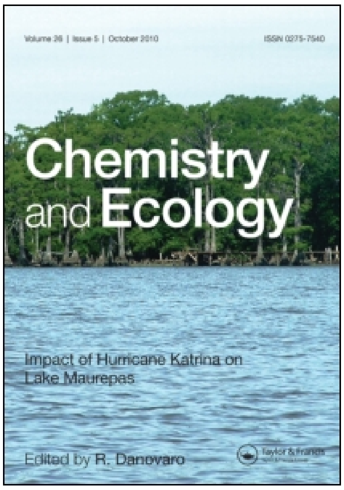

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Geochemical characteristics of surficial sediments in a tropical estuary, south-west India

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Geochemical characteristics of surficial sediments in a tropical estuary, south-west India

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Geochemical characteristics of surficial sediments in the Panangad region of Cochin estuary, the largest brackish-water humid ecosystem in the south-west coast of India, were analysed. Temporal variations in nutrient stoichiometry, seasonal characteristics of redox elements Fe and S, and the phosphorus geochemistry were employed for the purpose. The stoichiometric analysis pointed towards autochthonous origin of organic matter, possibility of nitrogen limitation, and allochthonous modification of redox conditions. Seasonal variations were not statistically significant for all the geochemical parameters, whereas significant spatial variations were observed with lower values at sandy stations, suggesting that the texture of the sediments is the main factor influencing the sediment geochemistry. Significant inter-relations between the geochemical parameters also suggest a common control mechanism. Based on these geochemical characteristics, the study region can be effectively categorized into two distinct zones, viz. (1) erosion and transportation and (2) deposition zones.

Keywords: Geochemistry; Nutrient dynamics; Diagenesis; Autochthonous production; Tropical estuary

1. Introduction

Sediments conserve important environmental information [1] and are increasingly recognized as both a carrier and a possible source of contaminants in aquatic systems [2]. Estuaries are particularly vulnerable to such input changes because of the limited water exchange [3]. Sediments effectively trapped by estuarine circulation processes [4] may be eroded, transported, and deposited many times before they accumulate below the actively reworked surface layer [5]. Since sediment quality assessment is considerably complex as a result of the many site-specific parameters, detailed information on interacting hydrodynamical, biological, and geochemical processes is essential [6].

The biogeochemical processes operating in the system will lead to chemical transformations of the element and will ultimately affect the bioavailability of the element. In aquatic systems,

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in situ identification and monitoring of individual processes and their contribution to the biogeochemical process is a difficult task. Hence, an index should be developed in such a way that it will have the signals of all the possible processes. If we consider the chemical transformations as redox reactions, a better index can be developed by potential elements, which exhibit a definite redox character and sufficient concentration to monitor the transformations. Two elements that can generally be considered as having these qualities are iron and sulfur, with varying oxidation states and a high environmental reactivity. Another possibility is the nutrient elements. Stoichiometric ratios of nutrients have been utilized in many estuarine studies to determine the origin of organic matter sources and documenting organic transformations [7].

The Vembanad-Kol wetlands (09° 50′ N, 76° 45′ E) is the largest estuarine system in the south-west coast of India. It lies parallel to the coastline with several islands and small arms. The permanent openings to the Arabian Sea are at Kochi (about 450 m wide) and at Azheekode. The region around Cochin barmouth is generally referred to as Cochin backwaters. Its length is about 80 km with a NW–SE orientation, and the width varies from a few hundred metres to about 4 km. The estuary is generally shallow with depths ranging from 0.75 to 5 m [8]. The depth of the navigation channel for the ships to reach Cochin port varies from 8 to 12 m. Rich biodiversity and ecological values of this estuary qualified for the designation as a Ramsar Site (No. 1214).

This is a typical monsoon-influenced estuary, which contributes to about 71% of annual rainfall [9]. Accordingly, there are three seasonal conditions prevailing, viz. monsoon (June–September), post-monsoon (October–January), and pre-monsoon (February–May). There are several rivers joining on either side of the Cochin barmouth with maximum discharge during south-west monsoon periods. Tides at Kochi are of a mixed semi-diurnal type, with the spring tide range of about 1 m [10]. This is one of the highly productive estuarine systems, with an annual gross production ranging from 52 to 183 $mg\,C\,m^{-3}\,h^{-1}$ [11].

The main objective of the present study is to identify the geochemical characteristics of the sediments in the study region through monitoring the spatial and temporal variations in nutrient stoichiometry and seasonal characteristics of redox elements, iron and sulfur.

2. Materials and methods

The study area is the Panangad region of the Cochin estuary and is situated about 10 km from the barmouth. The area is mainly the inner arm of the Lake and surrounds Nettoor and Panangad islands. Six stations were selected for the present study (figure 1). Only stations 2 and 6 are in the main arm of Cochin estuary, and all the other stations represent the narrow inner parts of the estuary, the estuarine characteristics of which were least studied [11]. Depth of the stations varied from 1 to 5 m with an average of 2.5 m. Monthly samples of surficial sediments were collected from these stations during January to December 2003 using a van Veen grab (0.042 m^2). Samples during the month of May could not be collected. Samples were stored in airtight polyethylene bags, transported to lab on ice, and stored in a deep freezer.

Textural analysis of the wet sediment was done based on Stoke's law using the method of Krumbein and Pettijohn [12]. Finely powdered air-dried sediment samples were used for the analyses of rest of the parameters, and the values are expressed as percentage dry weight. The total carbon, nitrogen, and sulfur of the surficial sediments were analysed using a CHN analyser (VarioEL lll CHNS). Organic carbon was also determined using the CHN analyser by removing the inorganic carbon with diluted HCl [13]. Total phosphorus was calculated as the sum of different fractions obtained from sequential extractions [14]. About 1 g of the sediments was carefully digested with a tri-acid mixture ($HClO_4$, HNO_3, and HCl in a ratio of

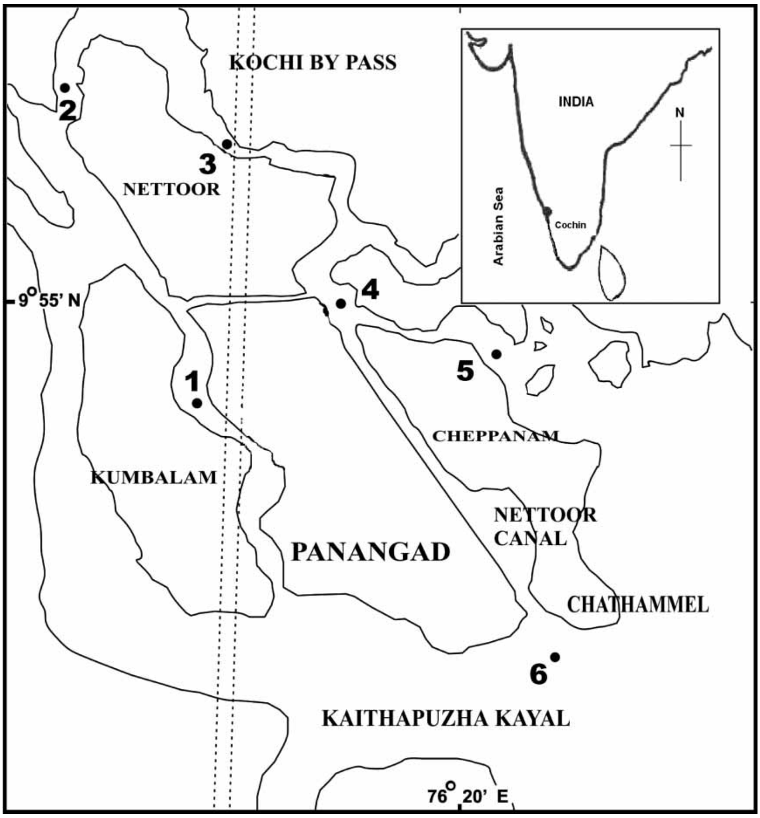

Figure 1. Panangad region of Cochin estuary. Sampling locations are marked as 1–6.

1:1:3), and total iron concentrations were determined by atomic absorption spectrophotometry (Perkin-Elmer, 3110). The accuracy of the analytical procedures for total iron determination was checked using BCSS-1 (standard reference material for marine and estuarine sediments). A replicate analysis of BCSS-1 showed a good accuracy, with a recovery rate of 93%.

3. Results

Data (including standard deviations) are reported as seasonal averages of the monthly observations (table 1). Substratum generally represented a combination of clay, sand, and silts. The textural composition of the sediment showed a distinct spatial variation, but the seasonal variations were minimal. Coarser fractions were found at stations 1, 2, and 3, while stations 4, 5, and 6 were dominated by finer fractions. By applying Folk [15] classification, sediments at stations 2 and 3 were sandy, whereas they were muddy at stations 5 and 6. Sandy mud nature was observed at station 1 and sandy silt at station 4.

On a seasonal basis, the total carbon content showed a wide variation, ranging from 0.1 to 3.61% dry weight pre-monsoon and from 0.07 to 3.86% during the monsoon, and ranging between 0.10 and 3.74% post-monsoon. Organic carbon content showed similar distributional characteristics to that of total carbon content and varied from 0.08 to 2.51% dry weight pre-monsoon. The monsoon and post-monsoon variations were 0.06–2.48% and 0.06–2.36% respectively. The percentage of organic carbon to total carbon did not show any seasonal trend.

Table 1. Seasonal averages of geochemical parameters in the study region (percentage weight ± S.D.), and results of ANOVA (two-way without replication).

	Station 1			Station 2			Station 3			ANOVA (p value)	
Parameters	Pre	Mon	Post	Pre	Mon	Post	Pre	Mon	Post	Spatial	Seasonal
Sand	82.5 ± 1.20	82.7 ± 1.20	81.9 ± 0.90	92.4 ± 4.20	93.9 ± 4.20	90.1 ± 1.30	0 ± 0.00	0 ± 0.00	0 ± 0.00		
Silt	7.3 ± 1.90	6.6 ± 1.30	8.2 ± 1.30	1.4 ± 0.60	1.2 ± 0.70	1.7 ± 0.20	54 ± 1.90	53.1 ± 1.30	55 ± 1.40		
Clay	10.2 ± 0.70	10.8 ± 0.5	9.9 ± 0.50	6.2 ± 3.50	4.8 ± 3.70	8.2 ± 1.10	46 ± 1.90	46.9 ± 1.30	45 ± 1.40		
Total carbon	0.68 ± 0.10	0.69 ± 0.05	0.81 ± 0.24	0.1 ± 0.03	0.07 ± 0.01	2.53 ± 1.87	2.83 ± 0.91	3.5 ± 0.14	3.37 ± 0.12		
Organic carbon	0.54 ± 0.12	0.5 ± 0.03	0.59 ± 0.19	0.08 ± 0.05	0.06 ± 0.02	1.87 ± 1.61	2 ± 0.88	2.48 ± 0.29	1.99 ± 0.22		
Total nitrogen	0.12 ± 0.02	0.1 ± 0.06	0.15 ± 0.09	0.06 ± 0.03	0.09 ± 0.04	0.26 ± 0.24	0.27 ± 0.18	0.42 ± 0.03	0.46 ± 0.09		
Total phosphorus	0.08 ± 0.02	0.08 ± 0.03	0.09 ± 0.04	0.03 ± 0.00	0.04 ± 0.00	0.09 ± 0.05	0.19 ± 0.06	0.28 ± 0.05	0.23 ± 0.05		
Total sulfur	0.27 ± 0.01	0.26 ± 0.09	0.32 ± 0.08	0.04 ± 0.03	0.03 ± 0.00	0.92 ± 0.74	0.88 ± 0.27	1.13 ± 0.06	1.09 ± 0.08		
Total iron	2.4 ± 0.23	2.34 ± 0.32	2.33 ± 0.52	0.45 ± 0.15	0.34 ± 0.14	2.08 ± 1.15	5.91 ± 2.17	7.19 ± 0.27	7.54 ± 0.79		
	Station 4			Station 5			Station 6				
Sand	97.6 ± 0.70	98.1 ± 0.70	97.2 ± 0.20	26.4 ± 6.00	27 ± 7.00	30.9 ± 0.90	0.4 ± 0.10	0.4 ± 0.10	0.4 ± 0.00	1.01E–15	0.85
Silt	0.6 ± 0.20	0.4 ± 0.30	0.8 ± 0.10	51.5 ± 6.20	52.1 ± 4.40	47.9 ± 4.40	67.2 ± 2.70	68.5 ± 1.90	65.9 ± 1.70	2.78E–14	0.82
Clay	1.8 ± 0.40	1.5 ± 0.40	2 ± 0.20	22.1 ± 0.80	20.9 ± 0.50	21.2 ± 0.60	32.4 ± 2.60	31.1 ± 1.80	33.7 ± 1.80	1.21E–12	0.55
Total carbon	0.21 ± 0.17	0.09 ± 0.02	0.1 ± 0.04	2.65 ± 0.83	2.68 ± 0.20	2.35 ± 0.21	3.61 ± 0.08	3.86 ± 0.13	3.74 ± 0.03	9.80E–05	0.41
Organic carbon	0.16 ± 0.12	0.07 ± 0.03	0.06 ± 0.03	1.72 ± 0.66	1.86 ± 0.26	1.62 ± 0.24	2.51 ± 0.15	2.47 ± 0.10	2.36 ± 0.08	0.0004	0.65
Total nitrogen	0.08 ± 0.02	0.09 ± 0.01	0.03 ± 0.05	0.32 ± 0.10	0.29 ± 0.05	0.3 ± 0.06	0.33 ± 0.02	0.35 ± 0.04	0.36 ± 0.08	0.0002	0.23
Total phosphorus	0.04 ± 0.01	0.08 ± 0.03	0.1 ± 0.04	0.18 ± 0.05	0.19 ± 0.08	0.18 ± 0.08	0.17 ± 0.04	0.19 ± 0.03	0.13 ± 0.01	5.12E–05	0.22
Total sulfur	0.09 ± 0.06	0.04 ± 0.02	0.02 ± 0.01	0.82 ± 0.18	0.79 ± 0.12	0.83 ± 0.07	1.17 ± 0.22	1.14 ± 0.24	1.52 ± 0.20	0.0002	0.14
Total iron	0.72 ± 0.39	0.28 ± 0.08	0.68 ± 0.65	4.8 ± 1.08	5.29 ± 0.53	5.12 ± 0.99	7.52 ± 0.12	7.37 ± 0.29	6.98 ± 0.21	6.58E–08	0.34

Note: Pre: pre-monsoon; Mon: monsoon; Post: post-monsoon. [a]The post-monsoon samples of station 2 were not collected from same location as that of other seasons (inside the regularly dredged National Waterway). The data presented belong to a location just outside the waterway. Hence, these variations are not included in the general discussion.

Total nitrogen content in the sediment ranged from 0.06 to 0.33% pre-monsoon and from 0.09 to 0.42% during the monsoon, and ranging between 0.03 and 0.46% post-monsoon. The total phosphorus content ranged between 0.03 and 0.19% pre-monsoon and between 0.04 and 0.28% during monsoon. The post-monsoon range was 0.09–0.23%. The sulfur content was in the range of 0.04–1.17% pre-monsoon and 0.03–1.13% during monsoon. The post-monsoon range was from 0.02 to 1.52%. Iron content ranged between 0.45 and 7.52% pre-monsoon and between 0.28 and 7.37% during the monsoon. The post-monsoon range was 0.68–7.54%.

The results showed that the geochemical elements have a clear spatial variation with higher values at stations 4, 5, and 6 and lower values at stations 1, 2, and 3. No temporal trend was seen for any of the sediment parameters.

4. Discussion

An ANOVA (two-way without replication) was carried out to determine the spatial and temporal variations of the geochemical parameters in the study region (table 1). Significant spatial variations ($p < 0.001$) were observed with higher values at muddy stations and lower values at sandy stations. Seasonal variations of all the geochemical elements were not statistically significant. The seasonal averages of the sediment geochemical data were statistically analysed ($n = 18$) with a view to finding their inter-dependence, and the correlation matrix is presented in table 2.

Sediment textures are highly variable in estuaries, and this particular system also is not an exception. Grain size is related to hydrodynamics, and it generally showed an increase from the inner areas towards the barmouth direction. The texture of the sediments has a significant role in the physico-chemical processes as well as in the species diversity of the depositional environment [16]. The absence of seasonal variations suggests that direct effects of river discharge and land runoff are not influencing the texture of the study region. Correlation analysis showed that silt and clay fractions have high positive correlations with all the analysed sedimentary parameters. Sand fractions showed a similar negative behaviour. It has been well documented that fine particles often concentrate metals due to their greater surface area and amounts of organic carbon, clay, iron, or aluminium [17]. Since the organic matter generally decreased with increasing grain size, as evident from the correlation analysis, it seemed that coarse-grained sandy deposits lack the substrate to sustain significant biological activity. These correlations thus give a clear indication that the main factor influencing the geochemistry of

Table 2. Correlations between the seasonal averages of the geochemical parameters ($n = 18$) in the study region.

Parameter	Total carbon	Total nitrogen	Total phosphorus	Total sulfur	Iron	Sand	Silt	Clay
Total carbon	1							
Total nitrogen	0.96	1						
Total phosphorus	0.83	0.86	1					
Total sulfur	0.98	0.93	0.77	1				
Iron	0.94	0.93	0.87	0.90	1			
Sand	−0.91	−0.91	−0.87	−0.87	−0.98	1		
Silt	0.91	0.88	0.84	0.88	0.96	−0.98	1	
Clay	0.84	0.87	0.85	0.78	0.92	−0.94	0.87	1

Note: Correlation analysis showed that silt and clay fractions have high positive correlations with all the analysed sedimentary parameters. On the other hand, sand fractions showed a negative behaviour. The results give a clear indication that the main factor influencing the geochemistry of the surficial sediments in the study region is the sediment texture. The spatial variations in the geochemical parameters are the direct results of the granulometry. The interdependence of geochemical parameters, as evident from their highly significant inter-correlations, suggests a common control mechanism.

the surficial sediments in the study region is the sediment texture, and the spatial variations are the direct results of the grain-size variations.

Nutrient elements in the study region did not show any seasonal trend as reported in the case of other Indian estuaries [18, 19]. Seasonal changes are difficult to observe in surface sediments of estuaries due to periodic resuspension by tidal currents, bioturbation, and post-depositional chemical reactions [20]. Nutrients varied widely with respect to the grain-size compositions of sediments and decreased with increasing grain size of the sediment. Fine-grained sediments are richer in organic matter than coarse sand [21]. The maximum values of nutrients were recorded in the muddy stations, evident from the high positive correlations of nutrient elements with the silt and clay and their high negative correlations with sand. The positive correlation of sediment carbon with total nitrogen and phosphorus indicates a common source of organic matter to these elements.

Stoichiometric ratios of nutrients (figure 2) are utilized to determine the origin and transformation of organic matter. Variations of C:N ratios were generally lower than 10, and seasonal averages were 6.6, 7.8, and 7.3, respectively, during pre-monsoon, monsoon, and post-monsoon. The data indicate that organic matter in the sediments is labile and originates mainly from the water column (autochthonous), and phytoplankton-derived matter is presumably a major fraction of this material. Organic matter should have a C:N ratio lower than 17 in order to be of nutritional use to invertebrates [22]. Hence, this organic-matter input is characterized by a high nutritional value and represents a high-energy source for benthic organisms. The shallowness of the water column and higher primary [11] and benthic productivity [23] provide a better supply of labile sedimentary organic matter to this estuary.

By mass, Redfield [24] predicts a C:P ratio of 40 and N:P ratio of 7 for algal material, while Hecky *et al.* [25] indicated that a wider range of C:P and N:P ratios in lakes can still be considered to follow Redfield (C:P = 28–56 and N:P = 4–9). The C: P ratio varies widely in the study region ($\sim$1–28) and was higher in the muddy stations than in sandy ones. However, the N:P ratio did not show considerable variations among stations and ranged between 0.3 and 2.7. Both these ratios did not show any seasonal variations and were far below the Redfield ratio. Hence, there is a possibility of phosphorus enrichment in this estuary. Hydrodynamical data [11] also suggested the lack of phosphorus limitation. The lower N:P ratios also indicate that benthic nitrogen recycling is in excess of phosphorus, and denitrification, and the benthic release of nitrogen might play a role in sustaining the productivity of the system.

The S:C value in sediments did not show any significant variations; values were in the range of 0.3–0.5 in most cases. This ratio, which is considerably higher than the average ratio in abyssal plain sediments (0.13), showed no spatial variations, maintaining the same levels in sandy and muddy sediments. Very high levels of sulfur indicated an anthropogenic source. This could be by the active transport of raw sulfur to a fertilizer plant (FACT, Cochin Division) through the National Water Way, which passes through the study region. The presence of such a high level of sulfur can also cause a higher accumulation of metals in sediments, through coagulation and precipitation [26].

Generally, redox characterization of the system is done in terms of sulfur dynamics. But in systems where external addition of sulfur is dominant, iron chemistry can be used to define the system. Comparison of iron content with the shale average [27] showed no significant enrichment, suggesting the absence of any anthropogenic source as in the case of sulfur. In this study, iron was observed to be behaving as reflections of the geochemical parameters, as evident from the correlation analysis.

The geochemical distribution patterns of various elements in the study area indicated that the texture of the sediments is the major controlling factor on sediment geochemistry. The bottom dynamic conditions are highly significant in the geochemistry, and accordingly three areas can be defined [28], viz. areas of erosion, transportation, and accumulation. From the

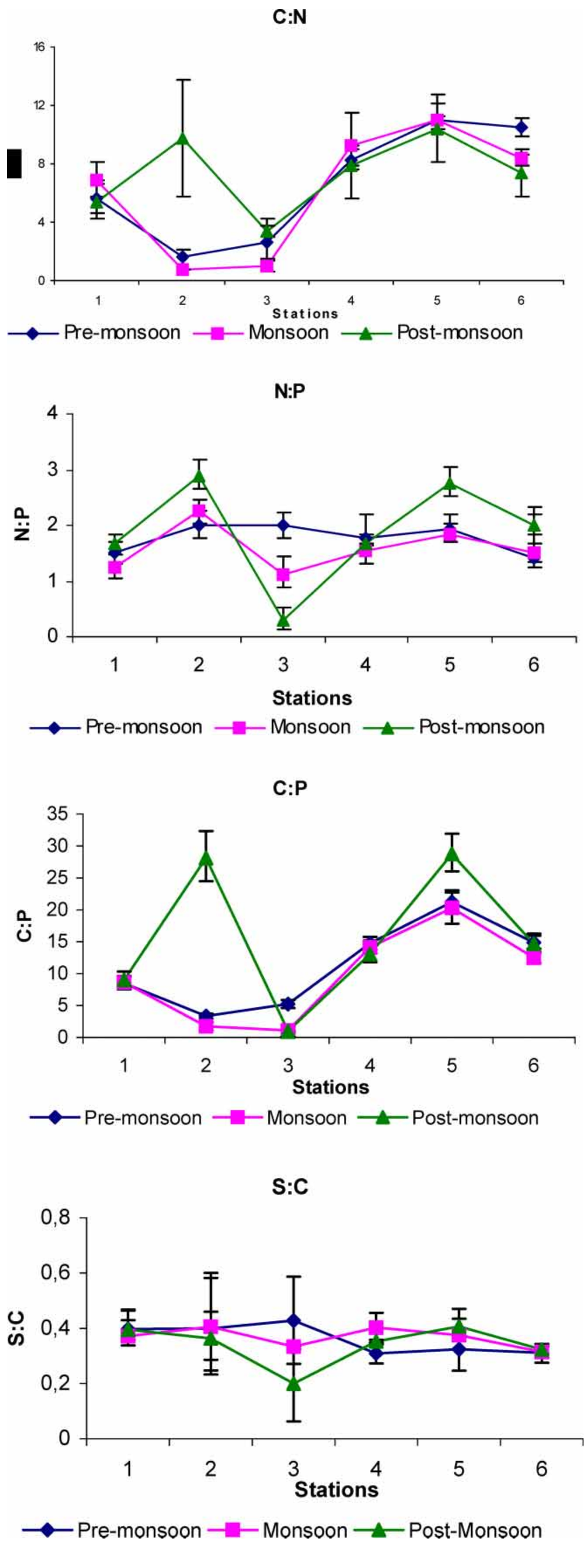

Figure 2. Seasonal and spatial variations of nutrient stoichometry in the study region.

geochemical characters and also from the hydrodynamical data [11], stations 1, 2, and 3 can be confined to the first two classes, whereas the other three can be confined to the areas of accumulation. In the erosion zone, the deposited particles are not being stored, as indicated by the low total carbon content. The organic carbon content was about 70–85% of the total carbon in these areas, and the sulfur content was also low, suggesting slow progress of diagenetic processes. The deposition zone is organically rich and anoxic. An enhanced input of sulfur by anthropogenic addition may also stimulate the diagenesis, substantially altering the cycling of elements.

5. Conclusion

The study showed that the seasonal distributions of nutrient stoichometry and redox elements have similar trends. The main factor influencing the geochemistry of the surficial sediments in the study region is the sediment texture, and the spatial variations are due to the grain-size variations. The significant inter-correlations between the geochemical parameters suggest a common control mechanism. These results indicate that these elements could give a general idea about the geochemical characteristics prevailing in the estuary. Micro-level speciation studies are essential to derive the complete geochemical dynamics.

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