their uptake, accumulation and potential effects have been studied in more detail in soil organisms and plants than in aquatic organisms. Certain soil microorganisms can easily absorb REE ions. It has been shown that the ecological structure of microorganisms in soil may be changed at high REE concentrations, although the effects are smaller than those of heavy metals. The REE transfer from soil into plants seems to be very low but the results are controversial, indicating that the accumulation in plants varies with the application method.

Aquatic plants can easily bioaccumulate REEs even when they are exposed to low concentrations, but only low bioaccumulation has been observed in fish such as carp and tuna. The lethal concentrations (LC50) to freshwater zebrafish (*Danio rerio*) in short-term exposures range between 14 and 25 µg/L and the no observed effect concentrations (NOEC) in chronic exposures (30 days) between 1.2 and 3.8 µg/L, with yttrium (Yt) being slightly more toxic than the rest of REEs included in that study[2] .

In a study with marine bacteria (*Vibrio fischeri*) the heavier lanthanides were up to two orders of magnitude more toxic than the lighter ones, and their toxicity was of the same order as that of the metals cadmium, copper, lead and zinc. Because REE concentrations in natural waters are low due to their low solubility, toxic effects on biota are only expected under extreme conditions, for example in water with low pH and low ligand concentrations. REEs share common mechanisms of action and often substitute for each other. Therefore, it is not clear yet whether REEs should be evaluated as a group (such as PCBs) or individually in environmental risk assessment.

Literature

Kulaksız, S. and Bau, M. (2013) Anthropogenic dissolved and colloid/nanoparticle-bound samarium, lanthanum and gadolinium in the Rhine River and the impending destruction of the natural rare earth element distribution in rivers. *Earth and Planetary Science Letters*, 362, 43-50.

Useful links

Development of Environmental Quality Standards: Report from the Dutch National Institute of Public Health and the Environment
http://www.rivm.nl/bibliotheek/rapporten/601501011.html

Info page on rare earth elements of the US Geological Survey
http://www.usgs.gov/science/science.php?term=1553&type=theme

Website of the R&D activities on rare earth minerals and metals processing, including environmental aspects, of Natural Resources Canada.
http://www.nrcan.gc.ca/minerals-metals/technology/4475

Contact

Carmen Casado-Martinez, phone +41 21 693 0896,
carmen.casado@centreecotox.ch

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[2] For Yt, La, Ce, Pr, Nd, Sm, Gd, and Dy.