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Geochemical Characteristics of Heavy Metals Concentration in Sediments of Quiberon Bay Waters, South Brittany, France

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ABSTRACT

Cr, Co, Cu, Zn, Cd and Pb in the bottom sediments from 93 sites at *Quiberon bay* were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICPMS) after acid extraction. The ranges of the concentration in the sediments are as follows: 27.3 µg/g (Cr), 11.6 µg/g (Co), 13.8 µg/g (Cu), 42.0 µg/g (Zn), 0.08 µg/g (Cd) and 17.8 µg/g (Pb). Potential contamination of the bay was assessed by Igeo and pollution load index whether the concentration observed represent background or contaminated levels. Based on the results, it can be concluded that the bay is unpolluted for the studied metals.

Key words: Quiberon bay, ICPMS, Igeo, Pollution load index.

INTRODUCTION

Marine sediments, including materials originating from the terrestrial and land inputs, as well as atmospheric deposition and autogenetic matter from ocean itself, preserve a continuous record of regional and global environmental changes, which can be employed in reconstructing environmental evolution (Wan *et al.,* 2003; Dai *et al.,* 2007). To some extent, sediment is the mirror of any sedimentary environmental changes, which can reflect the biological and geochemical process of former conditions. On the other side, environmental changes are not only driven by natural forces, but also by anthropogenic effects (Kalis *et al.,* 2003). Especially in recent years, the anthropogenic impacts on the environment have been leading to eutrophication in coastal zone and offshore and the interaction of the natural force and human activities have exerted great effects on the whole environmental system (Cobelo–Garcia and Prego 2003; Meng *et al.,* 2008).

In this work, Cr, Co, Cu, Zn, Cd and Pb total concentrations have been determined in bulk sediment of 93 surface sediments from Quiberon Bay, in order to increase the knowledge on metal levels in this area, which is not been studied very much. Geo–accumulation index and pollution load index has been calculated to assess sediments contamination and establish if metals concentrations represent background levels for the Northwest France (Loska *et al.,* 1997; Ruiz 2001). Moreover, analytical results have been elaborated by using Geographical Information System (GIS) ArcGIS 9 software, to show metals' accumulation areas. Multivariate statistical analysis has been used to evaluate the possibility to distinguish sampling stations, in relation to their geographical location (Guillen *et al.,* 2004; Buccolieri *et al.,* 2006). The aim of this paper is to describe the distribution of heavy metals, to provide preliminary data on the environmental conditions, and to evaluate the risks from metal contamination, the impact of the human activities and the mariculture areas, in this area compared with other bay in this region.

MATERIALS AND METHODS

Description of sampling sites

Quiberon Bay is a large well–sheltered expanse of open sea at the south coast of Brittany and made up of two complementary areas with an equivalent surface area, approximately 120 km² (Figure 2). The bay is roughly triangular in shape, almost completely surrounded by land on the north and east sides, open to the south with the Gulf of Morbihan to north–east and the narrow peninsular of Presqu'île de Quiberon of providing protection from the Atlantic Ocean to the west (Chaumillon *et al.,* 2008). The Belle Island, Houat Island and Hœdic Island add to the bay's protection (Guillaud *et al.,* 2008).

Sample collection

This oceanographic fieldwork was accomplished with the vessel from Regional Committee of Conchyliculture (CRC), South Brittany. A total of 93 sediment samples were collected randomly in Quiberon Bay with Orange Peel Grab. Sediment samples were collected from the top 3–5 cm of the surface at each sampling point. During sampling, precautions were taken to minimize any disturbance in the grain–size distribution of the original sediment. Samples 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 sample was removed and only the inner part was kept. After collection the samples were placed in plastic containers and kept at 4°C until analysis.

Reagents and calibration

The reagents used were all of analytical reagent grade certified for high purity. Ultrapure water (water resistivity > 18.2MÙ at 25°C) was produced with a Mili–Q Integral Water Purification System. High purity concentrated HNO3, HCl and HF (Merck) were used in aqua regent digestion. Calibration was done using external and internal standards. The external standard was prepared by diluting the ICP multi–element standard solution VI for ICP–MS CentiPUR® with the same acid mixture used for sample digestion. A mixture of scandium (Sc), indium (In) and bismuth (Bi) was used as an internal standard. All glass and plastic wares were cleaned by soaking overnight in 5% HNO_3 and were then rinsed with Mili–Q water.

Analytical procedures

The sediment samples were digested and the analyses for total heavy metals carried out following published methodologies with some modifications (Ong and Kamaruzzaman 2009; Kamaruzzaman *et al.,* 2008). An inductively coupled plasma mass spectrometer (Perkin Elmer Elan 6000) was used for the quick and precise determination of Cr, Co, Cu, Zn, Cd and Pb in the digested sediment with acid. The digestion method involved heating of 50mg 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 at 150°C for 5 hours. After cooling, a mixed solution of HBO and EDTA was added, and the vessel was heated again at 150°C for 5 hours. After cooling at room temperature, the solution of the vessel was transferred into a polypropylene test tube and was dilute to 10mL with deionized water. A clear solution with no residue should be obtained at the last stage. The accuracy was also examined by analyzing

duplicate Standard Reference Material 1646a Estuarine Sediment, the results of which were within ±3% of certified values. Recoveries of elements ranged from 96.3–102.6%.

RESULTS AND DISCUSSION

The distribution of metals in bottom sediment of Quiberon Bay has been examined in order to enhance the data inventory for the region, characterize the geochemistry of Cr, Fe, Co, Cu, Zn, Cd, and Pb in bottom sediments and to help understand the influence of anthropogenic activities on biogeochemical process in this bay system. Meanwhile, the distribution patterns were depicted through the interpolation of metal concentration by using ArcGIS 9.3 software (Figure 2). Concentrations of the heavy metals show a wide range of values; Cr (8.52–61.9 µg/g); Co (2.12–19.7 µg/g); Cu (3.45–40.9 µg/g); Zn (8.96–87.1 µg/g); Cd

Table 1: Correlation matrix between heavy metals in sediment samples from Quiberon Bay

	Cr	Fe	Co	Cu	Zn	Cd	Pb	Mean Size
Cr	1							
Fe	0.560	1						
Co	0.412	0.760	1					
Cu	0.632	0.845	0.652	1				
Zn	0.534	0.928	0.805	0.779	1			
Cd	0.352	0.569	0.557	0.462	0.670	1		
Pb	0.485	0.569	0.393	0.570	0.648	0.431	1	
Mean size	0.071	0.170	0.266	0.148	0.283	0.278	0.056	1

Table 2: I_{geo} classification (Miller 1979)

I_{geo}	I_{geo} class	Description of sediment quality
<0	0	Uncontaminated
0–1	1	Uncontaminated to moderately contaminated
1–2	2	Moderately contaminated
2–3	3	Moderately to strongly contaminated
3–4	4	Strongly contaminated
4–5	5	Strongly to extremely strongly contaminated
>5	6	Extremely contaminated

Table 3: Geoaccumulation index value of heavy metals in sediment

	Igeo		Sediment quality
	Average	Min / Max	
Cr	–2.40	–3.99 / –1.13	Uncontaminated
Fe	–2.67	–5.28 / –0.79	
Co	–1.50	–3.75 / –0.53	
Cu	–2.45	–4.29 / –0.72	
Zn	–1.94	–3.99 / –0.71	
Cd	–2.59	–4.53 / –1.77	
Pb	–0.78	–1.76 / –0.10	

(0.02–0.13 µg/g); and Pb (8.88–28.0 µg/g). The mean values of the study area was 27.3 µg/g for Cr, 11.6 µg/g for Co, 13.8 µg/g for Cu, 42.0 µg/g for Zn, 0.08 µg/g for Cd and 17.8 µg/g for Pb, allowing to arrange the metals from lower to higher mean content as; Cd < Co < Cu < Pb < Cr < Zn.

Pearson's correlation coefficient matrixes among the selected heavy metals in the sediment are depicted in Table 1. The matrix summarizes the strength of the linear relationships between each pair of variables. All the metal pairs in the surface sediment exhibit positive relations and some of them

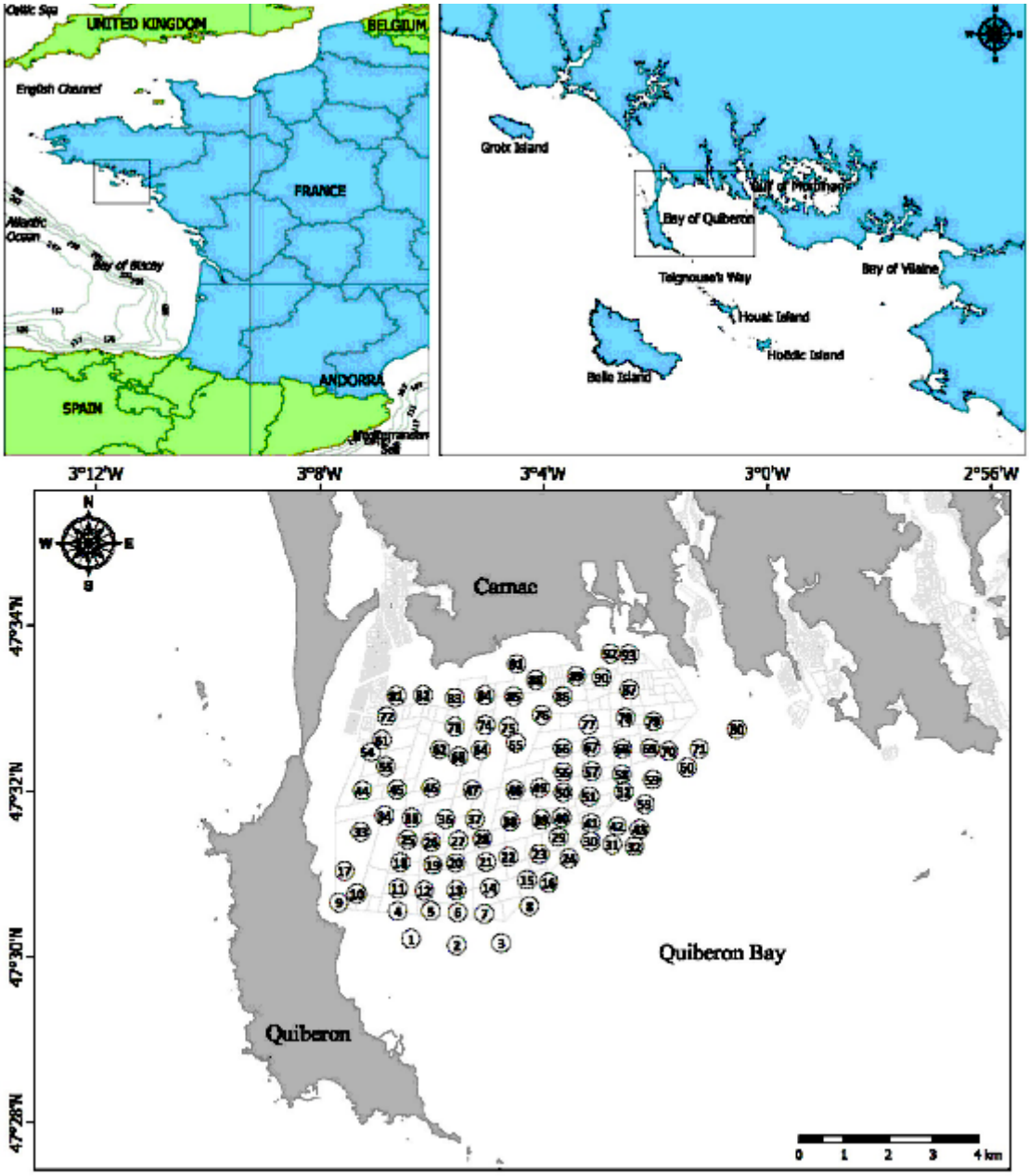

Fig. 1: Surface sediment sampling locations in Quiberon Bay, Brittany, France

were significant at the 95% and 99% confidence levels. Fe–Co, Fe–Cu, Fe–Zn, Co–Zn pairs are significantly positively correlated with each other at the 99% confidence level, which may suggest a common pollution sources or a similar geochemical behaviour for these metals (Ahdy and Azza 2009) and a similar terrigenous source or a result of similar mechanisms of transport and accumulation within the sediments.

Significant correlation between all metal studied and Fe suggested Fe has a strong correlation with other oxides which have a higher affinity with most elements (Cardoso *et al.,* 2001; Zabetoglou *et al.,* 2002). Meanwhile, positive correlation also been found between the metals and sediment size suggested fine–grained sediments tend to have relatively high metal contents, due in part to the high specific surface of the smaller particle size.

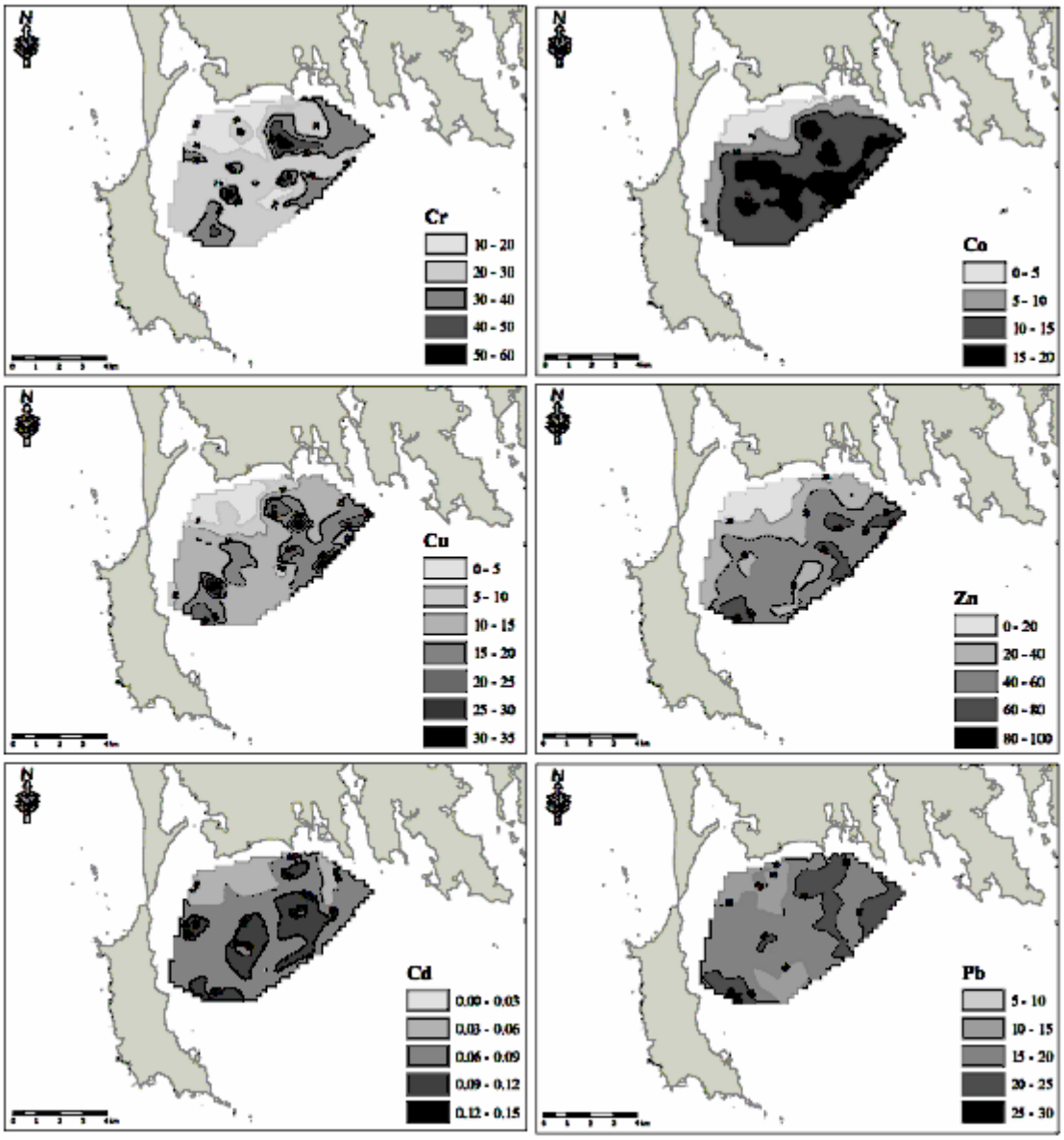

Fig. 2: Heavy metal distribution (in µg/g dry weight) in Quiberon Bay

Many authors prefer to express the metal contamination with respect to average shale to quantify the extent and degree of metal pollution (Muller 1969). In order to compare present day heavy metal concentrations with background values, we computed the "Index of Geoaccumulation", which was introduced by Müller (1979). The formula used for the calculation, $I_{geo} = \log_2 (C_n/1.5B_n)$, where C_n is the measured content of element "n", and B_n the element's content in "average shale" (Turekian and Wedepohl 1961). The factor 1.5 is introduced to include possible variations of the background values due to lithogenic effects. Muller (1979) has distinguished seven classes of geoaccumulation index (Table 2).

The world average shale aften used to provide background metal levels. The regional background value for these metals are not available, thus the background concentration of Cr, Cu, Zn, Cd and Pb in the average shale obtained from Turekian and Wedepohl (1961) are used in this study. These values are commonly used as background values in sediment studies to quantify the extent and degree of metal pollution (Cevik *et al.,* 2009; Nobi *et al.,* 2010)

According to the Muller scale, the sediments of Quiberon Bay were found to be in class 0, uncontaminated (Table 3). On the basis of the mean values of Igeo, sediments are enriched for metals in the following order: Cd<Cu<Cr<Zn<Co<Pb.

The extent of pollution by metals has been assessed by employing the method on pollution load index (PLI). PLI, for a particular site, has been evaluated following the method proposed by Tomilson *et al.,* (1980). This parameter is expressed as, $PLI = (CF_1 \times CF_2 \times CF_3 \times .....CF_n)^{1/n}$, where n is the number of metals (six in the present study) and CF is the contamination factor. The contamination factor can be calculated from the following equation, CF = (metal concentration in the sediment/ background value of the metal). Because we do not have the background values of the metals of interest, same as we did in enrichment factor calculation, we will adopt the average shale values (Turekian and Wedepohl 1961) in index of geoaccumulation calculation.

The following terminology has been used in this pollution index to get a uniform way of describing the contamination factor. The PLI value > 1 is polluted whereas PLI value < 1 indicates no pollution (Chakravarty and Patgiri 2009; Seshan *et al.,* 2010). The PLI value range from 0.23 to 0.79 confirmed that Quiberon bay superficial sediments are in unpolluted condition. The pollution load index does not show much fluctuation. Lower values of PLI imply no appreciable input from anthropogenic sources.

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