Geochemistry of Metallic Trace Elements in Surficial Sediments of the Gulf of Morbihan, Brittany, France

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Abstract: Concentration of selected Metallic Trace Elements (MTEs), chromium, manganese, iron, cobalt, copper, zinc, lead and cadmium in surficial sediments from gulf of Morbihan were studied in order to understand the current MTEs contamination due to urbanization and mariculture economic development surrounding the gulf region. Therefore, the distribution, enrichment and accumulation of MTEs in 101 surficial sediments collected by Orange Peel grab were characterized for MTEs content using ICP-MS after mixed acid digestion. The average concentrations of selected MTEs were 36.2±23.9 µg g⁻¹ dry weight (Cr), 278±140 µg g⁻¹ dry weight (Mn), 2.40±1.29% (Fe), 14.4±5.31 µg g⁻¹ dry weight (Co), 16.4±10.3 µg g⁻¹ dry weight (Cu), 38.1±19.1 µg g⁻¹ dry weight (Zn), 34.6±13.9 µg g⁻¹ dry weight (Pb) and 0.11±0.06 µg g⁻¹ dry weight (Cd), respectively. Results from the analysis showed that MTEs studied have relatively low index of geo-accumulation and enrichment factors values and were in value to conclude practically uncontaminated within the gulf. Overall, the geochemistry of the sediment of gulf of Morbihan was influenced by both natural and anthropogenic inputs to the catchment. However, direct comparison with upper continental crust indicated that natural processes were more dominant than anthropogenic input in concentrating metals.

Keywords: Heavy metals, surficial sediments, Gulf of Morbihan, index of geo-accumulation, enrichment factors

INTRODUCTION

In recent years, awareness of the marine has greatly increased, especially relating to the presence of anthropogenic pollutants and their possible to biological effects to the marine organisms to the human. These pollutants such as Metallic Trace Elements (MTEs) entering the aquatic environments by fine-grained particulates and will accumulate in the bottom sediments (Farkas et al., 2007). These sediments which are an important component in aquatic and marine ecosystems also provided a habitat for variety of benthic organisms and juvenile forms of pelagic organisms (Unlu and Alpar, 2009; Adams et al., 1992).

Sediments have known to be one of the important carriers for MTEs in aquatic environment and they can reflect the recently quality of status of the aquatic system (Celò et al., 1999). Therefore, they can act as a sink for the organic pollutants that derived from human activities such as from agricultural activities (Apitz et al., 2005), industrial and urban habitation surface runoff (Hatje et al., 2002) and transportation or recreational activities (Zulkifli et al., 2010) and by direct natural input by atmospheric deposition (Lacerda et al., 1991). Coastal environments such as estuary are particularly sensitive to the input of MTEs since urban and industrial wastes are usually drained to the nearby river system and the contaminant waste quickly reaches and settled down to the coastal zone (Garcia et al., 2008). These MTEs are mainly associated with particulate and colloidal matters and deposit to the surface sediments once they reach the coastal environment (Gibbs, 1983; Loring and Rantala, 1992).

MTEs occur naturally and are ubiquitous contaminants in the aquatic sediments around the world. These elements become toxic to aquatic organisms and
humans if the concentrations above certain threshold bio-available levels (Blackmore, 1998; Shazili et al., 2006). MTEs residues in contaminated habitats may accumulate in biota especially filter feeding organism such as mollusk and bivalve species which in turn may enter into the human food chain and result in human health problems (Cook et al., 1990; Sin et al., 2001). In the aquatic environment, these MTEs are persistence and non-degradable, thus they represent one of the greatest ecological risks for coastal-marine ecosystems (Pekey, 2006).

Extensive study of MTEs is necessary in order to gain information to understand the possible threats of pollution to the gulf of Morbihan aquatic environment. In order to estimate the source of MTEs contamination, two approaches were applied, index of geo-accumulation and enrichment factors by using AI as a normalizer. Additionally, this region is influenced by the discharge plumes of three rivers; namely Auray, Marle and Noyalo rivers, whose catchment areas are affected by human population growth. Such information is crucial to ecological risk assessment and better management of marine areas with contaminant input since this area is important for shellfish mariculture activities. Hence, the present study was conducted to assess the preliminary concentrations of MTEs in surficial sediments collected randomly in the gulf as no geochemistry study has been conducted in the gulf before.

MATERIALS AND METHODS

Site description: The gulf of Morbihan is a natural harbor located at southern Brittany (northwest France), sheltered from the Atlantic Ocean by the peninsula of Rhuys, Belle Ile Island and the structural arc formed by peninsula of Quiberon, Houat and Hoedic islands (Fig. 1) (Menier et al., 2006, 2010). It is a close seawater body (11,500 ha), linked to the ocean by a narrow channel (900 m) and dotted with many islands (Henocque, 2003; Menier et al., 2011). With every tide, approximately 400 million m$^3$ of seawater pour in and out the gulf creating strong currents on the flat bottom, contributing to the creation of a great biodiversity of marine ecosystem. Across this entrance strong tidal currents affect the basin with water speeds that can reach 4.6 m sec$^{-1}$ at spring tides. Gulf of Morbihan has a semidiurnal tidal regime (tidal range 3 m at spring tide) with freshwater input from the Auray, Marle and Noyalo rivers (Blanc and Daguzean, 1998). Many areas along the coast are used as recreation areas by the public. The surrounding coast is successfully used for commercial shellfish (oysters and mussels) cultivation with a significant market around the region.

Sampling: This oceanographic fieldwork was accomplished with the SEPIOLA research vessel from University of Rennes 1. A total of 101 surficial sediments were collected randomly in gulf of Morbihan with Orange Peel Grab sampler from 7th to 9th Dec 2009. During sampling, precautions were taken to minimize any disturbance in the grain-size distribution of the original sediments. Sediments were taken only when the grab was firmly closed on arrival on the boat deck, so as to avoid any leaks of fine material withdrawn by water. In addition, to avoid metal contamination from the grab's wall, the outermost layer of the sediment samples were removed and only the inner part was kept for further analysis. After sampled, the samples were placed in plastic containers and preserved at 4°C until analysis.

Analysis: The sediment samples were digested and the analyses for total Metallic Trace Elements (MTEs) were carried out following published methodologies with some modifications (Ong and Kamaruzzaman, 2009; Kamaruzzaman et al., 2008, 2010). 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 150°C for 6 h. After cooling at room temperature, the solution of the vessel was transferred into a polypropylene test tube and was diluted to 10 mL with deionized water. A clear solution with no residue was obtained at the last stage. An inductively coupled plasma mass spectrometer (Perkin Elmer Elan 6000) was used for the quick and precise determination of selected MTEs (Cr, Mn, Fe, Co, Cu, Zn, Pb and Cd) 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.

RESULTS AND DISCUSSION

All the analyzed data were visualized using ArcGIS software and presented in the form of concentration isopleth map to identify the hotspot of the sediment concentrations as shown in Fig. 2. These visualization through overlying maps using a geographical information system makes these presentation even easier and more successful (Caeiro et al., 2005).
Cr concentrations ranged from 5.43 to 111.7 μg g⁻¹ dry wt., with an average of 36.2 μg g⁻¹ dry wt. The concentrations were nearly equal the Upper Continental Crust (UCC) values, 35 μg g⁻¹ dry wt. (Wedepohl, 1995). Meanwhile for Mn, the average concentration was 278.2 μg g⁻¹ dry wt., ranged from 16.6 to 732 μg g⁻¹ dry wt. This value was two times lower compared to UCC value, 527 μg g⁻¹ dry wt. (Wedepohl, 1995). For Fe, the average concentration, 2.40 μg g⁻¹ dry wt. was lower than UCC value, 3.5% (Wedepohl, 1995). The concentrations were ranged from 0.05 to 5.47%. UCC value for Co was 11.6 μg g⁻¹ dry wt. (Wedepohl, 1995) and the concentration of Co in our sediment samples was 14.4 μg g⁻¹ dry wt. and slightly higher compared to the UCC value. The lowest concentration was 4.71 μg g⁻¹ dry wt. while highest concentration was 31.3 μg g⁻¹ dry wt.

The average concentration of Cu was 16.4 μg g⁻¹ dry wt. and was lower compared to UCC value, 25 μg g⁻¹ dry wt. (Wedepohl, 1995). The concentrations of all sampling points ranged from 1.20 to 48.5 μg g⁻¹ dry wt.
Fig. 2: Metallic trace elements distribution (expressed in μg g$^{-1}$ dry weight except Fe in %) in gulf of Morbihan surficial sediments
The concentration of Zn ranged from 4.78 to 85.4 μg g⁻¹ dry wt., with an average of 38.1 μg g⁻¹ dry wt. This average value was two times lower compared to average shale, 71 μg g⁻¹ dry wt. (Wedepohl, 1995). In contrast, the average concentration of Pb was considerably higher compared to UCC, 20 μg g⁻¹ dry wt. (Wedepohl, 1995). The average of Pb was 34.6 μg g⁻¹ dry wt., ranged from 3.38 to 59.4 μg g⁻¹ dry wt. in all sampling points. Finally, the average concentration of Cd, 0.11 μg g⁻¹ dry wt. was comparable compared to UCC, 0.102 μg g⁻¹ dry wt. (Wedepohl, 1995). The highest value of Cd was 0.30 μg g⁻¹ dry wt. while the lowest was 0.02 μg g⁻¹ dry wt.

For better management of pollution control in the coastal environment, the contamination assessment should be easily understood by the decision makers and publics. Thereby, environmental quality indicators and indices are a powerful tool for analyzing and conveying general environmental information to all parties involved (Qingjie et al., 2008). Anthropogenic mainly by human activities had caused important transformation of organic contaminants in coastal environments during the last 150 years. MTEs were among the most widespread of the various contaminants originating from anthropogenic activities, particularly from mining and smelting waste sites (Mendil and Ulusozlu, 2007; Adamo et al., 2005), urban and housing discharge by surface runoff (MacFarlane et al., 2003; Freda and Cox, 2002) and transportation activities (Kishe and Machiwa, 2003).

The most often used approach to determine the sources of the pollutant is through the normalization of MTE data to a reference value. In order to a better estimation of anthropogenic input, index of geo-accumulation (Igeo) was computed based on the background values (Srinivasa Reddy et al., 2004, Yu et al., 2008). Igeo describes the relationship between the measured element concentration in the sediment fraction (Cₜ) and the geochemical value in sediment (average shale), Bᵢ. The Igeo value was calculated by using the following equation, Igeo = log₂(Cₜ/Bᵢ). The constant value, 1.5 allows natural fluctuations in the content of a given substance in the environment and has very small anthropogenic influences (Chatterjee et al., 2007; Audry et al., 2004). The index of geo-accumulation consists of seven grades or classes, with Igeo of 6 indicating almost a 100-fold enrichment above background values (Muller, 1981). The author has distinguished seven classes of the Igeo (Table 1). Based on the classification, all MTEs have calculated Igeo values less than 0 except for Pb (0.03). Based on the Igeo estimation, the gulf of Morbihan surficial sediments can be classified as practically uncontaminated to moderately contaminated (Table 2).

Beside Igeo, Enrichment Factors (EFs) was used as a second criteria in the MTEs pollution assessment of the gulf surficial sediments. The reference metal must therefore be an important constituent of one or more of the major fine-grained trace metal carriers reflect their granular variability in the sediment. The most often used reference metal is Al which represents a chemical tracer of Al-silicates, particularly the clay minerals (Van der Weijden, 2002; Liaghati et al., 2003; Daessle et al., 2004). Therefore, for a estimation of anthropogenic input, an EFs was calculated for each MTEs by dividing its ratio to the normalizing element by the same ratio found in the chosen background. EF values were applied to evaluate the dominant source of the sediments and as indicators for pollution (Hung and Hsu, 2004; Mil-Homens et al., 2007) and were described as: EF = (MTE/Al)ₜ/(MTE/Al)ᵣᵽ, where, the relative concentrations of the respective element, MTE and Al in the sediments and in the crustal material, respectively (Prudencio et al., 2007; Zhang et al., 2007). EF values close to 1 point to a crustal origin, while those with a factor more than 10 were considered to have a non-crustal source or anthropogenic input. In this study, the MTEs studied were proven to be categorized to minimal enrichment except for Pb which was classified as moderate enrichment (Table 3).

<table>
<thead>
<tr>
<th>Igeo : Index of geo-accumulation</th>
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<tr>
<th>Table 1: Sediment contamination categories based on Igeo value</th>
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<tr>
<td>Class</td>
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Igeo : Index of geo-accumulation

<table>
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<tr>
<th>Table 2: Contamination categories based on Igeo value</th>
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<tr>
<td>Igeo value</td>
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<tr>
<td>------------</td>
</tr>
<tr>
<td>Chromium</td>
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<td>Manganese</td>
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<tr>
<td>Iron</td>
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<td>Cobalt</td>
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<td>Copper</td>
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<tr>
<td>Zine</td>
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<tr>
<td>Cadmium</td>
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<td>Lead</td>
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Igeo : Index of geo-accumulation
Fig. 3: Distribution of water current speed (m sec⁻¹) and direction in gulf of Morbihan

<table>
<thead>
<tr>
<th>Elements</th>
<th>Mean</th>
<th>Average</th>
<th>Contamination category</th>
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<tr>
<td>Chromium</td>
<td>0.45</td>
<td>0.05-1.49</td>
<td>Deficiency to minimal enrichment</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.36</td>
<td>0.01-1.17</td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>0.54</td>
<td>0.01-1.49</td>
<td></td>
</tr>
<tr>
<td>Cobalt</td>
<td>0.64</td>
<td>0.15-1.41</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>0.34</td>
<td>0.02-0.97</td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>0.62</td>
<td>0.06-1.61</td>
<td></td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.64</td>
<td>0.07-1.90</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>1.94</td>
<td>0.10-2.78</td>
<td>Moderate enrichment</td>
</tr>
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Based on the Igeo and EFs estimation, it can be suggested that generally the sources of MTEs in gulf of Morbihan surficial sediments are solely natural and free of anthropogenic input. Some higher concentration of MTEs especially Pb levels in the Auray, Marle and Noyal rivers system may due to sources coming from surface and river runoff along the rivers. On the other hand, the relative MTEs deficiency measured in the gulf surficial sediments may be due to dilution of the MTEs by high tidal range and water current speed in the coastal environment of the gulf (Fig. 3). This strong current in the bottom can disperse the sediments containing MTE in the gulf and flush out to the open sea.

Surficial sediment characteristic in the gulf were also determined and showed in Fig. 4. With these sedimentary facies data, the relationship between types of sediment and MTEs were investigated. Most MTEs are bound mostly in the fine-grained fraction (<63 μm) because of its high surface area-to-grain size ratio and organic substance content (Horowitz and Elrick, 1987; Moore et al., 1989) whereas they have a potentially greater biological availability than those in the larger (2 mm-63 μm) sediment fraction (Bryan and Langston, 1992; Everaarts and Fischer, 1992). MTEs may be mobilized as a result of natural processes such as weathering and erosion of geological formation. In the mobilization process, MTEs may be adsorbed by fine-sediment and can combine with organic compounds or co-precipitate with oxide and hydroxides (Wang and Chen, 2000). Because of their large adsorption capabilities, fine-grained sediments represent a major repository for MTEs study and a record of the temporal changes in MTE contamination. These relationships were clearly evident in gulf of Morbihan surficial sediments where variations in absolute MTEs concentrations are linked clearly with variations in grain size. Figure 5 shows the plotted graph of MTEs concentration against grain...
Fig. 4: Types of sediment distribution and sedimentary map in gulf of Morbihan surficial sediments

Fig. 5(a-h): Continue
mean size. All MTEs studied show a significant positive correlation with grain mean size. The r-value range from 0.15 to 0.55 (very negligible relationship to moderate correlation) from plotted graph can prove this MTEs–grain size correlation.

CONCLUSION

A comparison between heavy metals and grain size distributions show a strong degree on correlation between concentration and finer particles. The results indicate that <63 µm fractions have the highest concentration of metals. A decrease in these element concentrations can be observed towards the higher grain size fractions. The fine sediment has a higher availability to absorb most of the considered metals and some organic contaminants and govern their transport throughout the water body.

Identification and quantification of heavy metal sources are important environmental issues. This study present useful tools, methods and indices for the evaluation of sediment contaminant. The calculation of enrichment factors showed that all metals studied have a low value of EF value except Pb (1.94) and category as deficiency to minimal enrichment. The results of geoaccumulation index reveal that sediments of Gulf of Morbihan are moderately polluted with Pb, whereas the other metals are practically uncontaminated. It is clear that concentrations of selected heavy metals were not greatly caused by anthropogenic activities but moderately occurs naturally. Some of the elevated concentration of Pb are due to anthropogenic sources including fishery activities, urban run-off from human population around the gulf and boating recreation may be the reason contributing insignificant to the sediment. Briefly, it can be concluding that there were no serious heavy metal contaminations in Gulf of Morbihan. Continuous monitoring and further studies of the area are recommended to ascertain long-term effects.

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