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# Examination of rare earth element concentration patterns in freshwater fish tissues

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## HIGHLIGHTS

- We surveyed rare earth element concentrations in different tissues of 10 freshwater fish species.
- Concentration patterns are summarized for different fish tissues.
- We examined concentration patterns for different ages and sizes of fish.
- Evaluated bioaccumulation potential of lanthanides in different species and tissues of fish.
- Report a large data set for fish that adds to limited information in the published literature.

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## ABSTRACT

Rare earth elements (REEs or lanthanides) were measured in ten freshwater fish species from a reservoir in Washington State (United States). The REE distribution patterns were examined within fillet and whole body tissues for three size classes. Total concentrations (ΣREE) ranged from 0.014 to 3.0 mg kg$^{-1}$ (dry weight) and averaged 0.243 mg kg$^{-1}$ (dry weight). Tissue concentration patterns indicated that REEs accumulated to a greater extent in organs, viscera, and bone compared to muscle (fillet) tissues. Benthic feeding species (exposed to sediments) exhibited greater concentrations of REEs than pelagic omnivorous or piscivorous fish species. Decreasing REE concentrations were found with increasing age, total length or weight for largescale and longnose suckers, smallmouth bass, and walleye. Concentration patterns in this system were consistent with natural conditions without anthropogenic sources of REEs. These data provide additional reference information with regard to the fate and transport of REEs in freshwater fish tissues in a large aquatic system.



## 1. Introduction

Rare earth elements (REEs or lanthanides) encompass a group of metals that are essential for emerging technologies (*e.g.*, cell phones, hybrid vehicles, and wind turbines). They include fifteen elements (atomic numbers 57 [lanthanum] through 71 [lutetium]) with similar physicochemical properties (Long et al., 2010; USEPA, 2012). Two additional elements (yttrium and scandium) share similar properties and often are found in minerals containing lanthanides (Long et al., 2010; USEPA, 2012). Currently, North America imports the majority of its REE supplies from China. Due to increasing demands for these elements, new mining ventures are under development to increase domestic supplies and alleviate global supply shortages (Long et al., 2010; USEPA, 2012).

Extraction and processing of rare earth element ores, that are essential for emerging technologies, can generate multiple waste streams that require complex environmental management systems. Improper waste management may alter the quality of the local environment (USEPA, 2011; 2012). For example, environmental alterations to surface soils, surface waters, and soil–plant systems have been documented in REE mining areas of China (see review by Liang et al., 2013). Processing of REE compounds (for petroleum refining) or utilization of REE-containing products (*e.g.*, gadolinium contrast agents or nanomaterials) may also result in the release of REEs to the environment (Karn, 2011; Kulaksız and Bau, 2011a, 2011b). USEPA (2012) has recognized that there is limited information with regard to health and environmental issues related to REEs. Therefore, further study of REEs in the

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environment and their transport is relevant, particularly in aquatic systems, where significant waste releases may occur (USEPA, 2012).

Relative to common metals (*e.g.*, arsenic, copper, lead, mercury, and zinc), few studies are available in the published literature regarding the aquatic toxicity or bioaccumulation characteristics of REEs. Existing studies have focused on the acute toxicity of selected lanthanides in aquatic invertebrates (*e.g.*, Barry and Meehan, 2000; Moermond et al., 2001; Borgmann et al., 2005; Oral et al., 2010; Zhang et al., 2012) or aquatic plants (*e.g.*, Tai et al., 2010; Weltje et al., 2002). Few studies have examined the aquatic toxicity to fish species (*e.g.*, Sneller et al., 2000; Hongyan et al., 2002; Cui et al., 2012). Rare earth elements may accumulate in aquatic organisms and generally exhibit lower bioaccumulation potential in fish species relative to aquatic plants (Qiang et al., 1994; Hao et al., 1996; Yang et al., 1999; Weltje et al., 2002). Further, bioaccumulation studies have demonstrated that REEs are concentrated in internal organs and the skeleton to a higher degree than in muscle tissues (Ennevor, 1994; Qiang et al., 1994; Hao et al., 1996; Tao et al., 2002).

Field studies reporting REE concentrations in fish are generally lacking, particularly for North American species (Barber et al., 2006; Guo et al., 2003; Hatcher et al., 1992; Korda et al., 1977). Therefore, additional information regarding lanthanide concentrations in varying fish species (and tissues) may be useful for characterizing the fate and transport of these elements in the environment. Rare earth element concentrations have been collected as part of an ongoing study in the State of Washington (United States [U.S.]). Objectives of this analysis were to characterize the concentrations of REEs within several freshwater fish species from a large reservoir. The authors investigated REE concentrations in tissues and their relationships with tissue type, size, and trophic group. Further, collection of surface water allowed for an examination of potential bioaccumulation patterns within this aquatic system.

## 2. Methods

### 2.1. Site description

The present environmental investigation focused on a large reservoir that lies within the State of Washington (WA). Within the U.S., the study area extends approximately 150 miles from the U.S.-Canada border to Grand Coulee Dam which forms a reservoir approximately 100 miles in length. Rare earth element deposits or industrial activities have not been documented in this area (Long et al., 2010); therefore, trace REE concentrations may be representative of natural mineralogical conditions or other anthropogenic inputs. Fish tissue and surface water sampling were conducted (as described below) to provide baseline environmental information for the area.

### 2.2. Fish sampling and analysis

Fish tissue sampling was conducted during September and October, 2009 from six collection areas throughout the reservoir. Fish were collected primarily by boat-mounted electrofishing and gill nets and a variety of additional sampling equipment (*e.g.*, backpack electrofishing, traps, hoop nets, and seines). Composite samples for target fish species were collected for three size classes (⩽150 mm, 150 to ⩽300 mm, and >300 mm). Samples included the following fish species: burbot (*Lota lota*), kokanee (*Oncorhynchus nerka*), longnose sucker (*Catostomus catostomus*), largescale sucker (*Catostomus macrocheilus*), lake whitefish (*Corgeonus clupeaformis*), mountain whitefish (*Prospium williamsoni*), rainbow trout (*Oncorhynchus mykiss*), smallmouth bass (*Micropterus dolomieui*), sculpin (*Cottus* sp.), and walleye (*Sander vitreum*). These species were selected to represent diverse feeding ecologies and are prey items of larger fish, wildlife, and/or sought by recreational anglers. Life histories have been detailed for these species by Wydoski and Whitney (2003). Largescale and longnose suckers are benthic species with varied diets including algal periphyton, aquatic invertebrates, and detritus. Sculpin species inhabit shallow reaches with gravel or cobble substrates and primarily feed on aquatic insects, benthic invertebrates, and fish eggs. Mountain whitefish and Lake whitefish primarily forage for bottom-dwelling insects (by overturning rocks and disturbing substrates). Rainbow trout and kokanee are primarily pelagic and feed on zooplankton and aquatic invertebrates. Smallmouth bass inhabit cool still waters and consume small aquatic invertebrates as juveniles and shift to primarily fish and crustaceans at adult size. Burbot and walleye are top-level predators that are primarily piscivorous but may consume some aquatic invertebrates. Burbot mainly feed in deeper waters while walleye mainly feed at or near the bottom (*i.e.*, in low-light) in shallow waters.

Whole body tissues were collected for the two smaller size classes (⩽150 mm, 150 to ⩽300 mm), while fillet (with skin) and carcass samples were collected for the largest size class (>300 mm). Carcass samples included the head, viscera, fins, skeleton, and musculature remaining after the fillet tissues were removed. Whole body concentrations for >300 mm composites were estimated from the fillet and carcass samples relative to the mass of each tissue type. In addition, the >300 mm samples for largescale and longnose suckers were analyzed without the gastrointestinal contents to limit bias due to sediments present in the digestive tract. Total length, weight and age (based on otoliths, scales, or opercula) were recorded for each fish collected. Up to five fish were included in each composite sample (for >300 mm) or higher to obtain sufficient mass for analytical chemistry (100–300 g), which included common metals, minor metals, pesticides, dioxins/furans, polycyclic aromatic hydrocarbons, polybrominated diphenyl ethers, polychlorinated biphenyls, and semi-volatile organics (not discussed herein). A summary of the tissue composite characteristics is provided in Supplemental Table S1. Rare earth metal concentrations were analyzed using inductively coupled plasma-mass spectrometry (ICP–MS, USEPA Method 6020). Chemistry data were independently validated to ensure data quality and accuracy. The following REEs were analyzed in tissue samples: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), scandium (Sc), and yttrium (Y).

### 2.3. Water sampling and analysis

Surface water sampling was conducted over three seasons to capture chemistry information during low and high flows (*i.e.*, September to October, 2009; February to April, 2010; and April to June, 2010). Nine transects were positioned along the reservoir and each transect included samples along each riverbank, the center of the river, near the surface (*i.e.*, 1 meter below water surface), and near the river bottom (*i.e.*, 1 meter above the river bottom). The same REEs were analyzed in filtered surface water samples, as in fish tissues, using ICP–MS (USEPA Method 6020). Water quality characteristics were also measured: pH and temperature (using a field multiparameter water quality sonde), hardness (Method SM2340B), and dissolved organic carbon (Method SM5310C). Surface water data were independently validated to ensure data quality and accuracy. Statistical analysis found no differences in metal concentrations between sampling rounds, therefore mean surface water concentrations from transects co-located with fish sample collection areas were matched to evaluate surface water and tissue