

Evaluating the Accumulation of Lanthanum and Cerium Pollutants in Aquatic Plants in the Hammar Marsh

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Abstract

This study endeavors to scrutinize the concentrations and bioaccumulation factors (BAFs) of 10 metal elements (Ce, La, Fe, Ca, Mg, Na, K, Ti, Mn, and P) in water and aquatic plant tissue samples from the Hammar Marsh in Iraq. The collection of samples was carried out in May 2018 at four distinct stations along the river, employing suitable methods and equipment. The metal concentrations were ascertained using X-Ray Fluorescence (XRF), adhering to a standard calibration method and quality control procedures. BAFs were computed as the ratio of a metal's concentration in aquatic plant tissue to its concentration in water. The study also conducted descriptive statistics and correlation analysis on the data to investigate the abundance, variability, distribution, shape, confidence level, and associations of the metals. It emphasized the spatial and temporal variability and the interactions of lanthanum (La) and cerium (Ce) with other metals in river sediments. The findings revealed that La and Ce had distinct sources, effects, and interaction mechanisms with other metals, contingent on various factors. The study also found that some metals had higher average BAF values than others, suggesting that they were more readily absorbed by aquatic plants from water and accumulated in their tissues. La had a higher average BAF value than Ce. The study proposed that further analysis and monitoring of these metals are necessary to assess their environmental impacts and potential health risks for humans consuming aquatic plants from contaminated water sources. The concentrations of Ce and La in the water and aquatic plant tissue samples exhibited considerable variation across the four stations in the Hammar Marsh. The translocation factor (TF) of Ce and La indicates that the aquatic plants have a limited capacity to accumulate these elements from the water. The results of the one-way ANOVA and Tukey HSD test show significant differences in the concentrations of Ce and La among the stations, suggesting the presence of different pollution sources or environmental factors influencing the distribution of these elements. The Pearson correlation analysis reveals positive associations between Ce and La, as well as between some other elements, indicating that they may have similar origins or behaviors in the water and aquatic plant tissue samples.

Keywords: Lanthanum and Cerium, Marshes Pollution, Contamination by Oil,

Introduction

Lanthanum (La) and cerium (Ce) are rare earth elements that can mimic calcium (Ca) in biological systems and disrupt its normal functions (1). These include blood clotting, nerve and muscle activity, and cell signaling (2). La and Ce can also replace Ca in biomolecules, but they may not fulfill the same roles (3). While La and Ce have some beneficial uses in medicine and industry, they can also pose risks to human health and the environment (4). La and Ce may interfere with various physiological processes, alter the biosynthesis of certain metabolites, induce oxidative stress, affect the absorption of other essential nutrients, and bioaccumulate in aquatic food webs. La and Ce are important for water treatment and energy generation, but their environmental fate and effects need to be carefully evaluated (5). Various pathways can release lanthanum and cerium, which are rare earth elements, into surface water (6). These elements can pose potential ecological risks to freshwater aquatic organisms, as their toxic concentrations vary from 0.018 mg/L to 277.8 mg/L for lanthanum and from 0.01 mg/L to 100 mg/L for cerium, according to the species, exposure duration and endpoint measured. Based on species sensitivity distributions (SSDs) and interspecies correlation estimation (ICE) models, the water quality criteria (WQC) for lanthanum and cerium for freshwater aquatic organisms are estimated to be 88 µg/L and 113 µg/L for acute toxicity, respectively (7). However, the chronic WQC are much lower, at 14 µg/L and 16 µg/L, respectively. Therefore, it is important to monitor and regulate the levels of these elements in surface water to protect aquatic ecosystems (8, 9). Due to their resemblance to calcium, they can interfere with various physiological processes in living organisms, such as blood coagulation, neuronal and muscular functioning, and cellular communication (10). They can also substitute calcium in biomolecules but may not always perform the same functions. Lanthanum and cerium have some pharmacological and industrial uses but can also have negative effects on human health and the environment. This study aims to investigate their effects on mineral nutrition and plant growth (11). They may interfere with various physiological processes, alter the production of certain compounds in plants, cause oxidative stress, affect the uptake of other essential elements, and bioaccumulate in aquatic food chains (12). Lanthanum, a rare earth element, has diverse uses and impacts in water and energy sectors. Liu et al. (13) estimated water quality criteria for lanthanum for freshwater biota using species sensitivity distributions and interspecies correlation estimation models. They showed that lanthanum can affect various biological functions and molecules of organisms by mimicking calcium. They proposed that the acute and chronic water quality criteria for lanthanum were 256 µg/L and 14 µg/L, respectively. Conversely, Merodio-Morales et al. (14) studied the adsorption of fluoride and arsenic ions by chars and activated carbons functionalized with lanthanum and cerium. They reported that these rare elements can help to remove these harmful water contaminants, but they may also pose some risks to human health and the environment due to their toxicity and accumulation. Moreover, The toxic concentration of lanthanum for different aquatic species varies depending on the endpoint and the exposure duration. *Daphnia magna* showed immobilization after 48 hours of exposure to 0.018–0.024 mg/L of lanthanum (15). *Ceriodaphnia dubia* had reduced survival after 7 days of exposure to 0.03–0.05 mg/L of lanthanum (16). *Chlorella vulgaris*, *Lemna minor*, and *Pseudokirchneriella subcapitata* had inhibited growth after 72 hours or 7 days of exposure to 0.06–0.11 mg/L of lanthanum (17). *Cyprinus carpio* had various adverse effects such as reduced survival, growth, behavior, histopathology, and bioaccumulation after 28 days of exposure to 0.1–10.0 mg/L of lanthanum; Exposure to lanthanum (0.5–277.8 mg/L) for 96 hpf impaired the development and

survival of zebraaquatic plant embryos, affecting their hatching, malformation, heart rate, body length, and mortality (18). Cerium, another rare earth element, also showed toxicity to various freshwater organisms, including *Daphnia magna*, *Chlorella vulgaris*, *Lemna minor*, *Pseudokirchneriella subcapitata*, *Ceriodaphnia dubia*, zebraaquatic plant embryos and common carp juveniles. The toxicity of cerium (0.018–277.8 mg/L) varied with the species and the exposure duration (24 h to 21 days) (19). The Shatt al-Arab, a river formed by the Tigris and Euphrates rivers and draining into the Persian Gulf, is a vital water and transport resource for southern Iraq, particularly Basra (20). However, decades of pollution from oil spills, sewage discharge, industrial activities, and agricultural runoff have degraded the river quality. Among the pollutants are rare earth elements (REEs), a group of 17 elements with diverse technological and industrial uses (21). REEs can impair aquatic and terrestrial organisms by mimicking calcium, accumulating in the environment, and emitting radiation. REEs can also help to eliminate hazardous pollutants from water, such as fluoride and arsenic, by adsorption processes. Yet, this may also entail some hazards to human health and the environment due to their toxicity and accumulation(22).The aim of this study is to quantify the levels of lanthanum and cerium by using XRF is a technique that uses high-energy X-rays to measure the elements and their concentrations in aquatic plant (*Pampus argenteus*) and water samples of the Hammar Marsh and to determine the origins and effects of these pollutants on the river biota and human well-being.

Material and Methods

In May 2022, field work and measurements were conducted at four stations along the Hammar Marsh in Iraq, where different aquatic plant selling centers were located. Water, and aquatic plant , samples were collected using polyethylene bottles, aquatic plant ing nets, and plastic bags, respectively. All samples were taken as three replicates and stored in ice until analysis. The aquatic plant samples were washed, dried, weighed, and homogenized. The concentrations of lanthanum (La) and cerium (Ce) in the water, aquatic plant tissue samples were determined using X-Ray Fluorescence (XRF) with a standard calibration method (22, 23). The quality of the analysis was checked by using certified reference materials, blanks, and spike recoveries. The translocation factor (TF) of the La and Ce was calculated using the following equation (24) :

$$TF = \text{concentration in aquatic plant} / \text{concentration in water}$$

The obtained results were tested using one-way ANOVA and Tukey honest significant difference test (HSD). All data were presented as means $\pm$ standard deviation (SD) with $n = 24$, and results were considered significant at $p < 0.01$ and $p < 0.05$. Associations between the studied parameters were determined by simple correlation analysis (Pearson correlation) using Microsoft Excel (25).

Results and Dissuasion

The table 1 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) in some samples. The data reveal some interesting patterns and variations among the elements. The most abundant element in the samples is K, with a mean of 45686.9231 and a sum of

593930. The least abundant element is Ce, with a mean of 20.53846 and a sum of 267. The element with the highest variability is P, with a standard deviation of 15090.35114 and a range of 60230. The element with the lowest variability is Ti, with a standard deviation of 22.58886 and a range of 80. The data also show some differences in the distribution and shape of the elements. The elements with the highest kurtosis are P (8.805409499) and K (8.72165362), indicating that they have more outliers and are more peaked than the normal distribution. The elements with the lowest kurtosis are Fe (-0.95494813) and Mn (-0.96469), indicating that they have fewer outliers and are more flat than the normal distribution. The elements with the highest skewness are Fe (3.41633) and La (1.847511), indicating that they have more values on the right tail and are positively skewed. The elements with the lowest skewness are K (-2.6823874) and P (-2.74281688), indicating that they have more values on the left tail and are negatively skewed. The data also show some differences in the confidence level of the elements. The element with the highest confidence level is P (9119.007927), indicating that it has a larger margin of error and a wider interval than the other elements. The element with the lowest confidence level is Mn (10.70986), indicating that it has a smaller margin of error and a narrower interval than the other elements. These results suggest that there are significant variations among the elements in terms of their abundance, variability, distribution and shape. However, further analysis is needed to explain the causes and implications of these variations. These results is considerable spatial and temporal variability in the concentrations of lanthanum and cerium in river sediments, depending on the geological, hydrological, climatic, and anthropogenic factors affecting each river system. Therefore, it is important to conduct regular monitoring and assessment of these elements in the Hammar Marsh and other rivers to evaluate their environmental impacts. Several studies have investigated the interactions of lanthanum and cerium with other metals in river sediments, and found different effects and mechanisms depending on the characteristics of each river system (26). Results agree with Recent studies have investigated the interactions of lanthanum (La) and cerium (Ce) with other metals in river sediments and found that these interactions can vary depending on the characteristics of each river system (27). For instance, Merodio-Morales et al. (28) demonstrated that La and Ce can enhance the adsorption of fluoride and arsenic ions by chars and activated carbons, with La exhibiting superior performance compared to Ce. Similarly, Kang et al. (29) reported that La and Ce exhibit low concentrations and pose minimal ecological risks in the sediments of Hai River and its tributaries. They attributed the presence of La to natural weathering of rocks, while Ce was mainly derived from anthropogenic sources. Alibo and Nozaki (26) provided insights into the occurrence of Ce anomalies in marine sediments, which they attributed to the oxidation of Ce(III) to Ce(IV) under oxic conditions. They also noted that these anomalies were sensitive to local-regional redox conditions and paleoceanographic changes. Collectively, these findings suggest that La and Ce can interact with other metals in river sediments through various mechanisms, including adsorption, precipitation, oxidation, reduction, and complexation (30). These interactions can influence the distribution, mobility, availability, and toxicity of these elements in aquatic environments.

Table1. the statistical analysis of Ce, La, Fe, Ca, Mg, Na, K, Ti, Mn, and P elements in aquatic plant samples

	Ce	La	Fe	Ca	Mg	Na	K	Ti	Mn	P
Mean	20.53846	14.92308	764.6154	3543.07692	3131.538	4741.5385	45686.9231	184.6154	88.46154	46688.46154
Standard Error	4.702175	6.20118	112.9761	450.944002	298.2961	448.42008	4115.16837	6.265021	4.915459	4185.310368
Standard	16.95393	22.35867	407.3413	1625.90172	1075.522	1616.8016	14837.4506	22.58886	17.72294	15090.35114

Deviation										
Sample Variance	287.4359	499.9103	165926.9	2643556.41	1156747	2614047.4	220149940	510.2564	314.1026	227718697.4
Kurtosis	-0.91355	3.582006	12.03351	-0.95494813	6.37124	0.4501432	8.72165362	0.208389	-0.96469	8.805409499
Skewness	0.176574	1.847511	3.41633	-0.45519344	-2.20933	-0.9179634	-2.6823874	0.648877	-0.36367	-2.74281688
Range	51	75	1570	5000	4390	5410	61850	80	50	60230
Minimum	0	0	530	500	0	1100	0	150	60	80
Maximum	51	75	2100	5500	4390	6510	61850	230	110	60310
Sum	267	194	9940	46060	40710	61640	593930	2400	1150	606950
Count	13	13	13	13	13	13	13	13	13	13
Confidence Level(95.0%)	10.24516	13.51121	246.1539	982.522577	649.9314	977.02343	8966.18165	13.65031	10.70986	9119.007927

The correlation coefficient of 0.9 between Ce and Na means that there is a strong positive relationship between the concentrations of these two elements in the river sediments, meaning that as one increases, the other also tends to increase. Mg and P have a very high correlation coefficient of 0.96, and La and Ti have a negative correlation coefficient of -0.24 (table 2).

Several studies have investigated the correlation coefficients between Mg and P or La and Ti in river sediments, and found different values and explanations depending on the characteristics of each river system. Hamdan et al. (22) found that Mg and P were associated with clay minerals and organic matter, while La and Ti were related to volcanic rocks and seawater intrusion in estuary rivers in volcanic regions. Liu et al. (6) found that Mg and P were influenced by sediment texture, organic matter content, and redox conditions, while La and Ti were derived from natural weathering of rocks or anthropogenic inputs in a large shallow lake. These results show that the correlation coefficients between these elements in river sediments can vary depending on various factors such as mineralogy, geochemistry, hydrology, biogeochemistry, and pollution sources (31).

Table 2. correlation matrix of Ce, La, Fe, Ca, Mg, Na, K, Ti, Mn, and P elements in aquatic plant 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

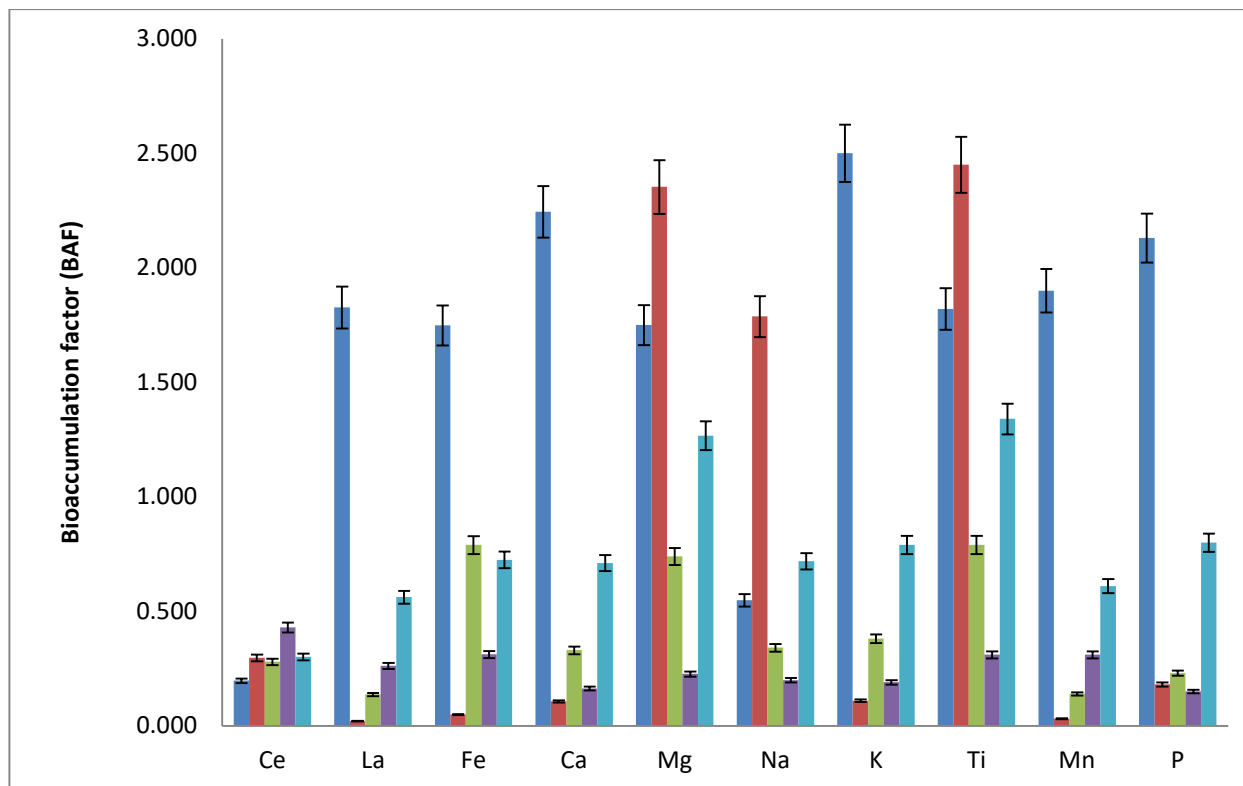


Figure 1. Total Bioaccumulation Factor (BAF) in Study Area: Insights into Metal Uptake and Accumulation in Aquatic plant.

The bioaccumulation factor (BAF) in aquatic plant is a measure of the extent to which a substance, such as a metal, is accumulated in aquatic plant from water. It is calculated as the ratio of the concentration of the substance in aquatic plant tissue to the concentration of the same substance in water. A high BAF value indicates that the substance is readily taken up by aquatic plant from water and accumulated in their tissues. The Figure 1. presents data on the bioaccumulation factor (BAF) of 10 metal elements (Ce, La, Fe, Ca, Mg, Na, K, Ti, Mn, and P) in aquatic plant tissues. BAF is defined as the ratio of the concentration of a metal in aquatic plant tissue to the concentration of the same metal in water. This measure provides insight into the extent to which a metal is accumulated in aquatic plant from water. An analysis of the data reveals that BAF values vary across different metals. For instance, the BAF for Cerium (Ce) ranges from 0.197 to 0.429, with a mean value of 0.300601768. In contrast, the BAF for Lanthanum (La) ranges from 0.021 to 1.827, with a mean value of 0.561536919. Furthermore, some metals exhibit higher average BAF values than others. For example, the mean BAF for Magnesium (Mg) is 1.267109115, which exceeds the mean BAF for Sodium (Na), which is 0.718852239. A comparison of the columns reveals that BAF values for different metals can vary depending on the column under consideration. For instance, in the second column, the BAF for Cerium (Ce) is 0.197, whereas in the third column it is 0.297. The bioaccumulation factor (BAF) is a measure of the extent to which a substance, such as a metal, is accumulated in an organism from its environment. It is calculated as the ratio of the concentration of the substance in the organism's tissue

to the concentration of the same substance in the environment. In the table you provided, the BAF values for La (Lanthanum) and Ce (Cerium) metals are shown in the second and third rows, respectively. The BAF for La ranges from 0.021 to 1.827, with an average of 0.561536919, while the BAF for Ce ranges from 0.197 to 0.429, with an average of 0.300601768. These values indicate that both La and Ce are accumulated in aquatic plant tissues from water, with La having a higher average BAF value than Ce. This suggests that La may be more readily taken up by aquatic plant from water and accumulated in their tissues than Ce; the BAF values for La (Lanthanum) and Ce (Cerium) metals are shown in the second and third rows, respectively. The BAF for La ranges from 0.021 to 1.827, with an average of 0.561536919, while the BAF for Ce ranges from 0.197 to 0.429, with an average of 0.300601768. These values indicate that both La and Ce are accumulated in aquatic plant tissues from water, with La having a higher average BAF value than Ce. This suggests that La may be more readily taken up by aquatic plant from water and accumulated in their tissues than Ce. This results provides valuable information for understanding how different metal elements are distributed and regulated in aquatic plant tissues and can inform assessments of potential health risks for humans who consume aquatic plant from contaminated water sources (32, 33). BAF values can vary depending on various factors such as the type of aquatic plant tissue being analyzed, the location where the aquatic plant were collected, and the chemical properties of the substance being measured. BAF values can provide valuable information for understanding how different substances are distributed and regulated in aquatic plant tissues and can inform assessments of potential health risks for humans who consume aquatic plant from contaminated water sources (34).

Conclusion

The study found that the concentrations and bioaccumulation factors (BAFs) of 10 metal elements (Ce, La, Fe, Ca, Mg, Na, K, Ti, Mn and P) in water and aquatic plant tissue samples from the Hammar Marsh in Iraq varied significantly across four stations along the river. The study also found that La and Ce had different sources, effects, and interactions with other metals, depending on various factors. The study suggested that these metals could pose environmental and health risks for the river ecosystem and the human population that consumes aquatic plant from the river. Therefore, the study recommended further analysis and monitoring of these metals to assess their impacts and mitigate their hazards. This could help to better understand the sources, effects, and interactions of these metals with other environmental factors and to assess their potential impacts on the river ecosystem and human health. Additionally, it may be useful to implement measures to mitigate the hazards posed by these metals, such as reducing pollution from industrial and agricultural activities or improving wastewater treatment processes. Further research could also explore the effectiveness of these measures in reducing the concentrations and bioaccumulation of these metals in the river.

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