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Assessment of Selenium Contamination in Sediments of the Aby and Tendo Lagoons in Côte d'Ivoire

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Abstract

Selenium is a trace element that can have both beneficial and harmful effects on aquatic life. The Aby Lagoon is a coastal environment in Côte d'Ivoire that receives selenium inputs from various natural and anthropogenic sources. The aim of this study was to assess the levels of selenium in the sediments of the Aby Lagoon and its tributaries, the Tanoe River and the Tendo Lagoon, and to examine the spatial and seasonal variations of selenium concentrations. Sediment samples were collected from different sites and seasons, and selenium concentrations were measured by atomic fluorescence spectrometry. The results showed that the average concentration of selenium in the sediments of the Aby Lagoon was 0.82 mg/kg, indicating moderate contamination. The concentration of selenium varied between sites and seasons, with higher values in the channel of the Tendo Lagoon and during the dry season. The study highlighted the complexity of selenium dynamics in aquatic ecosystems, and the need to take into account seasonal and spatial variability as well as interactions between environmental factors. The study also suggested potential ecotoxicological risks for some sensitive organisms in certain areas of the lagoon. This study contributes to the knowledge of the dynamics of selenium in lagoon ecosystems and to the assessment of the environmental risks associated with its presence.

Keywords

Tropical Estuarine, Selenium, Sediments, Aby Lagoon, Seasonal Distribution

1. Introduction

Selenium (Se) is a naturally occurring metalloid element in the Earth's crust [1]. It is essential for life in low concentrations, as it is incorporated into selenoproteins that play a crucial role in various metabolic processes [2] [3]. However, at higher concentrations, Selenium can become toxic to living organisms. Selenium can be released into the environment through natural and anthropogenic processes. Natural sources of Selenium include soil erosion, rock weathering, and volcanic emissions [4] [5]. Anthropogenic sources of Selenium include mining, fossil fuel combustion, agriculture, and pesticide use [6] [7]. Selenium in the environment occurs in different chemical forms, including selenite (SeO_3^{2-}), selenate (SeO_4^{2-}), elemental selenium (Se) and methionine selenea (MetSe) [8] [9]. The chemical form of selenium influences its bioavailability and toxicity to living organisms (Wang *et al.*, 2012). Sediment is an important reservoir of selenium in aquatic environments. Selenium can be adsorbed onto sediment particles or precipitated as insoluble compounds. The concentration of selenium in sediments can vary considerably depending on the sources of inputs, the physicochemical properties of the sediment and environmental conditions [8] [9] [10]. Selenium can be toxic to aquatic organisms at relatively low concentrations [11] [12]. The toxic effects of selenium may include reduced growth, reproduction and survival, as well as histological damage and endocrine disruption [13]. The toxicity of selenium to aquatic organisms depends on several factors, including the concentration of selenium, the chemical form of selenium, speciation of other metals in the environment, characteristics of the organism, and environmental conditions. The Aby Lagoon is an important coastal environment located in Côte d'Ivoire. It receives Se inputs from a variety of sources, including agriculture, mining, and domestic activities. The objective of the study is to determine the levels of selenium in the sediments of the Aby Lagoon and Tendo as a function of sites and seasons.

2. Materials and Methods

2.1. Area Study

The study was conducted in the Aby Lagoon, located in the southeast of Côte d'Ivoire, between latitudes 2˚40' and 3˚20' West and longitudes 5˚20' and 5˚40' North (**Figure 1**). The Aby Lagoon is the largest lagoon in the country, with an area of 1400 km^2 and an average depth of 3 m. The Aby Lagoon is fed by two main rivers, the Tanoé and the Bia, which drain a watershed of 19,000 km^2, covering forest, agricultural, and urban areas. The Aby Lagoon is bordered by a dense mangrove, dominated by the species Rhizophora racemosa and Avicennia germinans, and hosts a diversified fish fauna, including freshwater, brackish, and marine species.

2.2. Sampling

2.2.1. Frequency of Sampling

During each campaign and at each station, sediment samples were taken from

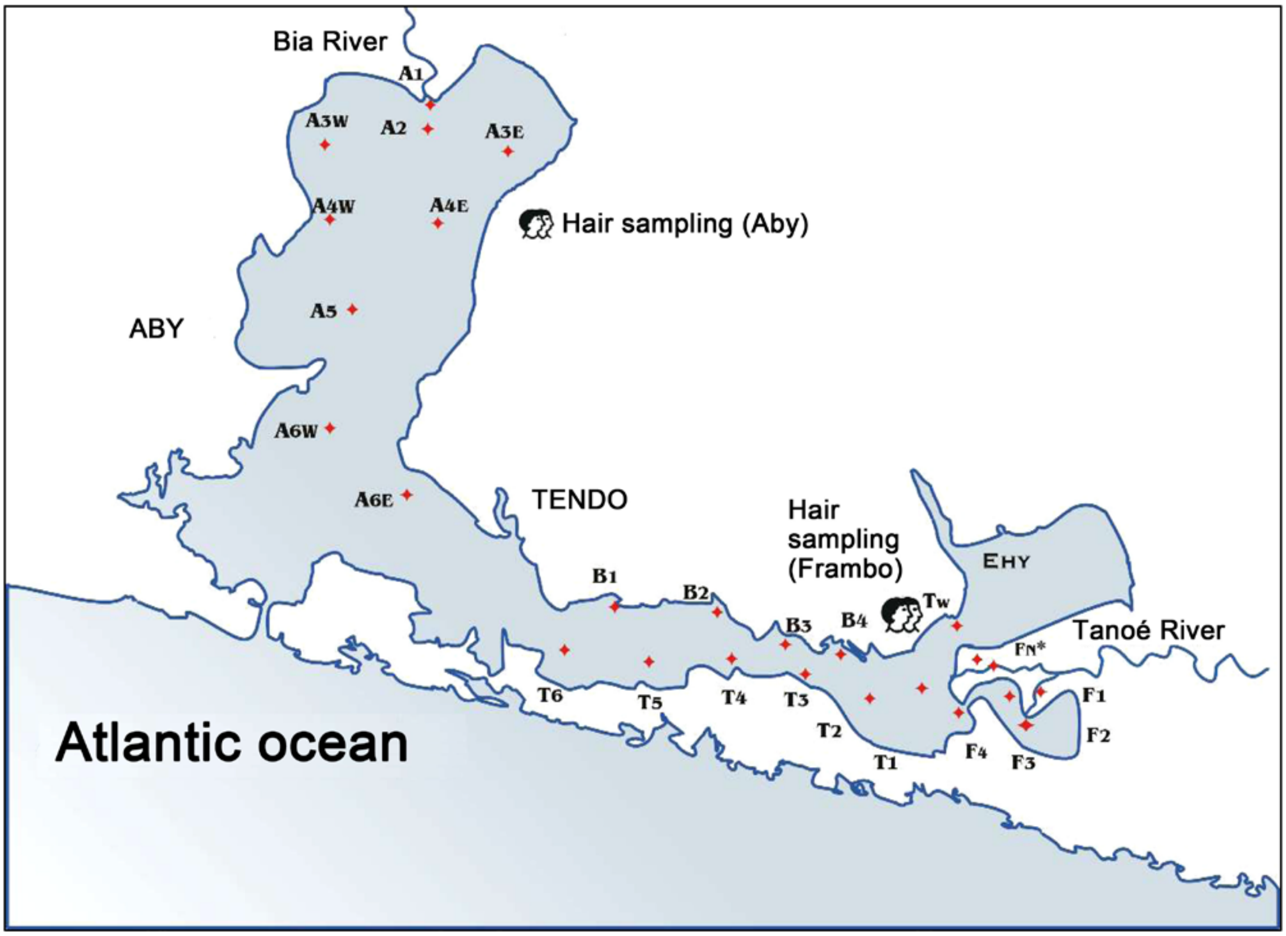

Figure 1. Sites for sampling areas.

the bottom of the lagoon. A total of four (04) campaigns were carried out, including two at the end of the main dry season (DS1 & 2) and two at the end of the main rainy season (RS1 & 2).

2.2.2. Distribution of Sampling Areas

Sediment and water samples were taken from the Aby Lagoon. The selection of sampling stations was made taking into account spatial, bathymetric and hydrological variations. Spatially and hydrologically, the influences of the rivers were taken into account, which led to the definition of two zones, identified as Tendo for the Tanoé River and Aby Nord. Within these zones, the stations were divided into four subzones, based on spatial variations, bathymetry and hydrodynamic data. These sub-areas include Aby North, the channel, the bays of the Tendo Lagoon, as well as the Tanoe River.

2.2.3. Frequency of Sampling

During each campaign and at each station, sediment samples were taken from the bottom of the lagoon. A total of four campaigns were carried out, including two at the end of the main dry season (DS1 & 2) and two at the end of the main rainy season (RS1 & 2).

2.2.4. Sediment Sampling Methods

Sediment samples were taken using a core barrel. Once brought to the surface, the core is extruded, and the top five centimeters are collected using a plastic spatula. Foreign bodies and organic detritus are carefully removed manually. Subsequently, the sample is thoroughly homogenized and stored in a polyethylene bag and stored in the dark in a cooler. Transport to the laboratory is carried out within 24 hours of collection.

2.2.5. Sediment Sampling

For each of the campaigns and at each station, sediment sampling was taken from the lagoon bottom. A total of four campaigns were carried out, including two at the end of the main dry season (DS 1 and DS 2) and two at the end of the main rainy season (RS 1 and RS 2).

At points where bathymetry is greater than 6 meters, two sets of measurements and sampling were carried out in the water column. The first at the surface (at 0.5 meters) and the second at a depth of 1 meter above the water-sediment interface. Seven points were selected for this double measure, four of which were in Tendo Lagoon.

Sediment was collected using a core barrel. Once brought to the surface, the core is extruded and the top five centimeters are collected using a plastic spatula. Foreign bodies and organic detritus are then removed manually. The sample is then homogenized, placed in a polyethylene bag, and stored in the dark in a cooler. Transport to the laboratory is carried out within 24 hours of collection. Sediment samples were air-dried, sieved to 2 mm, and then ground to 63 µm.

2.3. Sample Preparation

Sediment samples were air-dried, sieved through a 2 millimeters sieve and homogenized. Macrophyte and fish samples were washed in distilled water, dried at 60˚C for 48 hours, and ground into a fine powder.

Sediment Mineralization

The sediment was digested using a mixture of nitric acid and hydrogen peroxide (HNO_3/H_2O_2): Approximately 0.25 g of dried and homogenized sediment was precisely weighed in a container. Subsequently, 8 mL of concentrated nitric acid was added to the container, which was hermetically sealed with a reflux column. A plastic gasket has been placed between the backflow column and the container to prevent evaporation. The tube containing the mixture followed the following protocol:

- A first phase of microwave heating at 20 W for 5 minutes.
- Chill for 5 minutes, followed by the addition of 2 ml of hydrogen peroxide (H_2O_2).
- A second phase of microwave heating at 20 W for 5 minutes.

Finally, the mineralized was diluted with Milli-Q water in a volumetric borosilicate glass flask with a capacity of 50 ± 0.06 ml. The resulting mixture was then stored in the refrigerator in a polyethylene tube for further analysis.

2.4. Processing of Results

Student's test was used to determine whether differences in selenium concentration (Se) between the matrices studied. The Student's test is a statistical test used to compare the means of two independent samples. It is based on the null assumption that the two means are equal. If the test yields a p-value below the significance level (usually 0.05), then the null hypothesis is rejected and it is concluded that the two means are significantly different.

2.5. Determination of Total Selenium by Inductive Plasma/Mass Spectrometer Coupling

Analyses were performed using Perkin Elmer®'s Elan 6000 ICP-MS. The methodology used to optimize the instrument and analytical procedure was detailed by the US EPA (1998a) in Method 6020, specifically for selenium.

2.6. Expression of Results

The formula for calculating selenium levels in the samples was expressed as follows:

$$\text{Arsenic content}\left(\text{mg/kg}\right):\frac{\text{Selenium content}}{\text{Sample weight}}\times 1000 \quad (1)$$

Selenium content in miligrams per kilogram (mg/kg).

Amount of Selenium measured during analysis (micrograms).

Fresh weight test sample mass (kilograms).

3. Results and Discussion

3.1. Selenium Concentrations in Sediment

Table 1 presented descriptive statistics of selenium concentrations in sediments in the Aby lagoon system. The mean selenium concentration is 0.82 mg/kg with a standard error of 0.09. This indicates that the average is calculated with some uncertainty, which is quantified by the standard error. The 95% confidence interval for the mean is 0.64 to 0.99. This result implies that if the experiment were

Table 1. Descriptive statistics of selenium concentrations in sediments in the Aby lagoon.

Descriptive statistics	Se (mg/kg)
Mean (Standard Error)	0.82 (0.09)
95% CI of mean	0.64 - 0.99
Average truncated to 5%	0.77
Median	0.70
Standard deviation	0.69
75th percentile	1.29
Min. - Max.	0.02 - 2.96
Interval	2.94

repeated many times, 95% of the calculated confidence intervals would contain the true mean. The 5% truncated average is 0.77. This measure implies that the lowest 5% and the highest 5% were removed before the average was calculated. The median is 0.70, which is equivalent to saying that 50% of samples have a selenium concentration of less than 0.70 mg/kg. The standard deviation is 0.69, indicating the variability or dispersion of selenium concentrations around the mean. The 75th percentile is 1.29, which represents the fact that 75% of the samples have a selenium concentration of less than 1.29 mg/kg. The minimum selenium concentration is 0.02 mg/kg and the maximum concentration is 2.96 mg/kg. The interval is 2.94, which is the difference between the maximum and minimum value. The average of 0.82 mg/kg Se in the sediments of Aby Lagoon indicates moderate contamination compared to international threshold values. The high variability in concentrations (standard deviation of 0.69 mg/kg) highlights the influence of local factors such as sources of Se inputs, sediment properties, and biogeochemical processes. The median of 0.70 mg/kg shows that half of the samples have concentrations below this value, indicating an asymmetrical distribution of the data. Se concentrations in Aby Lagoon are comparable to those in other coastal lagoons in West Africa, such as Burullus Lagoon in Egypt [14] and a lagoon off the coast of Jeddah [15]. However, they are lower than those seen in areas heavily contaminated with selenium, such as the San Francisco Bay Area in the United States [16] [17]. The maximum concentration of Se in Aby Lagoon exceeds the EPA's proposed threshold value of 2 mg/kg for the protection of aquatic life. This suggests that potential ecotoxicological risks exist for some sensitive organisms in certain areas of the lagoon [18] [19].

3.2. Spatial Variation of Selenium in Sediments

Table 2 provided a description of selenium concentrations by site. The mean selenium concentration was lowest in Aby Lagoon north (0.66 mg/kg) and highest in Tendo Lagoon Bays (1.11 mg/kg). The average concentration in the Tanoe River was slightly higher in the rainy season (0.93 mg/kg) than in the dry season (1.13 mg/kg). The Tendo Lagoon channel had an intermediate average concentration (0.76 mg/kg). The standard deviation was highest in the Tendo Lagoon Bays (1.50 mg/kg), reflecting a high variability in selenium concentrations. The standard deviation was lower in the Tanoe River (0.42 mg/kg) and in the Aby Lagoon North (0.63 mg/kg). These results showed a more homogeneous distribution of selenium in these sites. The average selenium concentrations at the different sites in Aby Lagoon were comparable to those of other coastal lagoons in Africa [14]-[21].

Figure 2 showed the box plots and the scatter plot of selenium concentrations in sediment at the different sites. In North Aby Lagoon, the median selenium concentration was relatively low and the variability of the data was low, as evidenced by the length of the boxplot whiskers. In addition, the individual values were distributed around the median. At the channel, the median selenium

Table 2. Descriptive statistics of selenium concentrations by site.

Statistical settings (mg/kg)	Tanoe River	Aby North	Tendo		
			Chenal	Bays	Concentrations
Samples number	6	24	13	15	28
Average	0.93	0.66	0.76	1.11	0.95
Mean 95%	0.49 - 1.37	0.39 - 0.93	0.32 - 1.22	0.66 - 1.55	0.65 -1.25
Average truncated to 5%	0.95	0.62	0.74	1.05	0,90
Median	1.07	0.44	0.47	0.91	0.86
Standard deviation	0.42	0.63	0.75	0.79	0.78
75th percentile	1.22	1.00	1.37	1.50	1.39
Min - max	0.17 - 1.35	0.03 - 1.94	0.02 - 2.04	0.17 - 2.96	0.02 - 2.96
Interval	1.18	1.91	2.02	2.79	2.94

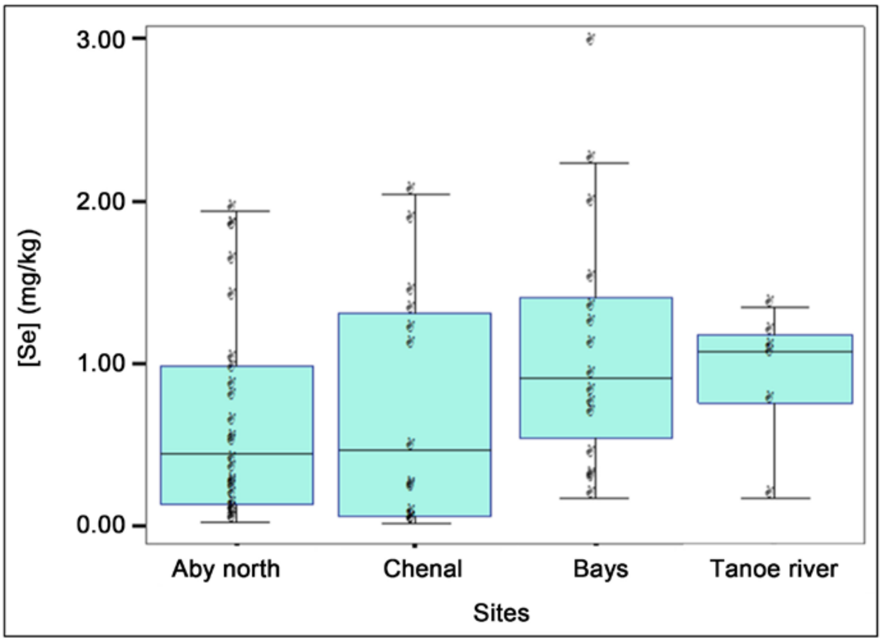

Figure 2. Boxplots and scatter plot of selenium concentrations from sediments in the Tanoe River, the channel and bays of Tendo Lagoon and in the Lagoon Aby North.

concentration was slightly higher than that of Aby-Nord, but the variability remained similar, with values scattered around the median. As for the bays of Tendo Lagoon, this site had a higher median selenium concentration and the variability of the data was greater, with values spread over a wider range.

In the River Tanoe, the median selenium concentration was the highest among all sites, and the variability was also greater, with more dispersed individual values. Overall, these results highlighted the variations in selenium concentrations between the different sites of the Aby Lagoon North. The box plots showed the distribution of the data, while the scatter plot showed the individual values. The median selenium concentration was significantly higher in the Tanoe River than in the other sites.

The bays of Tendo Lagoon had a higher median concentration than the North Aby Lagoon and the channel. The variability of the data was greater in the Tanoé River and the bays of the Tendo Lagoon than in the North Aby Lagoon and the channel. Indeed, differences in median selenium concentration between sites may be due to several factors, such as sources of selenium inputs, physicochemical properties of sediments, and biogeochemical processes [22] [23]. The high variability of the data in the Tanoe River and the bays of the Tendo Lagoon may be due to the presence of point sources of contamination or to selenium remobilization processes in sediments [24].

3.3. Intra-Seasonal Variations of Selenium in Sediments According to Medians, Minimum and Maximum Concentrations

Table 3 has presented data on concentrations and extreme values for two sites, Tendo and Aby North, during the dry (DS) and rainy seasons (RS) during two sampling campaigns.

3.3.1. For the Tendo Lagoon Site

During the rainy season (RS_1 and RS_2), for each season 1 and 2, the median concentration was 0.23 mg/kg and 0.28 mg/kg, respectively, with a concentration range from 0.02 to 1.50. During the dry season (DS1 and DS2), for the first and second seasons, the median concentration was 0.91 mg/kg and 1.37 mg/kg, respectively, with a concentration range from 0.28 mg/kg to 2.96 mg/kg.

3.3.2. For the Aby North Lagoon Site

The median concentration was 0.34 mg/kg and 0.23 mg/kg, respectively, with a concentration range of 0.08 mg/kg to 1.01 mg/kg. During the dry season (DS1 and DS2), the number of samples was 5 for the first season and 2 for the second. The median concentration was 0.15 mg/kg, respectively, with a concentration range of 0.03 to 0.25 mg/kg. The results showed significant differences in the

Table 3. Medians, minimum and maximum concentrations of Se in sediments from Tendo and Aby lagoons at RS 1&2 and DS 1&2.

Lagoons	Statistical parameters	Rainy seasons			Dry seasons		
		RS1	RS2	RS 1&2	DS 1	DS 2	DS 1&2
Tendo	Samples number	7	7	14	4	12	16
	Median	0.23	0.28	0.25	0.91	1.37	1.25
	Min - Max	0.02 - 0.91	0.02 - 1.50	0.02 - 1.50	0.28 - 1.32	0.47 - 2.96	0.28 - 2.96
Aby North	n	5	6	11	6	7	13
	Median	0.34	0.73	0.39	0.15	1.61	0.50
	Min - Max	0.08 - 0.52	0.03 - 1.01	0.03 - 1.01	0.03 - 0.25	0.50 - 1.94	0.03 - 1.94

median concentrations of the test substance between the wet and dry seasons, as well as variations between the two sites, Tendo and Aby North.

Based on the comparison between the rainy and dry seasons, the results showed that for the Tendo site, the median selenium concentrations during the dry season were significantly higher than during the rainy season. This suggested a potential accumulation of the substance in the soil during the dry season, possibly due to less leaching and greater bioavailability. Whereas for the Aby North site, selenium concentrations appeared to be lower during the dry season than during the rainy season. This could have been due to increased dilution during the rainy season or other site-specific environmental processes. This is because precipitation can influence the mobility of substances in the soil by diluting them or transporting them to other compartments of the ecosystem, such as groundwater or surface water [25] [26]. Studies have shown that precipitation can increase the leaching of substances from the soil during the rainy season, thereby reducing their concentration in the surface layer of the soil [27]. This is because seasonal variations in environmental conditions, such as soil temperature and moisture, can influence the sorption and desorption processes of substances in the soil. During the dry season, when temperatures are higher and the soil is drier, the holding capacity of substances in the soil can increase [28], resulting in an increase in observed concentrations. Referring to variations between sites, median selenium concentrations differed between the two sites, with Tendo having higher median concentrations than Aby North, especially during the dry season. Differences between sites could be related to site-specific agricultural practices and land use [29]. For example, the use of pesticides or fertilizers in agriculture can influence the presence and distribution of substances in the soil, and these practices may vary from site to site [30]. The results indicated the importance of considering both seasonal variations and differences between sites when assessing the environmental risks associated with the presence of this substance in soil.

Table 4 showed that, as with mercury, intra-seasonal variability is greater in the dry season. However, for selenium, it is the values of DR2 that are higher

Table 4. Comparisons of sediment selenium concentrations between RS1-RS2 and DS1-DS2 at different sites in Aby Lagoon (Student's test).

Sampling areas	Rainy Season 1&2 (RS1 - RS2)			Dry seasons 1 and 2 (DS1 - DS2)		
	t	ddl	p	t	ddl	p
Tendo Chenal	0.074	3	0.94		**	
Baies Tendo	−0.474	5	0.65	−1.783	6	0.12
Aby north	−0.489	9	0.63	−6.051	11	<0.01
Lagoon set	1.388	20.15§	0.18	4.583	26	<0.01

**Insufficient values to perform the test on Tanoe and Chenal at the SP, [§]Variance equal to the Student's test.

than those of DS1. At the site level, the Aby north lagoon shows significant variability during the dry and rainy seasons. Student's test applied to the search for significant differences between Se concentrations for identical seasons and by site yielded the results recorded in the Aby Lagoon north. For Aby Lagoon north, the results show a significant difference in the dry season between campaigns 1 and 2 and for all the data pooled at the same season. The results indicated several trends in selenium concentrations in soil, as well as significant seasonal and spatial differences. Indeed, the intra-seasonal variability of selenium is greater during the dry season. This could be due to a combination of factors, such as variations in precipitation, soil temperatures, and seasonal biogeochemical activities. During the dry season, when environmental conditions are more stable, selenium sorption and desorption processes in soil can be more influenced by factors such as sporadic rainfall and increased bioavailability due to lower soil moisture [31]. The spatial variability criterion showed that the North Aby Lagoon shows a significant variability in selenium concentrations during the dry and rainy seasons. This observation may be related to differences in geological features, hydrological conditions, and land use between sites. For example, human activities such as agriculture or industry can influence the distribution of selenium in the soil near the lagoon [32]. In addition, Student's tests revealed significant differences in selenium concentrations for identical seasons and by site. This reflects the idea that the observed variations are not simply due to chance but are influenced by environmental factors or human activities specific to each site and season [28]. The results highlighted the importance of considering both seasonal and spatial variations as well as the complex interactions between environmental factors to understand the dynamics of selenium in the lagoon environment.

3.4. Inter-Seasonal Variations of Selenium in Sediments

Table 5 shows median selenium concentrations in Aby lagoon sediments according to rainy season (RS) and dry season (DS). In Aby north Lagoon, the median selenium concentration during the rainy season is 0.39 mg/kg and during the dry season it is slightly higher at 0.50 mg/kg. In the Tanoé River, the median selenium concentration during the rainy season is 0.46 mg/kg and during

Table 5. Medians of sediment Se concentrations during the rainy season and dry season of Aby Lagoon and comparison by Student's test.

Sites	Samples number	Rainy season	Dry season	Student's Test		
				t	ddl	p
AbyN Lagoon	24	0.39	0.50	−0.06	22	0.55
Tanoe River	6	0.46	1.13	1.57	1.01$^{\$}$	0.35
Bays Lagune Tendo	15	0.81	1.21	−1.55	13	0.15
Chenal Lagune Tendo	13	0.04	1.31	6.04	6.41$^{\$}$	<0.01**

**Significant difference, $^{\$}$variance equal to the Student test.

the dry season it is significantly higher at 1.13 mg/kg. In the bays of Tendo Lagoon, the median selenium concentration during the rainy season is 0.81 mg/kg and during the dry season it is 1.21 mg/kg. Finally, in the Tendo Lagoon Channel, the median selenium concentration during the rainy season is 0.04 mg/kg and during the dry season it is significantly higher at 1.31 mg/kg. Selenium concentration is generally higher during the dry season than during the rainy season. The only significant difference is observed in the Tendo Lagoon channel, where selenium concentration is significantly higher during the dry season ($p < 0.01$).

For the other sites, the differences observed between seasons were not statistically significant. The results of this study suggest that the concentration of selenium in and around Aby Lagoon is generally low and does not pose a risk to human health. However, the concentration of selenium in the Tendo Lagoon channel is significantly higher during the dry season and could pose a health risk to local populations. The results indicate significant variations in selenium concentrations between the rainy and dry seasons, as well as differences between sampling sites. These results could be explained by seasonal effects on selenium availability, geographic and hydrological variations, biogeochemical processes, and interactions between seasons and sites.

In terms of seasonal effects on selenium availability, during the rainy season, precipitation could lead to selenium leaching into the sediment, which could lead to relatively lower concentrations in sediment samples. In contrast, during the dry season, with less precipitation, selenium may be less mobile and more likely to accumulate in sediments, resulting in higher concentrations [33].

In addition, with respect to geographic and hydrological variations, observed differences between sites could be attributed to geographic variations in sediment composition, hydrological conditions, and human practices such as agriculture or industry [34]. For example, sites near agricultural or industrial areas may have higher selenium concentrations due to fertilizer use or surface water contamination.

On the other hand, with regard to biogeochemical processes, selenium concentrations in sediment could also be influenced by phenomena such as sorption, desorption and bioavailability of selenium in sediment [35]. These processes could vary depending on seasonal environmental conditions as well as the specific characteristics of the sediment and vegetation present at each site.

Finally, interactions between seasons and sites revealed significant differences between seasons and sites, suggesting complex interactions between environmental factors and human practices that influenced selenium dynamics in sediment [36] [37].

Figure 3 showed the means and standard errors of selenium (Se) concentrations in sediments in the North Aby and Tendo lagoons. In the North Aby Lagoon, the average concentration of selenium in sediments is about 0.46 mg/kg. The rainy season samples (shown in orange) have a similar concentration to the

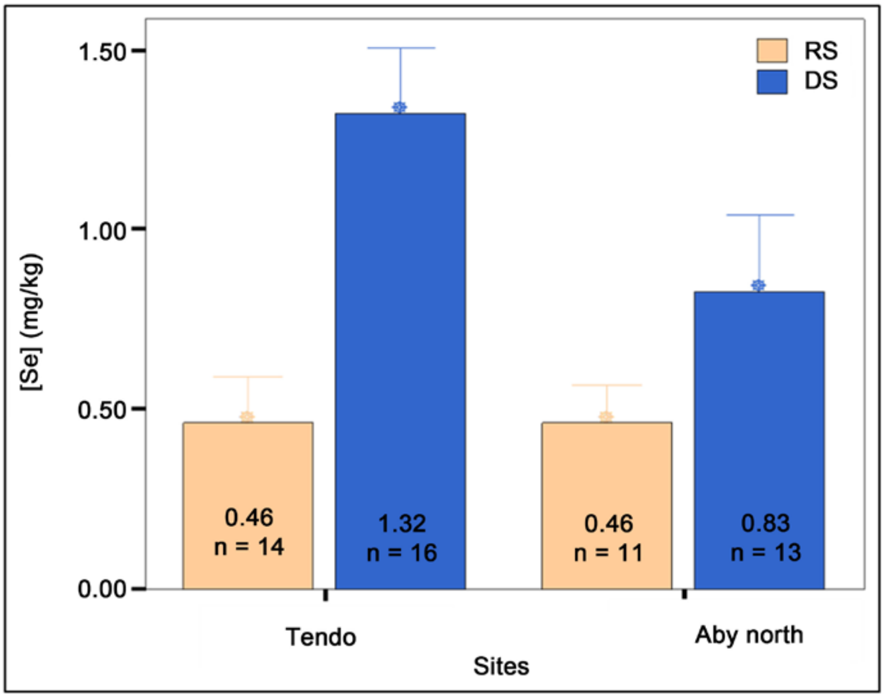

Figure 3. Standard means and error of Se concentrations in sediments of the AbyN and Tendo lagoons at RS 1&2 and DS 1&2.

dry season samples (shown in blue). The intensity of selenium enrichment varies from no enrichment to very high enrichment. Sediment pollution is also moderate, ranging from no pollution to heavily polluted. The main pollutants are copper, cadmium and lead. In addition, at the Tendo Lagoon, the average concentration of selenium in the sediments is about 0.46 mg/kg. However, dry season samples have a significantly higher concentration, reaching approximately 1.32 mg/kg. The selenium enrichment intensity is similar to that of Ab north, ranging from no enrichment to very high enrichment. Sediment pollution is moderate, ranging from no pollution to heavily polluted. In sum, these results highlight the need to take into account seasonal and spatial variability as well as interactions between environmental factors for a thorough understanding of selenium dynamics in aquatic ecosystems.

4. Conclusion

This study aimed to evaluate selenium contamination in the sediments of the Aby and Tendo lagoons in Côte d'Ivoire, taking into account variations across different sites and seasons. The findings revealed that the average selenium concentration in the sediments of the Aby Lagoon indicated moderate contamination when compared to international threshold values. Selenium concentrations varied across sites and seasons, with the highest values observed in the channel of the Tendo Lagoon during the dry season. These variations were influenced by several factors, including the sources of selenium inputs, the physicochemical properties of the sediments, biogeochemical processes, and seasonal environmental conditions. This research enhances our understanding of selenium dynamics in lagoon ecosystems and aids in assessing the environmental risks associated with its presence. The findings underscore the importance of considering seasonal and spatial variability, as well as the interactions between environmental factors, for a comprehensive understanding of selenium dynamics in aquatic ecosystems.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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