Heavy Metals Concentration in Sediments of South Brittany Waters, France: An Ecological Risk Assessment Approach

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Abstract

Distribution patterns of selected heavy metals content in sediments from the Bay of Quiberon and Gulf of Morbihan were studied to understand the current heavy metals contamination due to urbanization and mariculture activities in the coastal area. Therefore, a survey was conducted and 196 sediments collected were characterized for heavy metals content using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) after mix acid digestion process. The distribution maps of the concentrations of the heavy metals studied were produced as an isopleth map based on data interpolation by the ArcGIS software application. The association with the adverse effects on aquatic organisms was determined by the classification of the sediment according to the sediment quality guidelines. Therefore, two approaches were employed namely: direct comparison with Sediment Quality Guidelines (SQGs) by USEPA (United States Environmental Protection Agency) and comparison with other numerical SQGs, threshold effect level/probable effect level, and effect range low/effect range medium. In order to estimate the effect of multiple contaminations of heavy metals, the mean-ERM-quotient was calculated at each sampling point.

1. Introduction

Human pressures on the ocean are thought to be rising globally in diverse and
profound ways [1] [2]. The demand for marine space and resources is expanding
as the population grows and migrates toward coastal areas, resulting in new
challenges and risks for marine ecosystems [3] [4]. Nowadays, estuary and
coastal environments are contaminated through activities such as tourism, and
areas such as harbors and industrials sites. These release elevated concentrations
of heavy metals, nutrients, organic pollutants, and radionuclides into the marine
environment [5]. The pollution of coastal zones near metropolitan areas, caused
by this anthropogenic waste is due to the large human population and the
enormous amount of sewage discharged into coastal waters [6]. The addition of
waste products into rivers and estuaries, particularly those in industrial and po-
pulated centres, has led to a significant increase in contamination caused by
heavy metals [7].

Heavy metals, such as copper (Cu), zinc (Zn), cadmium (Cd) and lead (Pb),
have a great affinity for sediment in the aquatic environment. These pollutants
are persistent contaminants that bioaccumulate throughout the food chain with
potential toxicity for aquatic organisms and humans [8] [9]. It is difficult to re-
move the toxic heavy metals once they enter the body of organisms [10] [11].
Furthermore, heavy metals are enriched at consecutive trophic levels of food
chains resulting in biomagnification of these chemicals in the food web [12]
[13]. Top predators, such as marine mammals and humans, may be at a greater
risk from heavy metals due to their top position in trophic chains, resulting in
adverse health effects [14].

For example, lead can penetrate the body and cell membranes easily, and is
associated with nervous system disorders and lead encephalopathy [15]. Long-term
exposure or intake of food with a high concentration of Cd may cause itai-itai dis-
ease and kidney damage [16]. It occurred in numerous residents of the Jinzu
River basin in Toyama Prefecture, Japan, a region extremely polluted with Cd
that originated from a zinc mine located upstream [17]. Moreover, green-colored
oysters as a result of Cu contamination have been found in several estuaries and
harbors around the world, including the USA [18], Spain [19], Chinese main-
land [20] [21], and Taiwan area [22]. Chronic Cu toxicity can cause liver disease
and critical neurological damage [23]. Zn has been considered to be relatively
nontoxic; however, taking high levels of Zn-contaminated food can damage the
pancreas and disturb protein metabolism, causing health problems, such as sto-
mach cramps, bloody urine, liver failure, nausea, and anemia [24] [25]. As a

consequence, a systematic assessment of heavy metal pollutants is critical, especially for the coastal area.

Coastal areas are sensitive to both climate changes and human impacts, which make these areas ideal for studying environmental changes and the sequence of coastal sediments, and have become attractive targets for documenting paleoenvironmental changes. The Bay of Quiberon and Gulf of Morbihan on the south coast of Brittany Region, France, are an excellent example of the coastal sea with high terrestrial influence, a semi-enclosed bay, surrounded by densely populated areas and mariculture activities. Such an investigation is required if the environmental impacts of the region are to be understood quantitatively and qualitatively.

Accumulation of heavy metals in surface sediments from industrial effluents and urban discharged into the river without proper cleaning is easily identified by heavy metals spatial variations in sediments [26]. In this exploration, surficial spatial distributions of selected heavy metals; Cu, Zn, Cd, Pb (identified as priority contaminants in aquatic systems by the European Community (EC) Water Framework Directive 2000/60/EC) [27] were characterized in the surficial sediments which reflects the recent input to evaluate the contamination level resulting from anthropogenic inputs. This EC work recommends the monitoring of fluvial loads of heavy metals as a tool for sustainable management in the aquatic ecosystem [28].

Information on contamination background is required for managers and policymakers to make strategic regulations, guidelines, and monitor progress towards management objectives. In order to establish such a knowledge, the present study investigates the spatial distribution of four heavy metals (Cu, Cd, Pb and Zn) at 196 sampling points in the Bay of Quiberon and Gulf of Morbihan surficial sediments. The adverse effects on aquatic organisms were determined by direct comparison with the Sediment Quality Guidelines (SQGs) and the sediment toxicity and ecological risk indices, namely the effect low range (ERL)/effect range median (ERM), and the threshold effect level (TEL)/probable effect level (PEL) values. In order to estimate the effect of multiple contaminations of heavy metals in the study area, the mean-ERM-quotient was also calculated at each sampling point.

2. Materials and Methods

2.1. Study Area

The Bay of Quiberon is a large open-sea area on the south coast of Brittany, consisting of two additional areas with an equivalent surface area of approximately 120 km^2 (Figure 1). The bay is roughly triangular, almost completely surrounded by land on the north and east sides; open to the south with the Gulf of Morbihan to the north-east, and the narrow peninsula of Quiberon providing protection from the Atlantic Ocean to the west. The Belle, Houat, and Hœdic islands add to the protection of the bay [29] [30].
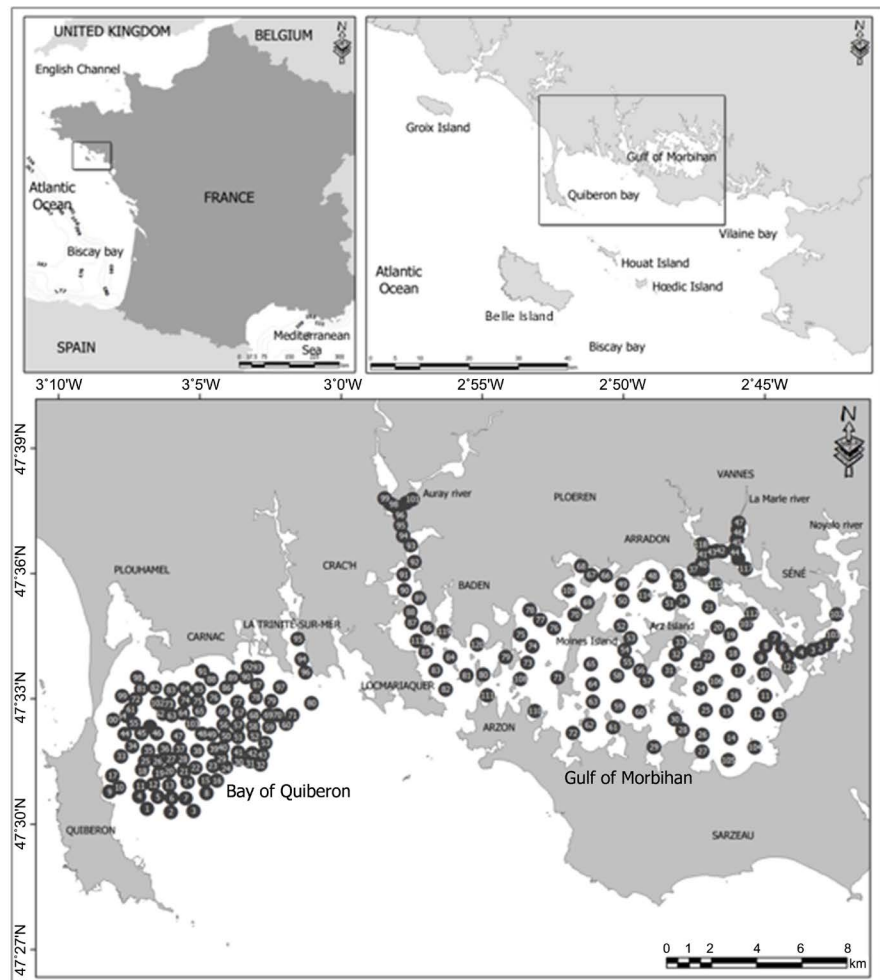
Figure 1. Map showing surficial sediment sampling points in South Brittany waters.

The tide is semi-diurnal with a mean spring tidal range of 4.5 m. The tidal were stronger in the vicinity of the coast and especially in the passage between the Quiberon peninsula and neighboring Houat and Hœdic islands, and are amplified in shallower water depths [31] [32]. Due to this water physical characteristic, the outer bay was much influenced by the strong water current and tidal wave compared to the inner bay.

The Gulf of Morbihan ("Morbihan" = "little sea" in Breton) is a natural harbor located in the South Brittany, northwest France (Figure 1). It is a close sea body (11,500 ha) and a shoreline of 250 km [33]. It is a shallow basin with a maximum depth of 30 m and is connected to the sea by a 900 m wide and 30 m deep tidal inlet at Port Novalo [34]. Institut Géographique National recorded that there are 37 islands located in the gulf where the two largest islands are Moine and Arz Islands. The gulf is sheltered from the Atlantic Ocean (Biscay bay) by the peninsula of Quiberon, Houat, Hoëdic, and Belle Islands.

Across the gulf entrance, strong tidal currents affect the basin with water speeds that can reach 2.2 m/s during ebb tides and 1.8 m/s during flood tide. This gulf has a semidiurnal tidal regime with freshwater input from Auray, La

Marle and Noyalo rivers [33]. The further from the entrance, the lower tidal range; 3 m at the eastern part and 5 m at the gulf entrance. Hence, tides are hypersynchronous, a characteristic feature of tidal dominated environments [35].

Many areas along the coast are used by the public as recreation areas. A number of shipping ports for recreational purposes and fishing activities are located in this region. In addition, the surrounding coast is successfully used for commercial shellfish (oyster and mussel) mariculture activities with a significant market around the region.

2.2. Sample Collection

This oceanographic fieldwork was carried out by the SEPIOLA research vessel of the University of Rennes1 at the Gulf of Morbihan and vessel of the Regional Committee of Conchyliculture (CRC), South Brittany at the Bay of Quiberon. A total of 196 surficial sediments were collected randomly in Bay of Quiberon and Gulf of Morbihan with Orange Peel Grab sampler. In addition, in order to prevent metals contamination from the wall of the grab, the outermost layer of the sediment samples were removed and only the inner part was kept for further analysis. After collected, the samples were stored in plastic containers and kept at low temperatures until analysis was carried out.

2.3. Laboratory Analysis

Sediment samples were digested and analyses for total heavy metals following published methodologies with some modifications [36] [37] [38] [39]. The digestion method involved heating of 50 mg of a finely powdered sample in a sealed Teflon vessel in a mixture with a mixed acid solution of concentrated HF, HNO_3 and HCl. The Teflon vessel was kept in an oven at 100˚C for 8 hours. After cooling at room temperature, the solution of the vessel was transferred into a polypropylene test tube. An inductively coupled plasma mass spectrometer (Perkin Elmer Elan 9000) was used for the quick and precise determination of selected heavy metals in the digested sediment samples. The accuracy was also examined by analyzing duplicate Standard Reference Material 1646a Estuarine Sediment, the results of which were within ±3% of certified values.

3. Results and Discussion

All the analyzed data were visualized using ArcGIS software and presented in the form of a concentration isopleth map to identify the sediment concentration hotspot as shown in **Figure 2**. Visualization by overlaying maps using a geographical information system makes this presentation even easier and more successful [40]. Generally, all studied metals' concentrations were higher in the Gulf of Morbihan compared to Bay of Quiberon waters. On the other hand, the inner part of both Gulf of Morbihan and Bay of Quiberon area with low and limited water circulation, also exhibit higher metals concentration.
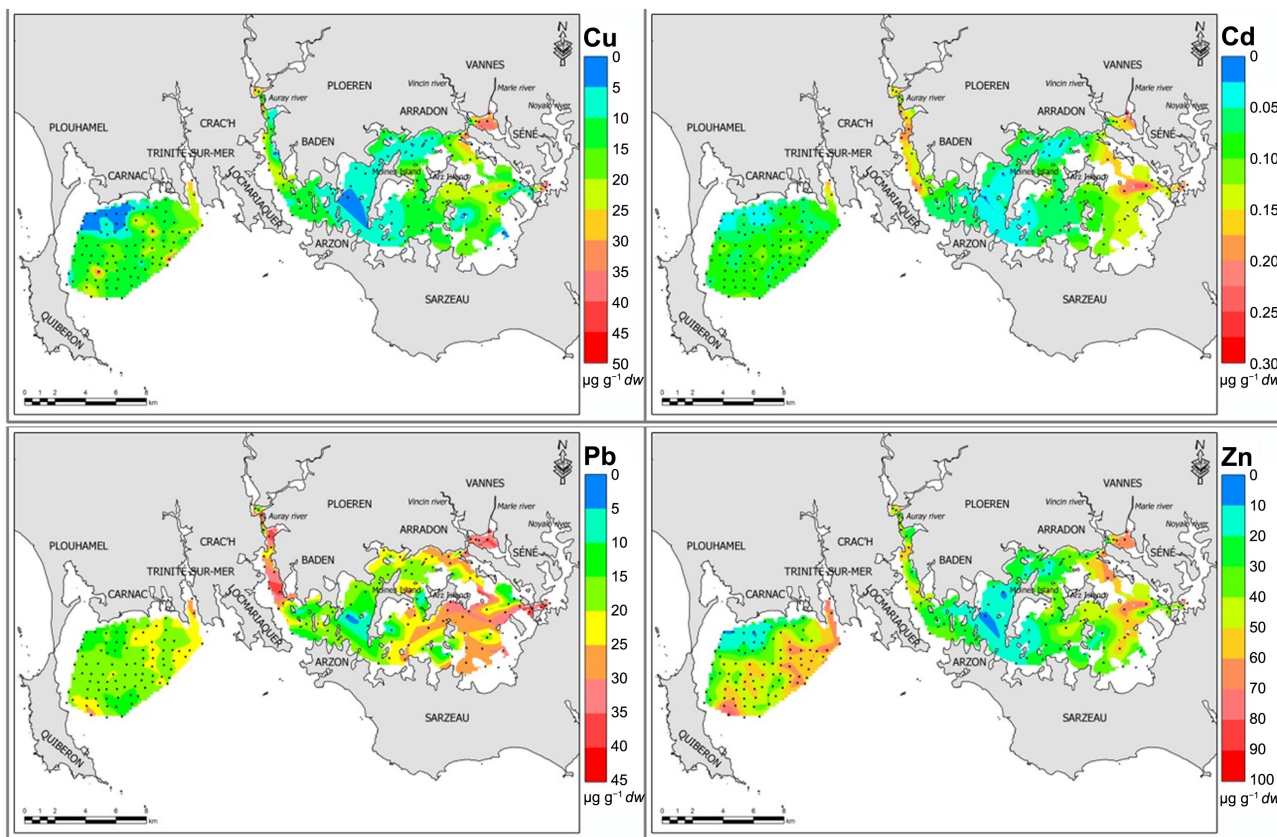
Figure 2. Concentration map for heavy metals distribution in South Brittany coastal waters surficial sediment.

Tomlison *et al.* [41] elaborated that the application of the pollution load index (PLI) provides a simple way to assess the quality of estuarine and coastal sediment. This assessment is a quick tool for comparing the status of pollution at different locations [42]. PLI represents the number of times the concentration of heavy metals in the sediment exceeds the background concentration and provides a summary indication of the overall level of heavy metal toxicity in a particular sample or location [43]. The PLI can provide the public in the surrounding area with some understanding of the quality of the components in their environment, indicating the trend both spatially and temporarily [44]. In addition, it provides valuable information to decision-makers towards better management of pollution levels in the Bay of Quiberon and Gulf of Morbihan regions.

PLI is obtained as contamination factors (CF). This CF is the quotient obtained by dividing the concentration of each metal with the background value of the metal. The PLI can be expressed in the following calculation:

$$\text{Pollution load index} \left(\text{PLI} \right) = \left(\text{CF}_1 \times \text{CF}_2 \times \text{CF}_3 \times \text{CF}_n \right)^{1/n} \tag{1}$$

where, *n* is the number of metals (4 in the present study) and CF is the contamination factor. The CF can be calculated from:

$$\text{Contamination Factor} \left(\text{CF} \right) = \frac{\text{Element concentartion in the sediment}}{\text{Background value of the element}} \tag{2}$$

The PLI value > 1 is categorized as polluted, while <1 indicates no pollution at the sampling point [45] [46].

PLI values of the analyzed surficial sediments were visualized by ArcGIS software and shown in Figure 3, which confirms that either Bay of Quiberon or Gulf of Morbihan is not seriously polluted with the heavy metals studied. PLI was found to be generally low (<1) in all the studied locations in the Bay of Quiberon, apart from Trinité-sur-Mer area. The eastern zone and rivers (Auray, Marle and Noyalo) zones also have a PLI value above 1; therefore these areas can be classified as moderate contamination factors [46].

Two approaches were used to assess sediment toxicity and ecological risk to benthic organisms for heavy metals studied in Bay of Quiberon and Gulf of Morbihan surficial sediments. The first approach was to compare the concentrations of heavy metals to the Sediment Quality Guidelines (SQGs) promulgated by the United States Environmental Protection Agency (USEPA) which were reviewed by Giesy *et al.* [47]. This approach was used only to screen contaminants of concern in aquatic ecosystems. On the other hand, the second approach was to apply two sets of SQGs developed for marine and estuarine ecosystems [48] to the assessment the ecotoxicology of the concentration of heavy metals in sediments, namely, 1) the effect range low (ERL)/effect range median (ERM) and 2) the threshold effect level (TEL)/probable effect level (PEL).

Based on the SQGs proposed by USEPA from Giesy *et al.* [47], sediment contamination is defined as three classes, non-polluted, moderately polluted and heavily polluted (Table 1). This classification of SQGs does consider the natural background or multiple elements [49]. By comparing the mean concentrations of heavy metals in Bay of Quiberon and Gulf of Morbihan surficial sediments with SQGs, sediments in both areas were classified as non-polluted for Zn, and Pb, and moderately polluted by Cu and Cd where these metals exceed SQGs. Surficial sediments from Trinité-sur-Mer zone in Bay of Quiberon, Auray, Marle, Noyalo river zones, and the eastern in Gulf of Morbihan catchment area
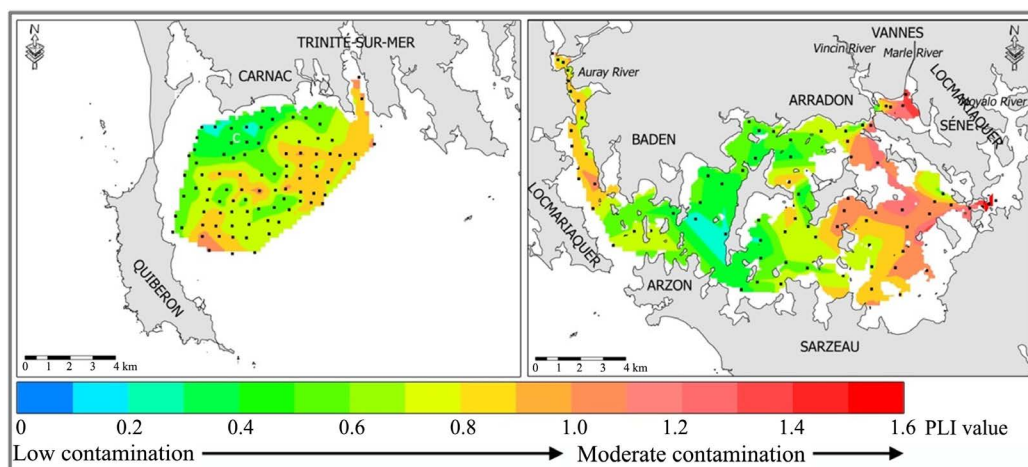

Figure 3. Contamination category based on PLI values in Bay of Quiberon and Gulf of Morbihan surficial sediments.

Table 1. Classification of sediment samples ($\mu g \cdot g^{-1}$) based on the proposed SQGs by USEPA.

	Bay of Quiberon		Gulf of Morbihan		Sediment Quality Guidelines (SQGs)		
	Mean	Min - Max	Mean	Min - Max	Non Polluted	Moderately Polluted	Heavily polluted
Cu	14.4	2.56 - 40.9	21.9	1.20 - 48.6	<25	25 - 50	>50
Zn	40.7	4.60 - 98.9	38.4	4.78 - 89.9	<90	90 - 200	>200
Cd	0.07	0.01 - 0.19	0.11	0.01 - 0.30	-	-	>6
Pb	15.1	3.61 - 28.0	23.8	2.43 - 42.7	<40	40 - 60	>60

were moderately enriched with these metals. However, no surficial sediments from both sampling areas were classified as heavily polluted with the heavy metals studied according to SQGs classification.

The concentration of heavy metals was evaluated in a screening-level ecological risk assessment by comparing them to another numerical SQGs, namely the threshold effect level (TEL)/probable effect level (PEL), and the effect range low (ERL)/effect range medium (ERM) which were proposed by Long and McDonald [50]. Low range values (*i.e.*, ERL and TEL) are less than expected to have adverse effects on sediment dwelling fauna. In contrast, ERM and PEL represent chemical concentrations above which adverse effects are likely to occur in the aquatic ecosystem [50].

The SQG values for heavy metals studied in the surficial sediments from the Bay of Quiberon and Gulf of Morbihan and the sediment classification based on these guidelines are shown in Table 2. Results of SQGs classification suggest that all heavy metals in sediments would rarely be expected to cause adverse effects on biota that living in the area.

The majority of heavy metals studied did not exceed the corresponding ERL and TEL guideline values and therefore do not pose a risk to marine organisms living in Bay of Quiberon and Gulf of Morbihan. Only a small percentage of surficial sediments would be classified as possibly posing an occasional threat to the organism due to concentrations of Cu. However, Cr, Cu, and Pb in a certain location exceeded the TEL value, particularly from the Gulf of Morbihan surficial sediments. Thus, at a concentration greater than the TEL, the toxic effect of long-term exposure to these heavy metals would be predicted to occur in the station sampled.

In order to estimate the effect of multiple contaminations on heavy metals, mean-ERM-quotient (M-ERM-Q) was calculated for each surficial sediment in the Bay of Quiberon and Gulf of Morbihan according to Tessier *et al.* [27], Long *et al.* [48] and Larrose *et al.* [51] as follows:

$$\text{M-ERM-Q} = \frac{\sum_{i=1}^{n}\left(C_i/\text{ERM}_i\right)}{n} \tag{3}$$

where C_i is the surficial sediment concentrations of element (*i*), ERM_i is the

Table 2. Classification of sediment samples based on the SQGs.

	SQGs (µg·g⁻¹)				Percentage of the samples exceeding SQGs (%)			
	ERL	ERM	TEL	PEL	ERL	ERL-ERM	TEL	TEL-PEL
Bay of Quiberon								
Cu	34	270	18.7	108.2	97	3	75	25
Zn	150	410	124	271	100	0	100	0
Cd	1.2	9.6	0.68	4.2	100	0	100	0
Pb	46.7	218	30.2	112.2	100	0	100	0
Gulf of Morbihan								
Cu	34	270	18.7	108.2	85.1	14.9	38.3	61.7
Zn	150	410	124	271	100	0	100	0
Cd	1.2	9.6	0.68	4.2	100	0	100	0
Pb	46.7	218	30.2	112.2	100	0	78.4	21.6

ERM for element (i) and n is the number of elements, e.g. four heavy metals in this study.

Long *et al.* [48] have defined several classes of toxicity probability for biota organisms in their study from US coast based on amphipod survival test: m-ERM-Q < 0.1 has a 9% probability of toxicity); 0.1 < m-ERM-Q < 0.5 has a 21% probability of being toxic; 0.5 < m-ERM-Q < 1.5 has a 49% of being toxic; and m-ERM-Q > 1.5 has a 76% probability of toxicity. Using the concentrations of the heavy metals studied, the m-ERM-Q value was calculated, and the obtained distribution visualized by ArcGIS software in Bay of Quiberon and Gulf of Morbihan is shown in Figure 4.

The m-ERM-Q distribution pattern in the Bay of Quiberon surficial sediments showed that the inner bay zone had values below 0.1, which indicated a 9% probability of being toxic to the benthic organisms in that area. In the outer bay, the m-ERM-Q values slightly exceed 0.1, but not more than 0.2 indicate that this zone is between 9% and 21% probability to be toxic to benthic organisms. However, in Trinité-sur-Mer area, m-ERM-Q ranged from 0.2 and 0.3; therefore, this area can be categorized as 21% probability of toxicity to the benthic organisms according to Long *et al.* [48] classification.

Meanwhile, in the gulf of Morbihan sediments, the m-ERM-Q values at the western zone of the gulf were lower than 0.1m, and therefore this zone can be categorized as 9% probability of being toxic to the benthic organisms. Towards the inner gulf of eastern zone, the values of m-ERM-Q were increased but do not exceed the 21% probability of toxicity to the benthic organisms, 0.2. Generally, some sampling locations located at the rivers zone (Auray, Marle and Noyalo) had the m-ERM-Q value higher than 0.3, which meant a 21% probability of toxicity to the benthic organisms. The impact of contaminated sediment probably on aquatic ecosystems is likely to be due to re-suspension and remobilization processes [52] [53].
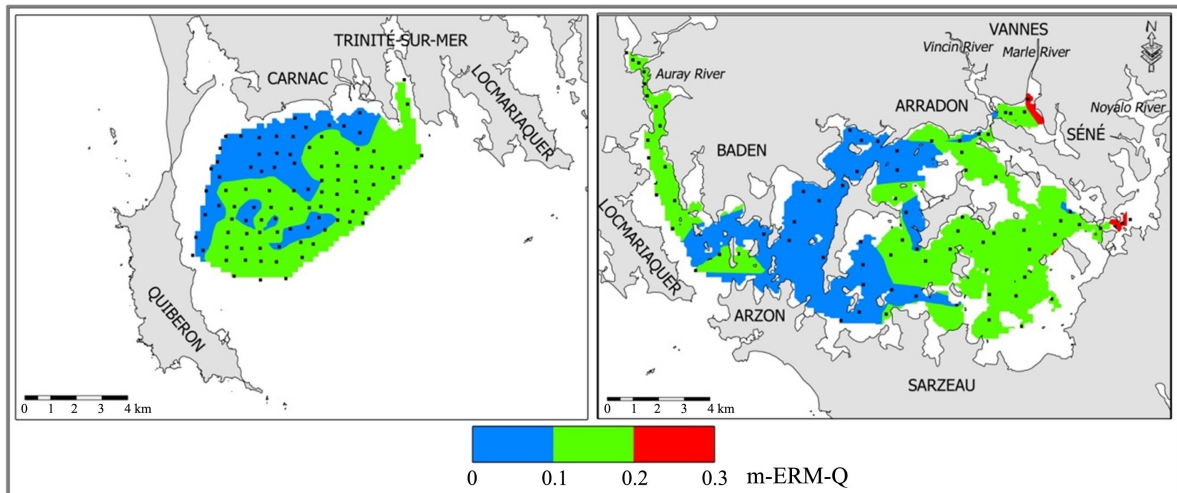
Figure 4. Contamination category based on m-ERM-Q values in Bay of Quiberon and Gulf of Morbihan surficial sediments.

4. Conclusion

In comparison with the sediment quality guidelines for the ecological risk assessment, generally, all metals studied were not exceeding the ERL and PEL classification. Hence, these metals were considered not toxic to the marine organisms. The multiple contamination evaluation by mean-ERM-quotient shows that the sediments do not have more than 21% probability of being toxic to the aquatic organism. However, it is suggested that continuous monitoring including other pollutants such as hydrocarbons, microplastics, nutrient and pharmaceutical wastes should be implemented as the site is important for the recreation area, fishing and oysters mariculture activities.

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Conflicts of Interest

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

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