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Assessment of lanthanum and cerium pollution in the Shatt al-Arab River

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Abstract
The current study investigates the concentrations and bioaccumulation exponents (BAFs) of ten metal compounds such as cerium (Ce), lanthanum (La), iron (Fe), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), titanium (Ti), manganese (Mn), and phosphorus (P) from water and fish tissue samples of Iraq's Shatt Al-Arab River. Samples were collected as May of the year 2018 from four sites distributed over a course of the river employing matching methods and gear. The metal grades were determined through X-ray Fluorescence (XRF) technology with proper calibration or standardization of a measuring device and method and quality control measures to provide reliable occurrences. The BAFs were derived as the proportion of the metal focus in fish tissues to its fixation in water. Descriptive factual studies were carried out to deconstruct the information and establish the normal, highest, lowest, and standard deviation qualities of every component. Information analysis unravelled massive differences in focuses of certain heavy metals between water and fish tissue tests from differing locations. The highest BAF values were noted for calcium, followed by titanium, magnesium and sodium, with very high bioconcentration of these metals in fish from the waterway. Overall, the results of this study present valuable information on natural presentation and health hazards posed by exposure to metals in fish and water samples from Shatt Al-Arab River.

Keywords: Oil pollution, Lanthanum and Cerium, river pollution , XRF technique.

1. INTRODUCTION

Lanthanum (La) and cerium (Ce), classified as rare earth elements (REEs), exhibit calcium (Ca)-mimicking behavior in biological systems. However, their substitution for Ca often disrupts critical physiological processes, including blood coagulation, neural signaling, muscle contraction, and cellular communication. Despite their utility in medical and industrial applications—such as batteries, catalysts, and water treatment—their potential toxicity to human health and ecosystems necessitates careful risk assessment [1, 2]. La and Ce interfere with essential metabolic pathways, induce oxidative stress, alter nutrient uptake, and exhibit bioaccumulative tendencies, particularly in aquatic food webs. Their environmental persistence remains poorly characterized, especially following industrial discharge or improper waste disposal, complicating ecological risk evaluations [3, 4]. Toxicity thresholds for La and Ce vary significantly across species, exposure durations, and biological endpoints. For lanthanum, adverse effects occur at concentrations ranging from 0.018 mg/L to 277.8 mg/L, while cerium exhibits toxicity between 0.01 mg/L and 100 mg/L. Using species sensitivity distribution (SSD) and interspecies correlation estimation (ICE) models, acute water quality criteria (WQC) were established at 88 µg/L (Ce) and 113 µg/L (La), with even stricter chronic limits of 14 µg/L (Ce) and 16 µg/L (La) [5–9]. The calcium-analog properties of La and Ce mean their presence can disrupt processes such as blood coagulation, nerve function, muscle contraction, and intercellular signaling in exposed organisms. Although these elements have legitimate pharmacological and

industrial uses, their potential for toxicity and environmental persistence poses significant challenges. Due to their Ca-analog properties, La and Ce impair blood clotting, neurotransmission, muscle function, and cellular signaling. Their industrial and pharmacological applications are counterbalanced by their environmental persistence and bioaccumulation risks, particularly in plant systems where they inhibit growth, alter metabolic pathways, and disrupt micronutrient uptake [10, 11, 13, 14]. Liu et al. [15] proposed acute/chronic WQC limits of 256 μg/L and 14 μg/L, respectively, for La in freshwater species. Merodio-Morales et al. [16] highlighted La/Ce-functionalized materials for contaminant removal (e.g., fluoride, arsenic) but cautioned against their ecotoxicological risks.

Case Studies in Aquatic Organisms; Daphnia magna: Immobilization at 0.018–0.024 mg/L La (48h); Ceriodaphnia dubia: Reduced survival at 0.03–0.05 mg/L Ce (7d); Algae (Chlorella vulgaris) and macrophytes (Lemna minor): Growth inhibition at 0.06–0.11 mg/L (72h–7d) [17]; Cyprinus carpio (common carp): Survival decline, growth impairment, histopathological damage, and bioaccumulation after 28d exposure to 0.1–10 mg/L La [18]; Zebrafish embryos (96h): Hatching failure, malformations, cardiac irregularities, and mortality at 0.5–277.8 mg/L La [19].

Cerium oxide, another rare earth element, has also demonstrated toxicity toward various aquatic species such as *Daphnia magna, Chlorella vulgaris, Lemna minor, Pseudokirchneriella subcapitata, Ceriodaphnia dubia*, and both embryos and juveniles of zebrafish. The degree of cerium toxicity (0.018–277.8 mg/L) was observed to vary among species and depended on the length of exposure, which ranged from 24 hours to 21 days [20, 21].

The growing use of La and Ce in technology necessitates stringent monitoring of their environmental release. Their potential to disrupt biological systems, bioaccumulate, and harm aquatic life underscores the need for improved regulatory frameworks to mitigate ecological and health risks. Rare earth elements (REEs), such as lanthanum and cerium, pose significant ecological risks due to their ability to mimic calcium, bioaccumulate in organisms, and, in some cases, emit ionizing radiation. Although REEs have been explored for water purification—such as the adsorption of fluoride and arsenic—their inherent toxicity and persistence in ecosystems raise concerns for environmental and human health [22].

The present study aims to:

1. Quantify lanthanum and cerium concentrations in water and fish (*Pampus argenteus*) from the Shatt al-Arab River using X-ray fluorescence (XRF), a non-destructive analytical technique that identifies elemental composition via high-energy X-rays.
2. Assess the sources, ecological impacts, and bioaccumulation potential of these REEs.
3. Evaluate exposure risks to riverine biota and human populations reliant on the river.

2. EXPERIMENTAL

Sample Collection and Preparation

Water and sediment samples were collected from various points along the Shatt al-Arab River, targeting areas with differing degrees of human impact. Surface sediments (0–5 cm) were obtained using a stainless-steel grab sampler and transferred into acid-washed polyethylene containers to avoid contamination. Water samples were collected at the same sites in high-density polyethylene bottles. Both types of samples were kept at 4°C during transport to the laboratory. In the lab, sediment samples were allowed to air dry at room temperature, then ground with a mortar and pestle, and sieved through a 63 μm mesh to ensure uniformity. Water samples were filtered using 0.45 μm cellulose acetate membranes prior to analysis.

Chemical Analysis of Elements

Ten elements—cerium, lanthanum, iron, calcium, magnesium, sodium, potassium, titanium, manganese, and phosphorus—were selected for analysis in both water and sediment samples. Sediment digestion was performed using approximately 0.5 grams of sample combined with a mixture of nitric and hydrochloric acids (aqua regia), followed by heating in accordance with EPA Method 3050B. The resulting digested solutions were then filtered and diluted to a known final volume.

Quantification of elemental concentrations in both water and digested sediment samples was carried out via X-Ray Fluorescence (XRF), with calibration performed using standard fish tissue samples to ensure analytical accuracy [23, 24].

Bioaccumulation Factor (BAF) Determination

Fish tissue samples were collected from the same locations, and species identification was performed for each specimen. Muscle tissue was dissected, rinsed with deionised water, and then freeze-dried. Approximately 0.2 grams of the dried tissue was digested using a mixture of HNO_3 and H_2O_2 in a CEM Mars 6 microwave digestion system, according to established methods.

Metal concentrations in the fish tissues were determined through X-Ray Fluorescence (XRF) analysis. The bioaccumulation factor (BAF) for each element was subsequently calculated using the standard equation. $C_{fish}=BAF\times C_{water}$

where:

- C_{fish} is the metal concentration in fish tissue (mg/kg),
- C_{water} is the metal concentration in water (mg/L),
- BAF is the bioaccumulation factor, which represents how highly the fish concentrates the metal relative to its water concentration.

Statistical Analysis

Descriptive measures like mean, standard deviation, standard error, sample variance, range, minimum, maximum, kurtosis, skewness, sum, and confidence interval were obtained for all elements in IBM SPSS Statistics [25]. Pearson's r correlation coefficients were used to quantify relationships between pairs of elements in sediment samples. Strength and direction of correlation were interpreted according to conventional criteria. In addition, multivariate analysis techniques were also considered to analyze spatial trend and clustering pattern of the elemental distributions.

Quality Control and Assurance

All measurements were done in triplicate to ensure analytical reproducibility. Instruments were calibrated after every 10 samples. Method blanks and certified reference materials were analyzed with the samples. The recovery was 90-110% that ensured method precision.

4. RESULTS AND DISCUSSION

The table shows the mean, standard error, standard deviation, sample variance, kurtosis, skewness, range, minimum, maximum, sum, count and confidence level of 10 elements (Ce, La, Fe, Ca, Mg, Na, K, Ti, Mn, and P) for certain samples. The data follow some interesting patterns and variations between the elements. The highest occurring element in the samples is K with a mean of 45686.9231 and a sum of 593930. The lowest occurring element is Ce with a mean of 20.53846 and a sum of 267. The most variable element is P with a standard deviation of 15090.35114 and a range of 60230. The least variable element is Ti with a standard deviation of 22.58886 and a range of 80. The data also provide some variation in the distribution and shape of the elements. The most kurtotic values are P (8.805409499) and K (8.72165362), which have more outliers and are more peaked than the normal distribution. Also, the most kurtotic values are Fe (-0.95494813) and Mn (-0.96469), which have fewer outliers and are more flat than the normal distribution. The most skewed elements are Fe (3.41633) and La (1.847511), indicating that they have more values on their right tail and are skewed to the right. The least skewed elements are K (-2.6823874) and P (-2.74281688), indicating that they have more values on their left tail and are skewed to the left. Variations in the confidence level of the elements are also apparent from the data. The most confident element is P (9119.007927), which means that it has a greater margin of error and broader interval compared to the rest of the elements.

The least confident element is Mn (10.70986), which means that it has a lower margin of error and narrower interval compared to the rest of the elements.

These observations suggest that there are huge variations between the fractions in their abundance, heterogeneity, spatial distribution and shape. These observations need additional analysis to emphasize the reasons and consequences of these variations. These observations show a significant spatial and temporal range in lanthanum and cerium concentrations in river sediments, depending on geological, hydrological, climatic, and anthropogenic processes affecting each river system. Therefore, there is a need to track and examine these components constantly in the Shatt al-Arab River and other rivers to determine their effects on the environment. There are numerous studies of interactions between lanthanum and cerium with other metals in river sediments, and different effects and mechanisms that depend on the nature of each river system [26]. Conclusions are uniform. The interactions between lanthanum (La) and cerium (Ce) with other elements in river sediments have been studied in recent research and it has been concluded that these interactions can be different depending on each river system's unique properties [27]. For instance, Merodio-Morales et al. [28] demonstrated that La and Ce can enhance the adsorption of fluoride and arsenic ions by activated carbons and char, with La proving to be more effective when compared to Ce. Similarly, Kang et al. [29] demonstrated that La and Ce are present in low concentrations and pose very minimal ecological hazards in Hai River sediments as well as its tributaries. They attributed the presence of La to natural weathering processes of rocks, and Ce was obtained mostly from anthropogenic sources. Alibo and Nozaki [26] provided data on the presence of Ce anomalies in marine sediments, which they attributed to the oxidation of Ce(III) to Ce(IV) under oxic conditions. They also observed that these anomalies responded to local-regional redox conditions and paleoceanographic alteration Together, these results indicate that La and Ce are capable of interacting with other metals in river sediments through a wide variety of processes, including adsorption, precipitation, oxidation, reduction, and complexation [30]. These interactions may impact the distribution, mobility, availability, and toxicity of these elements in aquatic systems.

Table 1 Statistical Summary of Metal Concentrations in Fish Samples

	Mean	SE	SD	Sample Variance	Kurtosis	Skewness	Range	Min	Max	Sum	Count	Confidence Level(95.0%)
Ce	20.53	4.702175	16.95	287.43	-0.91355	0.176574	51	0	51	267	13	10.24516
La	14.92	6.20118	22.35	499.91	3.582006	1.847511	75	0	75	194	13	13.51121
Fe	764.61	112.9761	407.34	165926.9	12.03351	3.41633	1570	530	2100	9940	13	246.1539
Ca	3543.07	450.944	1625.90	2643556	-0.95495	-0.45519	5000	500	5500	46060	13	982.5226
Mg	3131.53	298.2961	1075.52	1156747	6.37124	-2.20933	4390	0	4390	40710	13	649.9314
Na	4741.53	448.4201	1616.80	2614047	0.450143	-0.91796	5410	1100	6510	61640	13	977.0234
K	45686.92	4115.168	14837.45	2.2E+08	8.721654	-2.68239	61850	0	61850	593930	13	8966.182
Ti	184.61	6.265021	22.58	510.2564	0.208389	0.648877	80	150	230	2400	13	13.65031
Mn	88.46	4.915459	17.72	314.1026	-0.96469	-0.36367	50	60	110	1150	13	10.70986
P	46688.46	4185.31	15090.35	2.28E+08	8.805409	-2.74282	60230	80	60310	606950	13	9119.008

The very high correlation coefficient of 0.9 between Ce and Na shows a very high positive correlation between the two elements' concentrations in river sediments: if one increases, so does the other. Mg and P also show an extremely high correlation coefficient of 0.96, while La and Ti show a negative correlation coefficient of -0.24. There are studies that have checked the correlation coefficients of Mg and P or La and Ti in river sediments and presented different values and explanations based on characteristics of each river system. Hamdan et al. [22] found Mg and P to be correlated with organic matter and clay minerals, while La and Ti were correlated with volcanic rocks and seawater intrusion in estuary rivers in volcanic regions. Liu et al. [6] have stated that Mg and P were influenced by redox conditions, organic matter content, and sediment texture, while La and Ti were derived through natural rock weathering or anthropogenic activities in a huge shallow lake. These observations reflect the fact that correlation coefficients between these elements in river sediments differ based on a number of variables such as mineralogy, geochemistry, hydrology, biogeochemistry, and pollution sources [31].

Table 2. Correlation Matrix of Metal Concentrations in Fish Samples

	Ce	La	Fe	Ca	Mg	Na	K	Ti	Mn	P
Ce	1									
La	0.410116	1								
Fe	-0.32016	0.336757	1							
Ca	0.329393	0.246364	0.166468	1						
Mg	0.42182	0.058605	0.046908	0.75102466	1					
Na	0.462431	0.172574	-0.00559	0.77624792	0.885503	1				
K	0.338498	-0.06914	0.024181	0.57715755	0.927792	0.7061346	1			
Ti	-0.13324	-0.24014	-0.02606	-0.23707326	-0.113853	-0.276074	-0.10696733	1		
Mn	-0.22721	0.363494	0.362366	0.14622075	0.124732	-0.0656361	0.1130825	-0.02242	1	
P	0.400555	0.035259	0.073904	0.73583413	0.959534	0.7930252	0.96238835	-0.19389	0.072404	1

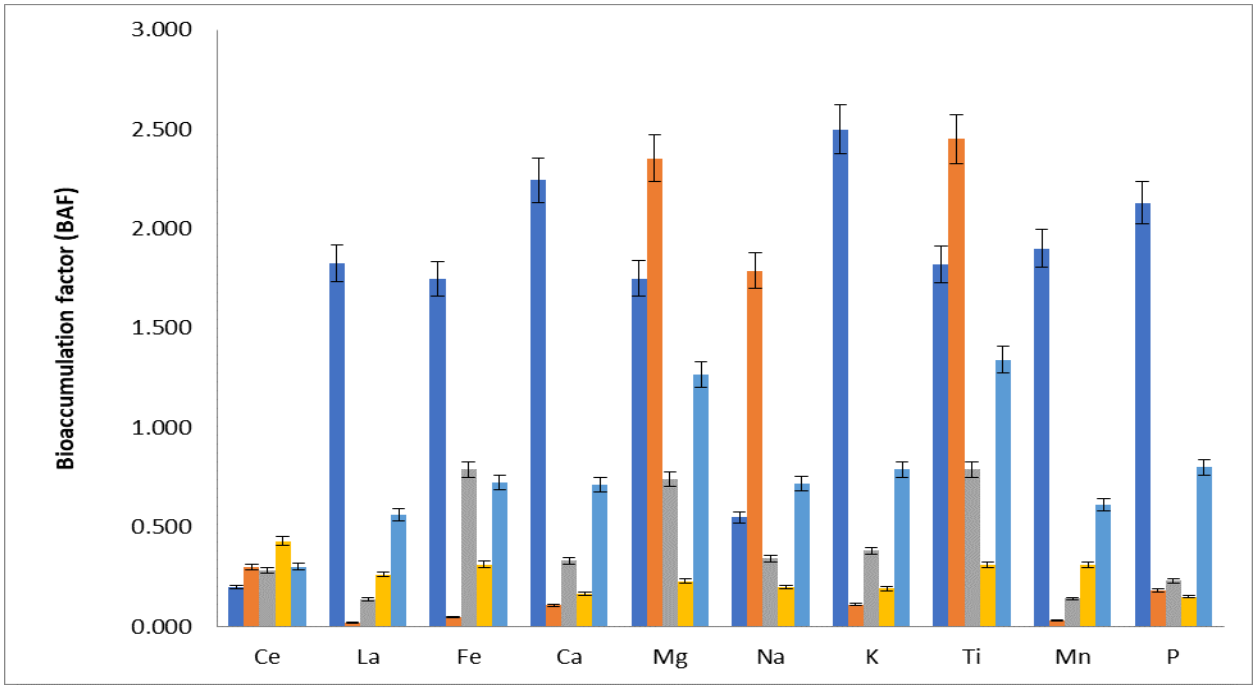

Figure 1. Total Bioaccumulation Factor (BAF) in Study Area: Insights into Metal Uptake and Accumulation in Aquatic Biota.

Metallic Element Bioaccumulation in Shatt al-Arab River: Implications for Ecosystem and Human Health

This study looked at ten metallic elements—cerium (Ce), lanthanum (La), iron (Fe), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), titanium (Ti), manganese (Mn), and phosphorus (P)—in the water and fish tissue (Pampus argenteus) from four spots along the Shatt al-Arab River in Iraq. The results showed that metal concentrations and how they build up in fish varied a lot from one place to another, pointing to local pollution issues and different environmental factors. This study investigated ten metallic elements—cerium (Ce), lanthanum (La), iron (Fe), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), titanium (Ti), manganese (Mn), and phosphorus (P)—in the water and fish tissue of Pampus argenteus collected from four locations along the Shatt al-Arab River in Iraq. Accumulated data pertaining to metal concentrations and their accumulation in fish show that localized pollution disturb the environmental equilibrium in a unique manner.

Lanthanum (La) and cerium (Ce) exhibited different trends concerning their accumulation in fish. The BAF of La, averaging 0.56 (ranging from 0.021 to 1.827), was much higher than the BAF of Ce with 0.30 (ranging from 0.197 to 0.429), indicating that La is likely absorbed more rapidly by fish than Ce because of some biological interactions. Among the elements considered, magnesium (Mg) had the highest BAF of 1.27, and sodium (Na) was at 0.72, suggesting that fish have different accumulation patterns for different metals.

BAF values described suggest that uptake of metals into fish is impacted by pollution sources and water chemistry. Certain metal BAFs found in ecosystems affected by such runoff thus symbolize human intervention in those ecosystems. Notably, the consumption of fishes from that river may pose a possible health risk, given that metals are accumulating in fish flesh due to human activities. The BAF for Ce ranged from 0.197 to 0.429, with an average of 0.30, whereas La ranged from 0.021 to 1.827, with a mean of 0.56. Many of these metals exhibit mean BAFs that are higher than for other metals, such as Mg, within 1.26 compared with Na at 0.72. There were a few differences in cerium BAF values from different sites, where one site recorded a BAF of 0.197 and the other had a value of 0.297. The bioaccumulation factor (BAF) shows the ratio of a particular concentration of the metal in fish to its concentration in water. The BAF values for La and Ce show the incorporation into fish tissue, with La typically metabolized greater than Ce. That data is essential for understanding the geographic distribution of metals in fish and assessing possible health concerns to humans who consume fish in polluted environments. Variations in BAF values can arise from differences in fish species, collection sites, and the chemical properties of the metals involved, offering insights into how various substances move through fish and informing health considerations for those eating fish from polluted environments [32, 33, 34].

5. CONCLUSIONS

The fish and water analysis of samples from the Shatt al-Arab River in Iraq revealed significant location-based variations. Lanthanum (La) and cerium (Ce) exhibited distinct distribution patterns, suggesting different sources and interactions with other metals. These differences suggest that various environmental factors affect how they spread in the river. This information raises concerns about possible harm to ecosystems and people, especially those who fish in the area. The report suggests more studies and continuous monitoring to better understand where these metals come from and what effects they might have. To reduce risks, it recommends cutting down industrial and farm waste and improving wastewater treatment systems. Keeping track of these efforts is crucial to lowering metal levels and safeguarding both the environment and public health.

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