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Effects of Lack of Basic Sanitation in Maricá Municipality (Rio de Janeiro/Brazil) and Resulting Endocrine Disruptors Dissemination Through Local Environments: Subsidies for Local Environmental Management

Moises Leão Gil , Estefan Monteiro da Fonseca * , Bruno Silva Pierri , Jessica de Freitas Delgado , Leonardo da Silva Lima , Danieli L. Cunha , Thulio Rigeti Correa , Charles Vieira Neves , Daniele Maia Bila

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Moises Leão Gil [1,2], Estefan Monteiro da Fonseca [1,3,*], Bruno Silva Pierri [1,2], Jessica de Freitas Delgado [1,2], Leonardo da Silva Lima [1,2], Danieli L. Cunha [1,2], Thulio Rigeti Correa [1], Charles Vieira Neves [1] and Daniele Maia Bila [4]

1 Aequor - Instituto de Geociências, Universidade Federal Fluminense, Avenida Litorânea s/n, 24210-340 Niterói, RJ, Brasil.
2 Department of Geology and Geophysics/LAGEMAR – Laboratório de Geologia Marinha, Instituto de Geociências, Universidade Federal Fluminense, Avenida Litorânea s/n, 24210-340 Niterói, RJ, Brasil.
3 Programa de Pós-Graduação em Dinâmica dos Oceanos e da Terra Av. Gen. Milton Tavares de Souza s.n., Gragoatá – Niterói
4 Universidade do Estado do Rio de Janeiro. Departamento de Engenharia Sanitária e Ambiental. Rio de Janeiro, RJ, Brasil.
* Correspondence: author, email oceano25@hotmail.com

Abstract: Endocrine-disrupting compounds (EDCs) are emerging pollutants that can potentially accumulate in aquatic ecosystems at significant levels, with the potential to impact the health of both animals and humans. Many scientists have correlated human exposure to high concentrations of EDCs with critical physiological impacts, including infertility, thyroid imbalance, early sexual development, endometriosis, diabetes, and obesity. Several substances, such as heavy metals, belong to this family, ranging from natural to synthetic compounds, including pesticides, pharmaceuticals, and plastic-derived compounds. Domestic sewage represents a significant source of EDCs in the surrounding aquatic ecosystems. To this day, most rural and urban domestic wastewater in the municipality of Marica is directly discharged into local aquatic environments without any treatment. The present study aimed to assess the potential contamination of the riverine and lagoonal environment in the municipality of Marica. Water and sediment samples were collected seasonally at 18 sites along the Maricá watershed and the main lagoon, where most of the watershed contributors flow. Water physico-chemical parameters (pH, Eh, dissolved oxygen levels, salinity, turbidity, temperature, and fecal coliforms) were analyzed to characterize the urban influence on the aquatic environment. Simultaneously, sediment samples were analyzed for grain size, total organic carbon percentage, and the potential bioavailable fraction of trace metals (Cd, Pb, Cu, Cr, Hg, Ni, Zn, and As). Finally, the sediment toxicity was assessed using YES assays. The results obtained already demonstrate the presence of estrogenic effects and raise concerns about water quality. The findings from the present study suggest that, despite the absence of agricultural and industrial activities in the city of Maricá, EDCs are already present and have the potential to impact the local ecosystem, posing potential risks to human health.

Keywords: Yes assay; sediment; heavy metal; toxicity

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1. Introduction

Human activities have introduced several emerging pollutants into global ecosystems. Among these pollutants, endocrine-disrupting compounds (EDCs) are a significant group of compounds widely found in aquatic environments. EDCs belong to various chemical groups, including xenobiotic chemicals also present in industrialized products such as children's toys, everyday

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utensils, plastic containers or bottles, polyvinyl chloride pipes, cleaning agents, and cosmetics [1,2]. As EDCs degrade and their constituent chemicals and by-products diffuse through the environment, they can influence the hormonal balance of living organisms by neutralizing or counteracting natural hormones [3,4]. Consequently, these pollutants can interact with the endocrine receptors in living species' bodies, generating "false" hormonal signals that can potentially stimulate or inhibit endocrine system function [5,6]. The presence of these contaminants in freshwater environments is a significant concern, as organisms are chronically exposed to them. Well-documented examples of harmful impacts resulting from EDC exposure include sexual effects and the feminization of male fish [7], inhibition of the molting process in crustaceans [8], and alterations in fish behavior [9]. Human exposure to EDCs can occur through ingestion, inhalation, and dermal absorption [10], and it may lead to various negative health impacts, such as the development of type 2 diabetes, obesity, cardiovascular abnormalities, and certain types of cancer [11]. Therefore, comprehensive knowledge of the fate of these pollutants in all the environmental compartments involved is crucial for assessing the potential risks associated with the discharge of domestic wastewater effluents.

The world's water circulation represents a dynamic system that plays a vital role in promoting biogeochemical cycles [12]. Rainfall runoff, which is dominated by rain events [13], washes pollutants from building walls, roofs, streets, land surfaces, and improperly disposed wastes, carrying them into local rivers and other aquatic bodies [14,15]. In the case of water receptor pools, such as lagoonal systems, these environments are sensitive ecosystems situated at the interface between terrestrial and marine coastal environments [16]. Globally, lagoonal environments make up 13% of Earth's coastline [17], each having unique features and sensitivities, making them essential natural habitats for Earth's biodiversity. Lagoonal systems are also significant for human activities, serving as protected sites for aquaculture, tourism, and recreational purposes. However, uncontrolled exploitation of these coastal environments can lead to negative ecological impacts and disrupt the local ecosystem. Lagoons typically have limited water circulation, making them susceptible to contaminant accumulation [18,19]. Therefore, assessing water quality in the contributing watershed and lagoonal ecosystem is crucial for ecological management, as it depends on the interaction of physical, chemical, and biological mechanisms.

In recent years, the revenue of the Maricá municipality has been rapidly increasing due to the policy of distributing royalties from oil production in the Santos basin [20]. Consequently, there is expected to be accelerated investment in the development and industrialization of the municipality. However, according to Nogueira and Barbosa (2018) [21], the municipality exhibits a low rate of basic sanitation infrastructure installation, with incomplete water supply and sewage networks.

Considering that urban sustainability is more effective when environmental policies are implemented while cities are still relatively small in size [22,23], the main objective of this article is to support the management of local urbanization and industrialization. Therefore, the present study aims to evaluate the potential presence of EDCs in Maricá's riverine complex and adjacent lagoonal complex, assess their potential toxicity, and diagnose current environmental toxicity. This assessment will help project potential environmental impacts associated with expected industrial development.

2. Study Site

The city of Maricá is located in the metropolitan area of the city of Rio de Janeiro, situated between the geographic coordinates of 22º53' and 22º58'S and 42º40' and 43º00'W. Currently, the municipality is home to more than 150,000 inhabitants [21] and continues to experience daily growth.

The local predominant climate is classified as tropical hot and super humid [24]. The average annual temperature has fluctuated between 27°C and 30°C in recent decades, with annual precipitation ranging from 1,015 mm to 1,635 mm [25]. The spring and summer seasons receive the highest levels of annual precipitation, and the relative air humidity typically falls between 80% and 90% due to marine influence [26].

The Maricá municipality is situated within a series of coastal plains that extend to the Jurubatiba National Park, which is located in the municipalities of Macaé, Carapebus, and Quissamã [27]. This coastal plain is characterized by the presence of double coastal ridges and associated lagoons,

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forming the Maricá-Guarapina Lagoon System. This system is connected to the Atlantic Ocean by a channel at the eastern end of this coast [28].

The Araçatiba Lagoon (also known as Maricá Lagoon) (Figure 1) has a total area of 18.2 km². Its associated drainage basin mainly receives water from the Ubatiba river basin, which is formed by small watercourses originating in the municipality. These watercourses flow into the lagoon system, including the Mumbuca river, Camburi, Imbassaí, Itapeba, and Burriche streams that flow into the Araçatiba Lagoon, as well as Padre Guedes, Caju, and Rangel streams, which have their mouth in the Barra Lagoon. Additionally, the rivers Doce, Bananal, Engenho, Nilo Peçanha, and Paracatu, along with their tributaries Manuel Ribeiro, Caranguejo, and Padeco, flow into the Guarapina Lagoon.

The selection of the Araçatiba Lagoon for this study is based on previous research [29,30] that identified this lagoon as one of the most degraded in the system. Furthermore, studies such as the one by Knoppers et al. (1991) [29] have already characterized the lagoon as eutrophic, with urban development and population growth in the municipality leading to deforestation, the presence of clandestine landfills, and the release of untreated effluents [31,32].

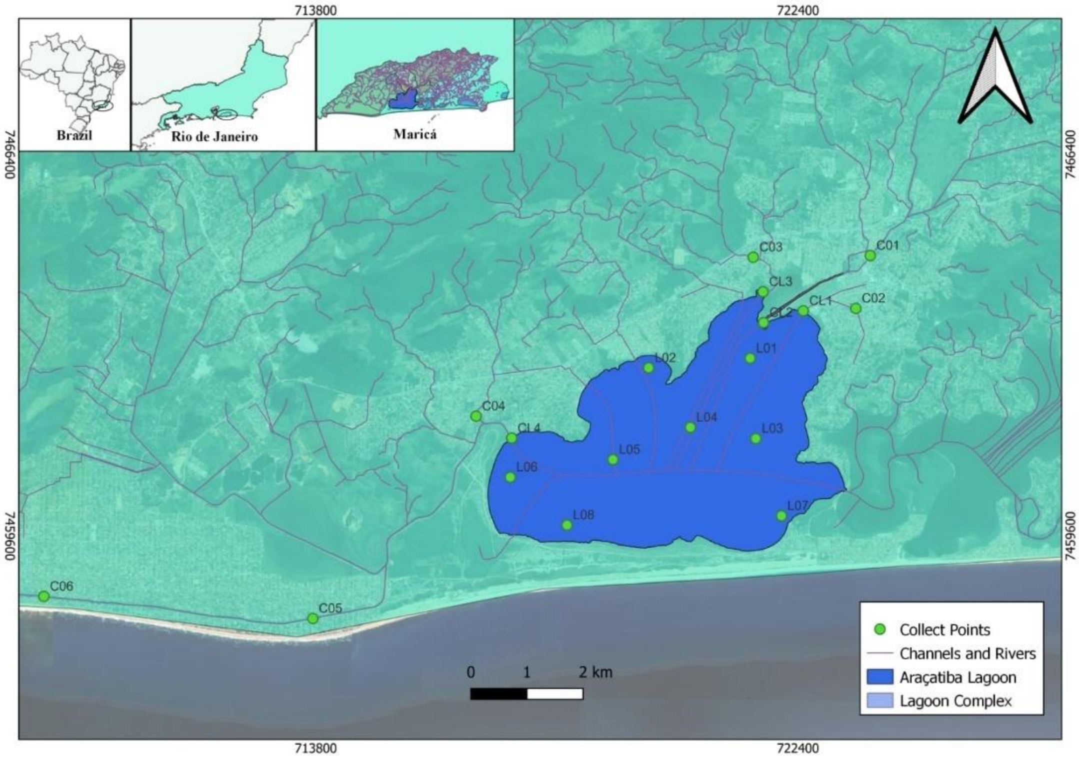

Figure 1. Study site and sampling stations.

3. Methodology

Five sub-basins within the Maricá watershed were selected as the study area, along with the Araçatiba Lagoon (Figure 1). The choice of sampling stations was influenced by the adjacent occupation scenario, which has been a result of the recent, uncontrolled growth in the municipality's population, potentially impacting water quality. Surface water samples were collected at 18 sampling stations during both the dry season (August/21) and the wet season (February/22). For water collection, a Van Dorn water sampler (5 L) was utilized.

Surface sediments were gathered using a Van Veen sampler and a spatula, both made of stainless steel, and were subsequently transferred to 200 mL amber glass bottles for the Yeast Estrogen Screen (YES Assay). Physicochemical parameters such as grain size, organic matter content, and heavy metal concentrations were analyzed using samples placed in polyethylene plastic bags.

The surface water samples collected for the analysis of E. coli were stored in 200 mL plastic bottles. Additionally, a pre-calibrated multiparameter probe (Horiba-U50) was employed to assess

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water column physicochemical parameters, including temperature, pH, redox potential, turbidity, dissolved oxygen (DO), and salinity.

Following the sampling campaign, all samples were stored at 4°C and transported to the laboratory. Surface sediment samples designated for the YES Assay underwent solid-phase extraction (EFS) and sonication within 48 hours of collection. Water samples for the determination of E. coli were also processed within the same timeframe.

In order to avoid interference with the final analysis results, all materials and glassware used in the collection and preparation of samples in the laboratory were previously decontaminated with sequential washing of neutral soap (Extran®), acetone, ultrapure water, hexane and ultrapure water.

3.1. Water Column Parameters

Regarding E. coli, its presence and quantity in water samples was determined using the most probable number method (MPN), according to the protocol described in Standard Methods for the Examination of Water and Wastewater [33]. Briefly, 100 mL of the water sample was filtered through a filter membrane (0.45 µm porosity), transferred to a selective culture medium for E. coli (incubated at temperatures between 35 and 37°C for 24 hours), and finally, we checked whether the E. coli colony had grown.

3.2. Sediment Parameters

The characterization of sediment quality was carried out through the analysis of Total Organic Carbon, (TOC%), and grainsize, trace metals (Cd, Pb, Cu, Cr, Hg, Ni, and Zn) and As. The TOC% and grainsize analysis were carried out according to the Embrapa Manual (1997) [34], respectively. Trace metal samples were maintained in pre-acidified plastic bowls and transported to the laboratory for analysis. For grainsize determination, organic matter was first removed with hydrogen peroxide (30%). Then a Microtrac S3500 grain size analyzer was used. The results were categorized into sand, silt, and clay classes. The fine class content (below 0.063 mm) was used for trace metal evaluation. The approach for the heavy metal and As determination in sediments was carried out using the method described by EPA (Environmental Protection Agency), method 3050b [35]. According to the referenced methodology, 15.0 mL of concentrated HNO3 is added with 0.50g of fine sediment in the pipes of the digestor block. Still, according to the cited method, after 12h, it is heated until 160oC, remaining at this temperature for 4h. Then, 8.0 mL of hydrogen peroxide 30% (v/v), was added, remaining at 160oC temperature for more 30min. Finally, the samples were transferred to a volumetric balloon of 100.0 mL and filtrated. Sample blanks and a reference sediment WQB-1 from the National Laboratory for Environmental Testing, Burlington, Canada were also used at regular intervals to monitor quality control. After centrifugation and further dilution, As, Cd, Pb, Cu, Cr, Ni, Hg, and Zn were read by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). The detection limits are Pb, 1.3 mg.Kg-1; Cu, 1.3 mg·Kg−1; Ni, 0.8 mg·Kg−1; Zn, 1.5 mg·Kg−1; Cd, 1.0mg·Kg−1; As, 1.2mg.Kg-1 and Cr, 1.5mg.Kg-1. The recovery rates for the trace metals varied between 87.8 and 102.5%. All utensils, tools, and equipment were acid-washed with 10% HNO3 and rinsed with distilled water to avoid potential procedure contamination. Certified standard material was used to assure the accuracy of the analytical procedures (SPEX-QC-21-16-85AS-traceable to NIST). The maximum value for precision data was 5%.

Mercury approach was performed according to USEPA - 7,471 method, through cold vapor atomic adsorption (USEPA 1997). This method involves mixing 0.2 g sample mass with 5 ml of reagent water and 5 ml of aqua regia, being after heated for 2 min in a 95 oC water bath before adding 50 ml of double deionized water and 15 ml of 10 % KMnO4 solution. After 30 min the samples were transferred from the bath and once cooled, 6 ml of a solution of 10 % sodium chloride-hydroxylamine sulphate was incorporated to reduce the residual KMnO4. The detection limit for Hg reached 0.0148 mg.Kg-1.

3.3. Estrogenic Activity (YES Assay)

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The methodology used to prepare the sediment sample was solid phase extraction (EFS), based on Routledge and Sumpter (1996) [36] with modifications, according to Gomes et al. (2023) [37]. The sediment samples collected for the YES assay were placed in an oven at 60 °C for 24 hours, macerated and 10 g were placed in a beaker for extraction by sonication with methanol (10 mL/5 min). Subsequently, they were centrifuged (2500 g/5 minutes) (NT 812 - Nova Técnica®) and the supernatant was collected and transferred to a 200 mL volumetric flask. This procedure was repeated three times, with the supernatants combined in the same volumetric flask, which was finally added to the volume with ultrapure water until 200 mL and HCL (3mol.L-1) was added to adjust the pH to 2.

Samples were purified using two EFS columns, Strata-X and Strata-SAX (Phenomenex®). Both were previously conditioned, the first with a sequence of 2 x 3 mL of hexane, 2 mL of acetone, 2 x 3 mL of methanol, followed by 10 mL of ultrapure water (pH 3); while the second, 2 x 5 mL of methanol and 2 x 5 mL of ultrapure water). The Strata-SAX cartridge was attached to the top of the Strata-X cartridge and 200 mL of the sample was then percolated through both cartridges in a manifold system with a flow rate of 3 ml s-1. In the end, the cartridges were uncoupled and the EFS procedure continued with just the Strata-X cartridge. The cartridges were cleaned up with a methanol: water solution (1:9 v/v) and followed by complete drying, through vacuum aspiration for 10 min. Finally, the analytes of interest retained in the cartridge were eluted in a vial with 2 x 2 mL of acetone. The extracts were evaporated under vacuum, reconstituted with 2 mL of ethanol, covered, homogenized in a vortex (2 min/30 rpm), and subjected to the YES Assay.

The in vitro assay uses the yeast Saccharomyces cerevisiae, which has a human estrogen receptor DNA sequence in its genome. In the presence of an estrogenic compound, it interacts with this receptor, causing the expression of a gene and, consequently, the production of the enzyme β-galactosidase. This enzyme is secreted into the medium and produces a colorimetric response, with the degradation of the chromogenic substrate chlorophenol red-β-D-ga-lactopyranoside (CPRG), which is yellow, into chlorophenol red (CPR), a pinkish product [38].

In a laminar flow hood, the assay was performed in sterile 96-well microplates with 12 serial dilutions of the samples in ethanol (HPLC grade). 17β-estradiol (E2) was used as a positive control and ethanol (HPLC grade) was used as a negative control. The dose-response curves of E2 (2724 to 1.33 ng L-1) were prepared by serial dilutions of E2 and ethanol from a stock solution at 54.48μg L-1. A 10μL aliquot of each sample dilution was transferred to microplates, in duplicate, and evaporated at room temperature. Next, 200 μL of analysis medium (growth medium, yeast and CPRG) were added to the wells. The microplates were sealed, shaken vigorously in a plate shaker (IKA MS3®) and incubated for 72 h at 30°C in an incubator (Nova Ética, 410®). After incubation, colorimetry and turbidity were measured at 575 nm and 620 nm, respectively, on a spectrophotometric plate reader (Spectramax M3, Molecular Devices®). The absorbance values read on the assay plate were corrected (Equation 1).

$$\text{Abs}_{\text{corrected}} = \text{Abs}_{\text{575 sample}} - \left(\frac{Abs_{620\ sample}}{Abs_{620\ blank}}\right) \quad (1)$$

The estrogenic activity of each sample was calculated based on the maximum induction of β-galactosidase in each sample extract, which was determined in 17β-estradiol equivalent (EQ-E2) by interpolating the sample curve data with that of the control curve. positive E2 (in ng L-1). To obtain the real EQ-E2 value of the sediment sample, it was necessary to divide the EQ-E2 value by the concentration factor used in the EFS.

Another calculation procedure carried out was cytotoxicity, that is, the inhibition of the growth of the yeast S. cerevisiae due to toxic compounds present in the sample, which translates into the absence of turbidity at the end of the test. To quantify this effect, absorbance control was performed at 620nm in each well (Equation 2), as described by Frische et al. (2009) [39].

$$\text{Citotoxicity} = 1 - \left(\frac{Abs_{620\ sample}}{Abs_{620\ blank}}\right) \quad (2)$$

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3.4. Statistical Analyzes

Spearman correlations (r) were calculated between the variables to evaluate the possible relationship between chlorophyll-a, E. coli and the physical-chemical parameters analyzed in the water and, for surface sediments, the possible relationship between EQ-E2 and physicochemical parameters. Correlation strengths were considered according to Dancey and Reidy (2006), values of $r < 0.4$ show a weak correlation, $0.4 \leq r < 0.7$ moderate and $r \geq 0.7$ strong. Correlations above 0.7 ($p < 0.05$) were considered significant. Principal Component Analysis (PCA) was also performed to further investigate the associations between all variables.

4. Results

4.1. Water

Throughout the research, salinity data exhibited distinct patterns among the various compartments studied, particularly between the sampling stations located within the water contributors and those within the lagoon. Sampling sites in the river basin generally displayed lower salinity values, indicating the presence of freshwater, except for sampling stations C05 and C06, where there appears to have been a potential momentary failure of the multiparametric probe used (Figure 2). As the stations approached the lagoon, salinity levels increased, indicating saline intrusion beginning at the mouths of rivers and canals. Seasonal fluctuations were evident, with the lowest values observed during the rainy season due to dilution from rainfall. However, the salinity values in the Araçatiba Lagoon suggested the influence of marine waters, despite the lagoon's isolated nature within the lagoon system. Furthermore, the absence of local tidal patterns consistent with the adjacent sea level implies a source of seawater intrusion other than surface intrusion.

Moore (1999) [40] defined the subsurface soil zone where meteoric groundwater mixes with saltwater as a subterranean estuary. In the specific case of Maricá, this term is not limited to groundwater. The overexploitation of groundwater, likely caused by a lack of sufficient fresh water for the local population's supply, has allowed the percolation of saltwater and subsequent salinization of surface water compartments. According to Mastrocicco and Colombani (2021) [41], one of the major concerns in coastal regions is the progressive salinization of freshwater compartments, which is driven by increasing demand for freshwater, climate change, and land use modifications. Consequently, freshwater salinization has garnered significant attention from the scientific community in recent years [42–45].

Regarding temperature, this parameter remained relatively stable, with winter temperatures ranging from 21.3°C to 27.1°C and summer temperatures from 26.7°C to 34.47°C (Figure 3). In contrast, pH values varied between 6.1 and 9.0 throughout the research. In terms of environmental quality, the pH values in the study area indicate relatively healthy environmental conditions since the water column's acidity is not significantly accentuated (Figure 4). Two main characteristics of the system likely contribute to this: the lagoon's shallow nature, allowing for effective atmospheric oxygen diffusion, especially during windy weather, and the presence of a relatively narrow sandy ridge separating the lagoon from the sea, which may buffer the lagoon's waters due to underground percolation of saltwater [46]. This is further supported by the moderate correlation between pH and salinity observed during statistical analysis (R: 0.63212).

Furthermore, the Eh (redox potential) did not exhibit extreme reduction characteristics during the winter, with the exception of points C03, C04, and C08 (Figure 5). In contrast, during the summer, particularly during the vacation season, the increased potential for waste disposal and the influence of rainfall may contribute to enhanced reducing conditions in the contributing channels. Once again, the most compromised conditions were observed in the more confined areas, which are potential locations for domestic sewage disposal. Dissolved oxygen data followed this trend, with levels ranging from 0.3 mg/L to 10.1 mg/L. Oxygen levels in the contributing channels were significantly lower than those in the lagoon, underscoring the importance of atmospheric oxygen diffusion and the distance from sewage sources in maintaining water quality (Figure 6). Turbidity, on the other hand, exhibited a random pattern with no clear trends in terms of seasonal or spatial variations (Figure 7).

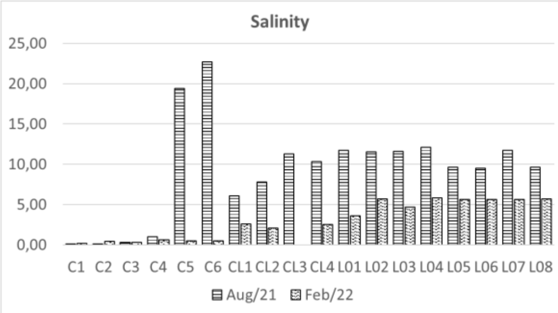

Figure 2. Salinity records along the studied area.

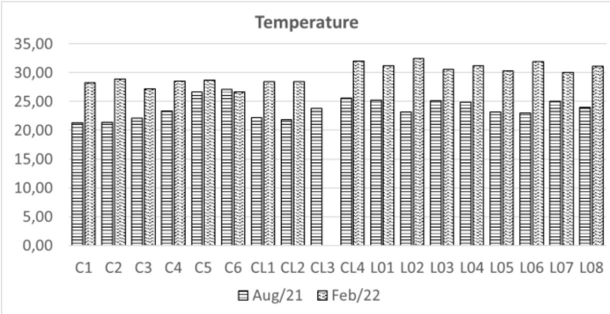

Figure 3. Temperature records along the studied area.

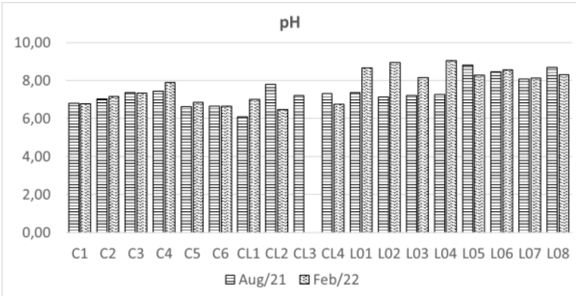

Figure 4. pH records along the studied area.

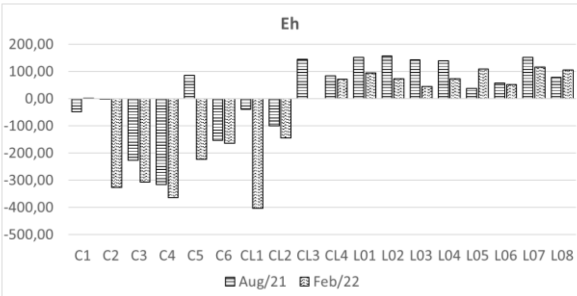

Figure 5. Eh records along the studied area.

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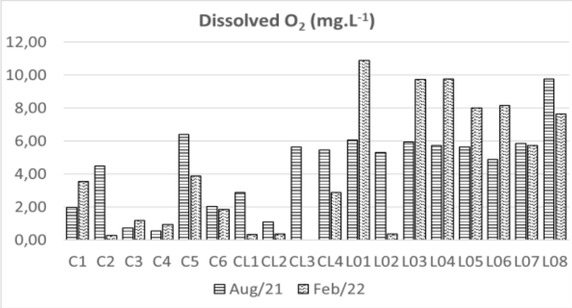

Figure 6. DO levels records along the studied area.

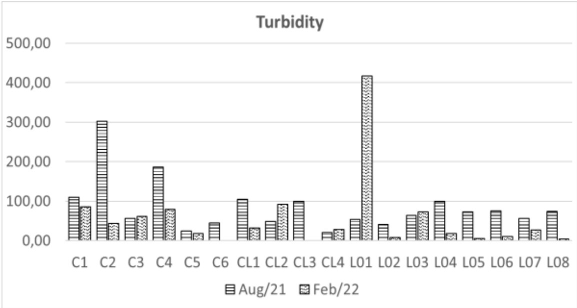

Figure 7. Turbidity records along the studied area.

Finally, concerning water quality, the coliform concentrations corroborate the domestic origin of the pollution within the watershed of the city of Maricá (Figure 8). Based on this data, with the exception of the collection points within the lagoon, all other points exhibited the presence of sewage waste discharge. Particular consideration should be given to point L1 inside the lagoon, especially during the summer, where coliform levels already indicate the influence of contributors into the lagoon.

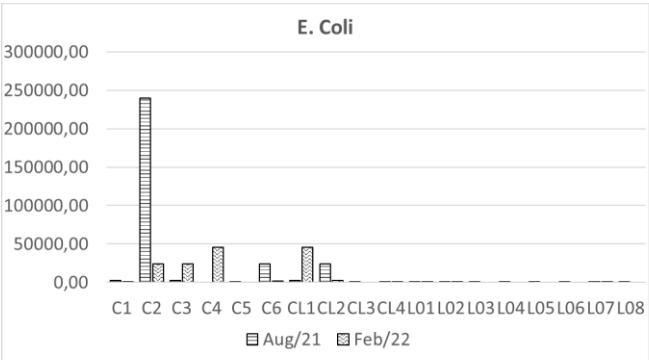

Figure 8. *Escherichia coli* concentrations along the studied area.

4.2. Sediment

Based on the results of sediment physicochemical analysis, there is a significant difference in the predominant grain size concentrations between the watershed contributors and the lagoonal sampling stations (Figure 9). Along the contributors' channels, coarse particles predominate, while in the lagoon, fine sediment particles are prevalent. This pattern can be attributed to the stronger water flow along the rivers and other channels that flow into the lagoon compartment. As water salinity increases, ions dispersed in the water column tend to group together and settle, a phenomenon known as flocculation. This leads to the accumulation of fine particles at the estuary mouths [47].

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Similarly, the percentage of total organic carbon (TOC%) was found to be higher in the lagoonal sampling stations (Figure 10). The increased fluxes in the contributing channels appear to prevent the accumulation of TOC in these channels, even in conditions of lower oxygen levels that would typically conserve organic matter loads. Another possible explanation could be the higher presence of TOC in the soluble phase, although this parameter was not analyzed in the current study.

Regarding heavy metal concentrations, all the studied elements generally exhibited low concentrations, when compared to the existing literature (Table 1). However, some isolated results already indicate potential threats to the ecosystem and living organisms. Nevertheless, the assessment of metal concentrations carried out in the present study confirmed the domestic source of pollution already present in Maricá's water bodies. It also revealed that despite climatic variations, these variations do not significantly affect the diffusion of metals, as no significant concentration variations were observed (Figures 11, 12, 13, 14, 15, 16 and 17).

Table 1. Concentration of heavy metals in sediments available in scientific literature.

Heavy Metal / Reference	Cu	Zn	Pb	Cd	Ni	As	Cr	Hg	Reference
Maricá's watershed and lagoon	n.d. – 47.9	5 - 232	1.07 – 34.41	n.d. – 2.89	n.d. – 22.9	n.d. – 9.62	0.42 – 77.42	n.d.	Present Study
Barra de Navidad and Colima Lagoon (Mexico)			42.7 – 123.9	0.02 – 0.42		10.7 – 25.4		n.d.	[48]
Global Average Shale	45	95	20	0.30	68	4.70	90	0.18	[49]
Red Sea	92	227	64	-	51	--	60		[50]
Shantou Bay (China)	19.0 – 48.0	44.4 – 962.6	21.9 – 102.9	0.2 – 3.6	8.2 – 48.0	-	23.7 – 80.0	-	[51]
ERL	34	150	47	1.2		8.2	81	.0.15	[52]
ERM	270	410	218	9.6		70	370	0.71	
Non - polluted	<25	<90	<40	-	-	<3	<25	≤1.0	[53]
Moderately polluted	25 – 50	90 - 200	40 - 60	-	-	3 - 8	25 - 75	-	
Heavely polluted	>50	>200	>60	>6	-	>8	>75	>1.0	

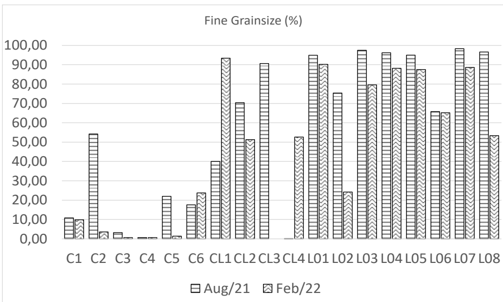

Figure 9. Grainsize records along the studied area.

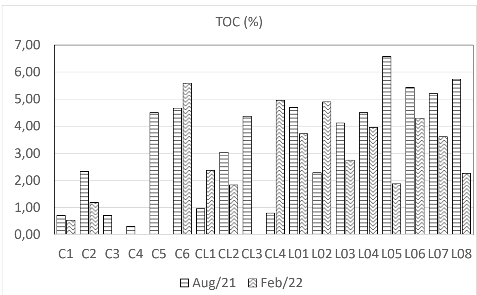

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Figure 10. TOC% records along the studied area.

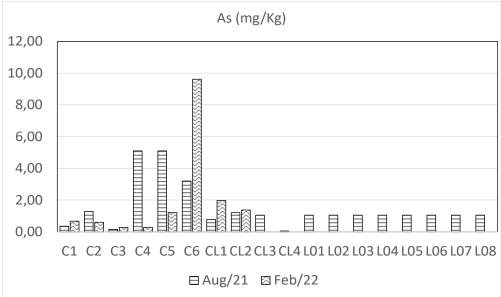

Figure 11. As records levels along the studied area.

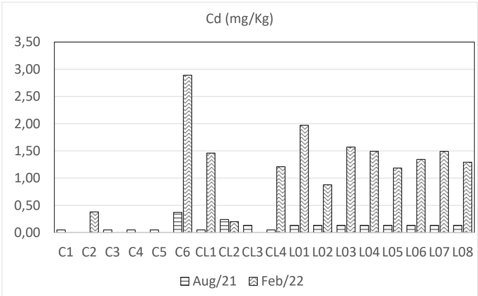

Figure 12. Cd levels records along the studied area.

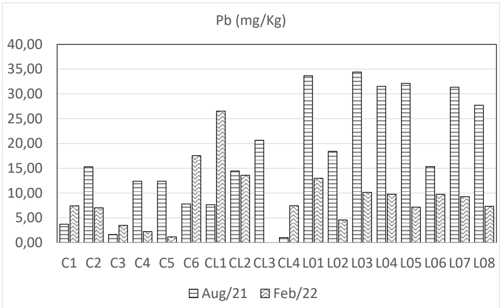

Figure 13. Pb levels records along the studied area.

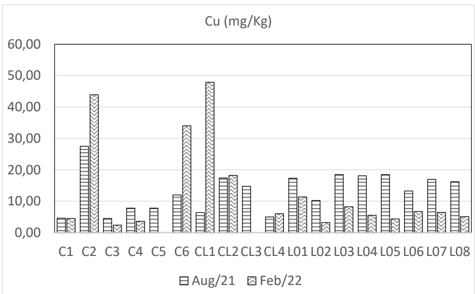

Figure 14. Cu levels records along the studied area.

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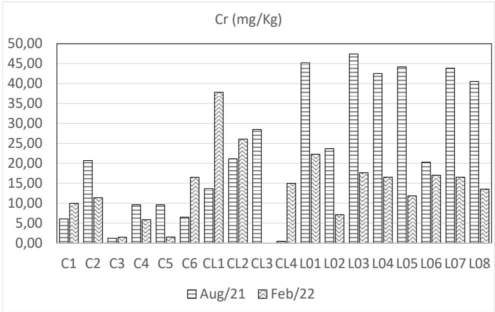

Figure 15. Cr levels records along the studied area.

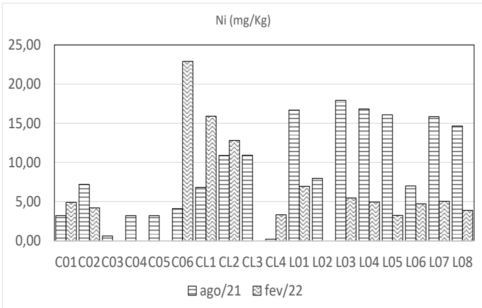

Figure 16. Ni levels records along the studied area.

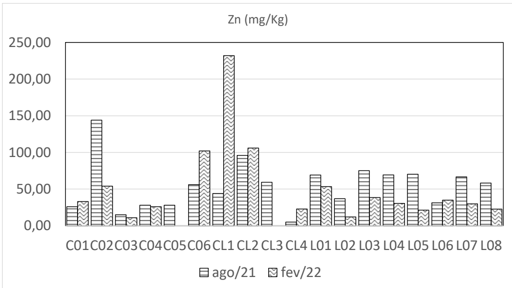

Figure 17. Ni levels records along the studied area.

4.3. Estrogenic Activity by the YES Assay

For the study's objectives, the results were deemed satisfactory. The estradiol dose-response curves (positive control) exhibited the anticipated sigmoidal shape, and no contamination was detected in the negative control (white). The average EC50 value for the estradiol dose-response curve for the sediment samples was 38 ± 10 ng.L-1, and the LD (Limit of Detection) was 0.02 ± 0.01 ng.L-1. The results of the estrogenic activity of the surface sediment samples obtained using the YES Test are depicted in Figures 18 and 19.

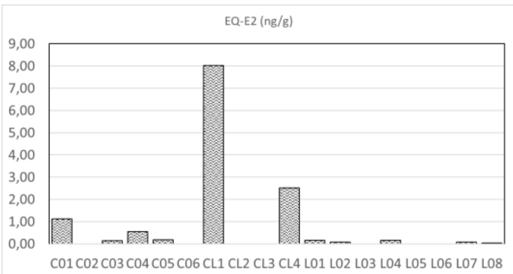

Figure 18. EQ-E2 levels records along the studied area.

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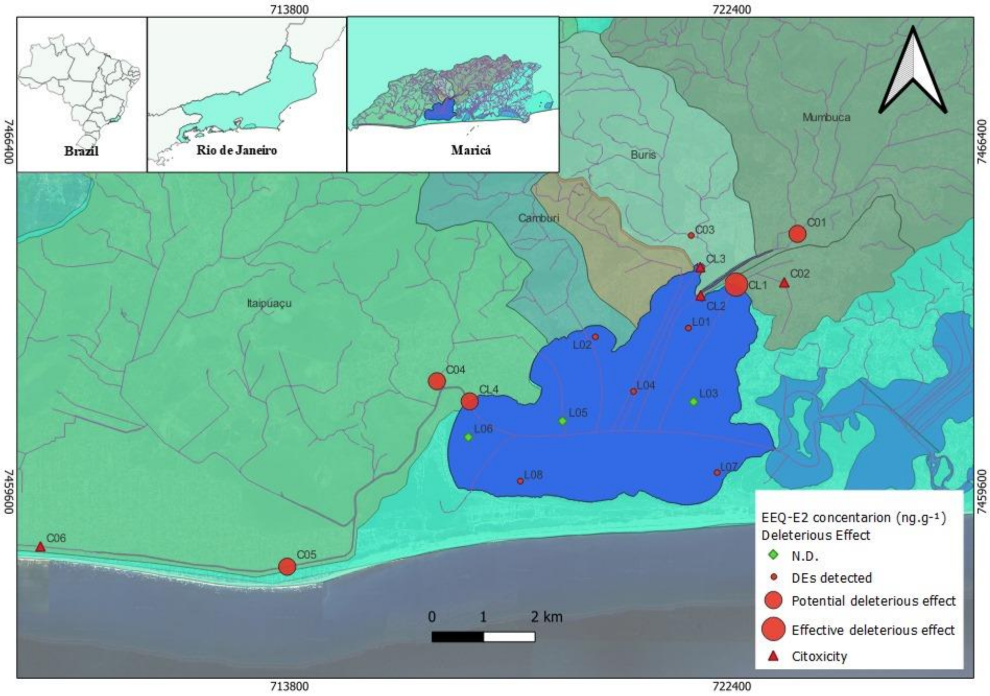

Figure 19. Estrogenic activity per sampling point of surface sediment samples in the river basins that flow into the Araçatiba lagoon, Maricá (RJ). ND – Not detected.

Concentrations ranged from below the limit of detection (<LD) to 8.03 ng.g-1. Among the 18 collection points, only four exhibited cytotoxicity (C02, C06, CL2, and CL3), preventing the assessment of estrogenic activity. In other words, the presence of other pollutants rendered the bioindicator strain unable to reproduce. Conversely, all sampling stations located in the channels and the areas where they connect with the lagoon demonstrated estrogenic activity, with particular emphasis on CL1, which had an EQ-E2 of 8.03 ng.g-1. Among the points within the lagoon, five did not exhibit estrogenic activity, while among the six that did, the one with the highest concentration was L04, situated in the middle of the lagoon, with an EQ-E2 value of 0.16 ng.g-1.

Pusceddu et al. (2019) [54] investigated the presence of estrogens in surface sediments of one of the most industrialized and urbanized estuary systems in Latin America, the Santos and São Vicente estuarine system in the state of São Paulo. They found significant levels of E3, E2, and EE2 in nearly all samples. The authors linked the presence of estrogens to proximity to domestic sewage outfalls, but they also detected contaminants in other areas originating from diffuse sources, such as irregular domestic sewage disposal from regions not covered by sewage services, underscoring the need for studies of these contaminants not to focus solely on point sources.

Lima et al. (2019) [55], in a study aiming to characterize anthropogenic and natural impacts in a coastal zone (Rio Pacoti – CE) involving emerging and traditional organic markers, found that the type of contamination is directly related to the source closest to the sampled points. Estrogens and steroids were quantified in greater quantities in areas near sewage discharges, while n-alkanes were associated with terrigenous sources and hydrocarbons with natural sources, particularly pyrogenic.

Pimentel et al. (2016) [56] examined the morphofunctional parameters of the tropical fish Sphoeroides testudineus (Baiacu Mirim) in an area (Rio Pacoti – Ceará) potentially contaminated by estrogens. Sediment analyses at the fish collection point indicated high contamination by natural (276 ng.g-1) and synthetic (523.97 ng.g-1) estrogens. Vitellogenin (VTG) expression was detected in mature males and undifferentiated fish, indicating endocrine dysregulation, and suggesting contamination with estrogens in the region.

Morais et al. (2020) [57] conducted an environmental diagnostic study to support the development of coastal environmental management policies in a coastal lagoon on the coast of the state of Ceará, with multiple anthropogenic sources related to urban and rural activities involving

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sterols and estrogens. Sediment analysis results indicated high contamination by synthetic estrogens (EE2 and DES), widely used in contraceptives and various female hormonal treatments, as well as in livestock production to improve productivity. These compounds have a higher octanol-water partition constant (Kow) compared to natural estrogens, contributing to their adsorption to sediment. Among natural estrogens, a higher concentration of E1 was found, possibly related to the oxidation of E2 to E1 in the environment. The environmental diagnostic study revealed moderate to high contamination by sewage.

The presence of estrogenic activity in sediments observed in this study is directly associated with points located near sewage disposal sources, corroborating findings from other studies [58–60]. Sediments from water bodies located along the lagoon's banks exhibited higher EQ-E2 values. This can be explained by the fact that they receive contributions from the basins before flowing into the lagoon, thus receiving a greater influx of domestic wastewater containing high concentrations of estrogenic compounds.

4.4. Statistical Analysis

According to the Spearman test applied to the results obtained in the present study (Table 2), a strong positive correlation was observed between the majority of the studied heavy metals in the present study and fine grain size (Pb - 0.91378, Cu - 0.74587, Cr - 0.94063, Ni - 0.94416, and Zn - 0.71178). This is attributed to the larger contact surface per unit volume of fine-grained sediments, a pattern widely recognized in the scientific literature [61–64]. As discussed earlier, it is suggested that the greater hydrodynamic flows in the watercourses within the hydrographic basin are responsible for the transport of fine grains in rivers and channels. When these fine sediments reach the mouths that flow into the lagoon, the slower currents allow for the deposition of these materials.

The moderate inverse correlation between salinity and turbidity also supports the idea that the flocculation phenomenon can stimulate the deposition of fine sediments in the Araçatiba Lagoon (R = -0.59152). Another moderate relationship is observed between the percentages of TOC and heavy metals (Cd - 0.60462; Pb - 0.66718, Cu - 0.57653, Cr - 0.61964, Ni - 0.61905, and Zn - 0.46225). This is due to the large quantity and variation of active sites available on the surface of the organic matter, promoting their association [65,66].

As for the results of the YES tests, they showed a moderate inverse relationship with pH. Given that the environmental conditions in the lagoon are better than those of its contributors, and that its salinity naturally tends to be higher due to the influence of the adjacent sea, an inverse relationship between both parameters is expected. The same can be said between the concentrations of dissolved O2 and fecal coliforms. In the channels, due to the direct disposal of sewage, oxygen concentrations tend to be lower as it is consumed by the bacterial degradation process of the organic matter carried by the sewage. In the lagoon, on the other hand, the maintenance of oxygen concentrations is mainly due to the diffusion of this gas through the air-water interface, allowing for an abundance of oxygen for the degradation of the sludge deposited on the lagoon floor. The rise in pH is also influenced by this trend, in addition to being stimulated by the buffering effect of carbonates present in seawater.

Table 2. Spearman correlation test applied in the present study.

	Temp (ºC)	pH	ORP	turbidity	DO (mg.L-1)	Salinity	E. coli	COT (%)	Fine Sediment	EEQ-E2	As	Cd	Pb	Cu	Cr	Hg	Ni	Zn
Temp (ºC)		0,78168	0,071271	0,014823	0,00824	2,85E-06	3,65E-02	0,11622	0,49648	0,99101	0,37143	0,49311	0,3296	0,82113	0,491	0,056701	0,52227	0,83226
pH	-0,07028		0,93997	0,98377	0,59932	0,63212	0,11802	0,060061	0,12407	0,021983	0,81756	0,28844	0,098122	0,19539	0,12498	0,16024	0,18078	0,46851
ORP	0,43492	0,019121		0,23589	0,000122	0,007643	1,42E-04	0,095315	0,003466	0,29345	0,63756	0,39162	0,004436	0,18149	0,005251	0,1141	0,011922	0,32828
turbidity	-0,56376	-0,00517	-0,29427		0,29905	0,009718	0,37673	0,52023	0,86121	6,56E-01	0,93767	0,40091	0,75073	0,50951	0,7322	0,44772	0,65609	0,44745

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DO (mg.L-¹)	0,60176	0,13282	0,78306	-0,25916		0,004925	0,000179	0,002411	0,001648	0,19935	0,92036	0,48976	0,002533	0,083402	4,44E-03	0,046943	0,009357	0,23711
Salinity	0,86912	-0,12112	0,60631	-0,59152	0,63166		0,039879	0,024156	0,093291	0,57995	0,27499	0,059901	0,080153	0,3862	0,13494	0,18203	0,11204	0,56472
E. coli	-0,51007	-0,3936	-0,79392	0,22896	-0,78672	-0,50235		0,056077	0,031332	0,087656	0,51824	0,79498	1,97E-02	0,71656	0,045332	4,19E-05	0,08778	0,65954
COT (%)	0,38346	0,4514	0,40517	-0,16219	0,66873	0,52847	-0,47146		0,001425	0,007105	0,35801	0,010139	0,002489	1,23E-02	0,006094	0,32052	0,006157	0,053431
Fine Sediment	0,1714	0,37603	0,65049	0,044376	0,68663	0,40745	-0,52272	0,69318		0,012163	**0,81098**	**0,017428**	**1,17E-07**	**0,00038**	**6,44E-09**	**0,36719**	**3,99E-09**	**0,000923**
EEQ-E2	-0,00332	-0,60466	-0,30233	0,13053	-0,36505	-0,16204	0,49202	-0,68293	-0,64824		0,27026	0,001132	0,012233	0,011342	0,015243	0,56386	0,03375	0,042629
As	0,22406	-0,05853	-0,1192	0,019857	0,025386	0,27194	0,16839	0,23025	0,060674	-0,31649		0,090331	0,40869	0,10441	0,57003	0,11507	0,64648	0,13202
Cd	0,17848	0,27334	0,22208	-0,21786	0,17984	0,46517	0,07061	0,60462	**0,56779**	-0,77495	0,42344		0,020883	0,000953	0,028166	0,40923	0,007972	0,000633
Pb	0,2438	0,40207	0,6374	0,080537	0,66632	0,42318	-0,55872	0,66718	**0,91378**	-0,64785	0,20705	0,55452		4,20E-05	3,33E-12	0,085608	7,35E-10	0,000689
Cu	0,057364	0,32006	0,32972	0,16632	0,41912	0,21739	-0,0951	0,57653	**0,74587**	-0,653	0,39534	0,72663	0,8124		4,20E-05	0,7787	1,38E-05	2,18E-09
Cr	0,17355	0,37519	0,6281	0,086732	0,6374	0,36627	-0,49104	0,61964	**0,94063**	-0,63235	0,14349	0,53136	0,97727	0,8124		0,23742	5,69E-12	0,000142
Hg	0,48532	0,36846	0,41066	-0,20437	0,50318	0,35138	-0,85851	0,26539	**0,24167**	-0,18547	0,40966	-0,23016	0,44312	0,076344	0,31327		0,53911	0,59322
Ni	0,16141	0,33023	0,57838	0,11272	0,5939	0,38756	-0,4265	0,61905	**0,94416**	-0,56889	0,11607	0,61969	0,95499	0,83851	0,97569	0,16593		3,68E-05
Zn	-0,05375	0,18252	0,24444	0,19112	0,29354	0,14545	0,11527	0,46225	**0,71178**	-0,54768	0,36884	0,74299	0,72351	0,94829	0,77829	-0,14457	0,81574	

The application of the PCA test confirms most of the results already obtained by Spearman (Figure 20). The proximity between the turbidity axes and E. Coli confirms the characteristics of high values of both parameters in the channels. The results of the YES tests are also found in the same quadrant. This test reflects the toxic effects of Endocrine Disruptors (EDs). Most of these compounds are not refractory in the environment and, therefore, must be continually released into the environment to maintain their negative effects on microorganisms. As a result, their concentrations are expected to be higher in the vicinity of the sources, confirming that in Maricá, the primary sources of EDs are domestic sewage flows.

The affinity between metals and fine sediments is also reflected in the PCA presented in this article. Finally, the physico-chemical parameters of the water (Dissolved Oxygen, Eh, Salinity, and Temperature) all appeared to be in agreement and varying in parallel between the different compartments studied in the Maricá environment.

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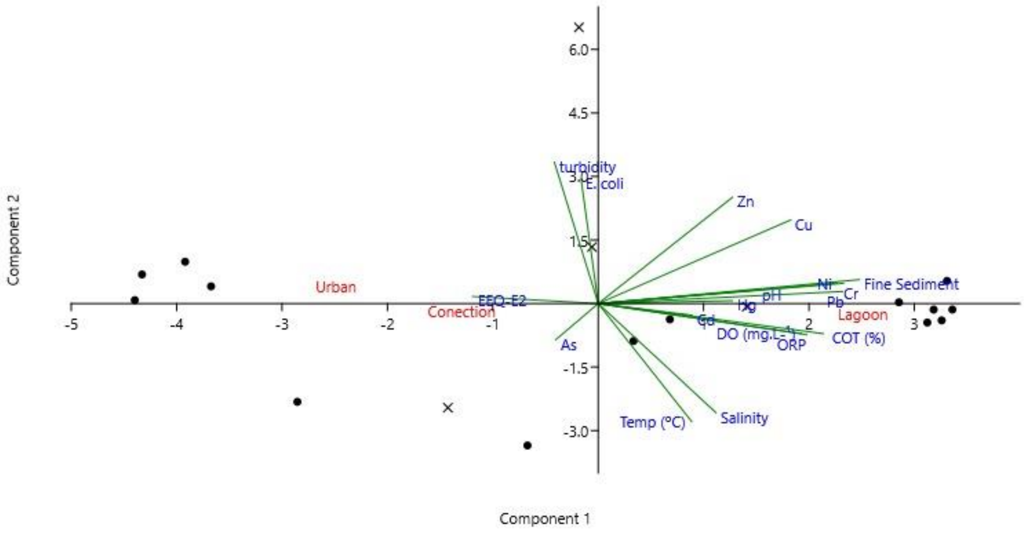

Figure 20. PCA test results (Comp 1 – 41,0% / Comp 2 – 19,5%).

5. Conclusions and Future Perspectives

Throughout Brazil's history, the oil production sector has consistently played a crucial role in the national economy. Current legislation mandates that municipalities adjacent to oil production areas receive compensation fees to address potential impacts generated by this activity. Maricá is one such municipality currently experiencing rapid development with a focus on industrialization and growth in other sectors. However, this intensive growth has not been accompanied by the necessary infrastructure to mitigate issues related to the exponential increase in its population. This study has examined the environmental conditions in the hydrographic basin of the Municipality of Maricá, as well as the Araçatiba Lagoon, which is the primary lagoon in the local lagoon system. The results clearly reflect the deficiencies in the municipality's basic sanitation infrastructure.

The streams and tributaries that flow into the Araçatiba Lagoon were found to have high concentrations of coliforms and heavy metals, which ultimately end up in the lagoon system. These conditions have already demonstrated adverse effects on the local natural ecosystem, potentially leading to hormonal imbalances in the species inhabiting this ecosystem. According to the YES tests, the channels exhibit greater toxicity related to endocrine disruptors. Furthermore, the potential contamination of groundwater, which also serves as a source of drinking water, is a concerning issue. Sinkholes, commonly used as a sanitation method in Maricá, may be contributing to groundwater contamination. Future studies should thoroughly investigate the contamination of groundwater by endocrine-disrupting compounds (EDCs).

Considering that Maricá currently lacks significant industrialization or agriculture, the situation is likely to worsen with the establishment of the industrial park, as part of the local government's plans. This study underscores the importance of implementing an adequate sanitation infrastructure to support the city's planned industrial development and its overall growth.

Data Availability Statement: Data sets generated during the current study are available from the corresponding author on reasonable request.

Conflicts of Interest Statement: The authors declare that they have no conflict of interest.

References

1. Jackson, J., Sutton, R. Sources of endocrine-disrupting chemicals in urban wastewater, Oakland, C. A. *Science of the Total Environment* **2008**, *405*, 153–160. https://doi.org/10.1016/j.scitotenv.2008.06.033
2. Flint, S. Bisphenol A exposure, effects, and policy: A wildlife perspective. *Journal of Environmental Management*, **2012**, *104*, 19–34. https://doi.org/10.1016/j.jenvman.2012.03.021
3. Céspedes, R., Lacorte, S., Raldúa, D., Ginebreda, A., Barceló, D., Piña, B. Distribution of endocrine disruptors in the Llobregat River basin (Catalonia, NE Spain). *Chemosphere*, **2005**, *61*, 1710–1719. https://doi.org/10.1016/j.chemosphere.2005.03.082.
4. Pojana, G., Gomiero, A., Jonkers, N., Marcomini, A. Natural and synthetic endocrine disrupting compounds (EDCs) in water, sediment and biota of a coastal lagoon. *Environment International*, **2007** *33*, 929–936. https://doi.org/10.1016/j.envint.2007.05.003
5. Zoeller, R.T., Brown, T. R., Doan, L. L., Gore, A. C., Skakkebaek, N. E., Soto, A. M., Woodruff, T. J., Vom Saal F. S. Endocrine-Disrupting Chemicals and Public Health Protection: A Statement of Principles from The Endocrine Society. *Endocrinology*, **2012**, *153*, 4097–4110.
6. Sharma, A., Mollier, J., Brocklesby, R.W.K., Caves, C., Jayasena, C.N., Minhas, S. Endocrine disrupting chemicals and male reproductive health. *Reproductive Medicine and Biology*, **2020**, *19*, 243–253. https://doi.org/10.1002/rmb2.12326
7. Kidd, K., Blanchfield, P.J., Mills, K.H., Palace, V.P., Evans, R.E., Lazorchak, J.M., Flick, R.W. Collapse of a Fish Population After Exposure to a Synthetic Estrogen. *Proceedings of the National Academy of Sciences of the United States of America*, **2007**, *104*, 8897-901. https://doi.org/10.1073/pnas.0609568104.
8. Zou, Enmin. Impacts of Xenobiotics on Crustacean Molting: The Invisible Endocrine Disruption. *Integrative and Comparative Biology*, **2005**, *45*. 33-8. 10.1093/icb/45.1.33.
9. Margiotta-Casaluci, L., Owen, S.F., Cumming, R.I., de Polo, A., Winter, M.J., Panter, G.H., Rand-Weaver, M., Sumpter, J.P. Quantitative cross-species extrapolation between humans and fish: the case of the anti-depressant fluoxetine. *PLoS One*, **2014**, *9(10)*, e110467. https://doi.org/10.1371/journal.pone.0110467.
10. Yılmaz, H., Karakuş, G., Tamam, L., Demirkol, M.E., Namlı, Z., Yeşiloğlu, C. Association of Orthorexic Tendencies with Obsessive-Compulsive Symptoms, Eating Attitudes and Exercise. Neuropsychiatric Disease and Treatment, **2020**, *14(16), 3035-3044.* https://doi.org/10.2147/NDT.S280047.
11. Encarnação, T., Pais, A.A., Campos, M.G., Burrows, H.D. Endocrine disrupting chemicals: Impact on human health, wildlife and the environment. *Science Progress*, **2019**, 102(1):3-42. https://doi.org/10.1177/0036850419826802
12. Moiseenko, T.I. Surface Water under Growing Anthropogenic Loads: From Global Perspectives to Regional Implications. *Water*, **2022**, *14*, 3730. https://doi.org/10.3390/w14223730
13. Pironti, C., Ricciardi, M., Proto, A., Bianco, P.M., Montano, L., Motta, O. Endocrine-Disrupting Compounds: An Overview on Their Occurrence in the Aquatic Environment and Human Exposure. *Water*, **2021**, *13*, 1347. https://doi.org/10.3390/w13101347
14. Pal, A., He, Y., Jekel, M., Reinhard, M., Gin, K.Y. Emerging contaminants of public health significance as water quality indicator compounds in the urban water cycle. *Environment International*, **2014**, *71*, 46–62. https://doi.org/10.1016/j.envint.2014.05.025
15. Zhang T. Xiao, Y., Liang, D., Tang, H., Yuan, S., Luan, B. Rainfall Runoff and Dissolved Pollutant Transport Processes Over Idealized Urban Catchments. *Frontiers in Earth Science*, **2020**, *8.* https://doi.org/10.3389/feart.2020.00305
16. Taner, M., Üstün, B., Erdinçler, A. A simple tool for the assessment of water quality in polluted lagoon systems: A case study for Küçükçekmece Lagoon, Turkey. *Ecological Indicators*, **2011**, *11*, 749-756. https://doi.org/10.1016/j.ecolind.2010.08.003.
17. Barnes, R.S.K. The Lagoons of Britain: an overview and conservation appraisal. *Biological Conservation*, **1989**, *49*, 295–313. https://doi.org/10.1016/0006-3207(89)90049-9
18. Johnson, D.E., Bartlett, J., Nash, L.A. Coastal lagoon habitat re-creation potential in Hampshire, England. *Marine Policy*, **2007**, *31*, 599–606. https://doi.org/10.1016/j.marpol.2007.03.004
19. Specchiulli, A., Pastorino, P., De Rinaldis, G., Scirocco ,T., Anselmi, S., Cilenti, L., Ungaro, N., Renzi, M. Multiple approach for assessing lagoon environmental status based on water bodies quality indices and microplastics accumulation. *Science of the Total Environment*, **2023**, *892*, 164228. https://doi.org/10.1016/j.scitotenv.2023.164228.
20. Filgueira, J. M., Pereira Júnior, A.O., Barbosa de Araújo, R.S., Silva, N.F.d. Economic and Social Impacts of the Oil Industry on the Brazilian Onshore. Energies (Basel), **2020**, 13 (8), 1–18. https://doi.org/10.3390/en13081922.
21. Nogueira, A., Barbosa, G. Challenges to Environmental Sustainability: an analysis of the territorial transformation in the production of the urban space of Maricá/RJ. **2018** https://doi.org/10.15341/mese(20181016-3)/01.09.2018/001.
22. Tripathi, S. Towards sustainable urban system through the development of small towns in India. *Regional Science Policy and Practice*, **2021**, 13, 777–797. https://doi.org/10.1111/rsp3.12424

23. Caldatto, F.C., Bortoluzzi, S.C., Pinheiro de Lima, E.. Gouvea da Costa, S.E. Urban Sustainability Performance Measurement of a Small Brazilian City. *Sustainability*, **2021**, *13*, 9858. https://doi.org/10.3390/su13179858
24. Barroso-Vanacôr, Perrin, P., Carmouze J.-P. (1994). Lesystème lagunaire de Maricá Guarapina (Brésil) et ses modifications écologiques récentes d'origine antropique. *Revue d'Hydrobiologie Tropicale, 27(3), 189-197*
25. INMET (All Weather Data). Instituto Nacional de Meteorologia (INMET); 2020. Available online: https://tempo.inmet.gov.br/TabelaEstacoes/# (accessed on 18 November 2021).
26. Cruz, C. B. M., Carvalho Júnior, W., Barros, R. S., Argento, M. S. F., Mayr, L. M. (1996). Impactos Ambientais no Sistema Lagunar de Maricá Guarapina. Anais VIII Simpósio Brasileiro de Sensoriamento Remoto, 137–141, 1996.
27. Folharini, S. de O., Oliveira, R. C., Furtado, A. L. dos S. (2020). Unidades geoambientais do Parque Nacional da Restinga de Jurubatiba, litoral norte fluminense. *Revista Do Departamento De Geografia*, 39, 154-168. https://doi.org/10.11606/rdg.v39i0.156779
28. Carvalho da Silva, A. L., da Silva, M. A. M., Gralato, J. C. A., Silvestre, C. P. S (2014). Geomorphological and sedimentary characterization of the Maricá coastal plain (Rio de Janeiro state). *Revista Brasileira de Geomorfologia*, *15*. https://doi.org/10.20502/rbg.v15i2.470.
29. Knoppers, B., Kjerfve, B., Carmouze, J.P. (1991). Trophic state and water turn-over time in 6 choked coastal lagoons in Brazil. *Biogeochemistry, 14(2)*, 149-166. https://doi.org/10.1007/BF00002903
30. Guerra, L. Savergnini, F., Silva, F., Bernardes, M., Crapez, M. (2011). Biochemical and microbiological tools for the evaluation of environmental quality of a coastal lagoon system in Southern Brazil. *Brazilian Journal of Biology*, *71(2)*, 461-468. https://doi.org//10.1590/S151998420110003000016
31. Lins de Barros, F.M. (2005). Risco, Vulnerabilidade Física à Erosão Costeira e Impactos Sócio-Econômicos na Orla Urbanizada do Município de Maricá, Rio de Janeiro. *Revista Brasileira de Geomorfologia*, *6(2)*, 83-90. https://doi.org/10.20502/rbg.v6i2.54
32. Sousa, L.G.R., Miranda, A. C. de, Medeiros, H. B. de (2013). O sistema lagunar de Maricá: um estudo de impacto ambiental. *IX Fórum Ambiental da Alta Paulista, 9 (2)*,153-165. https://doi.org/10.17271/19800827922013637
33. APHA (2017). Standard Methods for the Examination of Water and Wastewater (23rd ed.). Washington DC: American Public Health Association.
34. EMBRAPA (1997). Empresa Brasileira de Pesquisa Agropecuária Manual de métodos de análise de solos. EMBRAPA.
35. EPA (1996). Environmental Protection Agency - U.S.. "Method 3050B: Acid Digestion of Sediments, Sludges, and Soils," Revision 2. Washington, DC.
36. Routledge, E.J. & Sumpter, J.P. (1996). Estrogenic Activity of Surfactants and Some of Their Degradation Products Assessed Using a Recombinant Yeast Screen. *Environmental Toxicology and Chemistry*, *15*, 241–248. https://doi.org/10.1002/etc.5620150303
37. Gomes, G., Argolo, A. dos S., Felix, L. da C., Bila, D. M. Interferences in the yeast estrogen screen (YES) assay for evaluation of estrogenicity in environmental samples, chemical mixtures, and individual substances, Toxicology in Vitro, Volume 88, 2023, 105551, ISSN 0887-2333, https://doi.org/10.1016/j.tiv.2022.105551.
38. Cunha, D. L., S. Muylaert, Nascimento, M. T. L., Felix, L. C., Gomes, G., Bila D. M., Fonseca E. M. (2020). Occurrence of emerging contaminants and analysis of oestrogenic activity in the water and sediments from two coastal lagoons in south-eastern Brazil. Marine and Freshwater Research, *72* (2) 213-227. https://doi.org/10.1071/MF19391
39. Frische, T., Faust, M., Meyer, W., Backhaus, T. (2009) Toxic masking and synergistic modulation of the estrogenic activity of chemical mixtures in a yeast estrogen screen (YES). Environmental Science and Pollution Research, vol. 16, no. 5, pp. 593-603, DOI:10.1007/s11356-009-0184-7.
40. Moore, W. S. (1999). The subterranean estuary: a reaction zone of ground water and sea water, Marine Chemistry. 65(1–2), 111-125, https://doi.org/10.1016/S0304-4203(99)00014-6.
41. Mastrocicco, M. and Colombani, N. (2021) The Issue of Groundwater Salinization in Coastal Areas of the Mediterranean Region: A Review. Water, 13, Article No. 90. https://doi.org/10.3390/w13010090
42. Vengosh, A. (2003). 9.09 - Salinization and Saline Environments, Editor(s): Heinrich D. Holland, Karl K. Turekian, Treatise on Geochemistry, Pergamon, 1-35, https://doi.org/10.1016/B0-08-043751-6/09051-4.
43. Werner, A.D., Bakker, M., Post, V.E.A., Vandenbohede, A., Lu, C., Ataie-Ashtiani, B., Simmons, C. T., Barry, D.A. (2013). Seawater intrusion processes, investigation and management: recent advances and future challenges. Advances in Water Resources 51, 3–26. https://doi.org/10.1016/j.advwatres.2012.03.004
44. Bagheri R, Nosrati, A., Jafari, H., Eggenkamp, H.G.M., Mozafari, M. (2019). Overexploitation hazards and salinization risks in crucial declining aquifers, chemo-isotopic approaches. *Journal of Hazardous Materials. 5*(369), 150-163. https://doi.org/10.1016/j.jhazmat.2019.02.024.
45. Akpataku, K. V., Gnazou, M. D. T., Djanéyé-Boundjou, G., Bawa, L. M. & Faye, S. (2020). Role of Natural and Anthropogenic Influence on the Salinization of Groundwater from Basement Aquifers in the Middle

Part of Mono River Basin, Togo. *Journal of Environmental Protection*, *11*(1), 1030-1051. https://doi.org/10.4236/jep.2020.1112065.

46. Jiang, LQ., Carter, B.R., Feely, R.A., Lauvset, S. K., Olsen, A. (2019) Surface ocean pH and buffer capacity: past, present and future. Scientific Reports. 9, 18624 https://doi.org/10.1038/s41598-019-55039-4
47. Bartoli, G., Papa, S., Sagnella, E., Fioretto, A. (2012). Heavy metal content in sediments along the Calore river: Relationships with physical–chemical characteristics. *Journal of Environmental Management*, *95*:9-14. https://doi.org/10.1016/j.jenvman.2011.02.013
48. Ramírez-Ayala, E., Arguello-Pérez, M., Adrián, T., Mendoza, P., Jorge, A., Díaz-Gómez, J., Pérez-Rodríguez, R. Y., Núñez-Nogueira, G., & Sepúlveda-Quiroz, C., Zepeda-González, F., Lezama-Cervantes, C. (2021). Heavy metals in sediment and fish from two coastal lagoons of the Mexican Central Pacific. *Latin American Journal of Aquatic Research*, *49(5)*, 818-827. https://doi.org/10.3856/vol49-issue5-fulltext-2628
49. Turekian, K.K. and Wedepohl, K.H. (1961) Distribution of the Elements in Some Major Units of the Earth's Crust. Geological Society of America Bulletin, 72, 175-192. http://dx.doi.org/10.1130/0016-7606(1961)72[175:DOTEIS]2.0.CO;2
50. Mannaa, A.A., Khan, A.A., Haredy, R., Al-Zubieri, A.G. (2021). Contamination Evaluation of Heavy Metals in a Sediment Core from the Al-Salam Lagoon, Jeddah Coast, Saudi Arabia. *Journal of Marine Science and Engineering*, *9*, 899. https://doi.org/10.3390/jmse9080899
51. Zhang, Z. et al. (2022). Contamination of Heavy Metals in Sediments from an Estuarine Bay, South China: Comparison with Previous Data and Ecological Risk Assessment. *Processes*, *10*, 837. https://doi.org/10.3390/pr10050837
52. Long, E.R. (2006). Calculation and uses of mean sediment quality guideline quotients: a critical review. *Environmental Science & Technology*, *40*, 1726–1736. https://doi.org/10.1021/es058012d
53. Perin, G., Bonardi, M., Fabris, R., Simoncini, B., Manente, S., Tosi, L. & Scotto, S. (1997). Heavy metal pollution in central Venice Lagoon bottom sediments: evaluation of the metal bioavailability by geochemical speciation procedure. *Environmental Technology*, *18*, 593–604. https://doi.org/10.1080/09593331808616577
54. Pusceddu, F. H., Sugauara, L.E., de Marchi, M.R., Choueri, R.B., Castro, Í.B. (2019). Estrogen levels in surface sediments from a multi-impacted Brazilian estuarine system. *Marine Pollution Bulletin*, *142*, 576-580.
55. Lima, M.F.B., Fernandes, G.M., Oliveira, A.H.B., Morais, P.C.V., Marques, E.V., Santos, F.R., Nascimento, R..F, Swarthout, R.F., Nelson, R.K., Reddy, C.M., Cavalcante, R.M. (2019). Emerging and traditional organic markers: Baseline study showing the influence of untraditional anthropogenic activities on coastal zones with multiple activities (Ceará coast, Northeast Brazil). *Marine Pollution Bulletin*, *(139)* 256-262. https://doi.org/10.1016/j.marpolbul.2018.12.006
56. Pimentel, M.F., Pimentel, M. F., Damasceno, É. P., Jimenez, P. C., Araújo, P. F. R., Bezerra, M. F., de Morais, P. C. V., Cavalcante, R. M., Loureiro, S. & Costa-Lotufo, L. V. (2016). Endocrine disruption in Sphoeroides testudineus tissues and sediments highlights contamination in a northeastern Brazilian estuary. *Environmental Monitoring and Assessment*, *188(5)*, 1-13. https://doi.org/10.1007/s10661-016-5300-9
57. Morais, P.C.V. Lima, M.F.B., Martins, D.A., Fontenele, L.G., Lima, J.L.R., da Silva, Í.B., Pinheiro, L.S., Nascimento, R.F., Cavalcante, R.M. and Marques, E.V. (2020). Use of an environmental diagnostic study on a coastal lagoon as a decision support tool for environmental management policies in a coastal zone. Management of Environmental Quality: *An International Journal*, *31(1)*, 167-184. https://doi.org/10.1108/MEQ-11-2018-0195
58. Griffero, L., Gomes, G., Berazategui, M., Fosalba, C., Teixeira de Mello, F., Rezende, C., Bila, D., & Gacía-Alonso, J. (2018). Estrogenicity and cytotoxicity of sediments and water from the drinkwater source basin of Montevideo city, Uruguay. *Ecotoxicology and Environmental Contamination*, 13(1), 15-22. https://doi.org/10.5132/eec.2018.01.02
59. Cunha D., Muylaert, S., Nascimento, M., Felix, L., Andrade, J. J. D. D., Silva, R., Bila, D. (2021). Concentration and toxicity assessment of contaminants in sediments of the Itaipu–Piratininga lagoonal system, Southeastern Brazil. Regional Studies in Marine Science 46, 101873. https://doi.org/10.1016/j.rsma.2021.101873.
60. Gorga, M., Insa, S., Petrovic, M., Barceló, D. (2015). Occurrence and spatial distribution of EDCs and related compounds in waters and sediments of Iberian rivers. *Science of the Total Environment*, *503-504*, 69-86, https://doi.org/10.1016/j.scitotenv.2014.06.037
61. Zhang, C., Yu, Z.G., Zeng, G.M., Jiang, M., Yang, Z.Z., Cui, F., Zhu, M.Y., Shen, L.Q., Hu, L. (2014). Effects of sediment geochemical properties on heavy metal bioavailability, *Environment International*, *73*, 270-281, ISSN 0160-4120, https://doi.org/10.1016/j.envint.2014.08.010.
62. Tansel, B. & Rafiuddin, S. (2016) Heavy metal content in relation to particle size and organic content of surficial sediments in Miami River and transport potential. *International Journal of Sediment Research*, *31(4)*, 324-329, https://doi.org/10.1016/j.ijsrc.2016.05.004.

 doi:10.20944/preprints202411.0982.v1

63. Huang, L. Fang, H.. Ni, K., Yang, W., Zhao, W., He, G., Han, Y., Li, X. (2018). Distribution and Potential Risk of Heavy Metals in Sediments of the Three Gorges Reservoir: The Relationship to Environmental Variables. *Water, 10,* 1840. https://doi.org/10.3390/w10121840
64. Ali, A. & Talabani, M. (2018) Heavy Metals Distribution and Their Correlation with Clay Size Fraction in Stream Sediments of the Lesser Zab River at Northeastern Iraq. *Journal of Geoscience and Environment Protection*, *6*, 89-106. https://doi.org/10.4236/gep.2018.64006.
65. Yang , X., Xiong, B. & Yang, M. (2010). Relationships among Heavy Metals and Organic Matter in Sediment Cores from Lake Nanhu, an Urban Lake in Wuhan, China, *Journal of Freshwater Ecology, 25(2),* 243-249. https://doi.org/10.1080/02705060.2010.966507
66. Refaey, Y. Yansen, B., El-Shater, A., El-Haddad, A., Kalbitz, K. (2014). The Role of Dissolved Organic Matter in Adsorbing Heavy Metals in Clay-Rich Soils. *Vadose Zone Journal 13 (7),* vzj2014010009. https://doi.org/10.2136/vzj2014.01.0009