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ONG MENG CHUAN

EVALUATION AND MAPPING OF METALLIC TRACE ELEMENTS IN SURFICIAL SEDIMENTS AND OYSTERS FROM QUIBERON BAY AND GULF OF MORBIHAN, BRITTANY, FRANCE

Thèse soutenue le (date)
devant le jury composé de :

Olivier GEFFARD
Chargé de recherche, IRSTEA (France) / *rapporteur*

Kamaruzzaman YUNUS
Professeur, International Islamic University Malaysia (Malaisie) / *rapporteur*

Alexandra COYNEL
Maître de conférences, Université Bordeaux1 (France) / *examinateur*

Virginie DUPONT
Maître de conférences, Université de Bretagne Sud (France) / *examinateur*

Rejis PAJOT
Conseil Général du Morbihan (France) / *membre invité*

Pascal KOHAUT
SAUR; Société d'Aménagement Urbain et Rural (France) / *membre invité*

Alain DREANO
CRC; Comité Régional de la Conchyliculture Bretagne Sud (France) / *membre invité*

Noor Azhar MOHAMED SHAZILI
Professeur, University Malaysia Terengganu (Malaisie) / *Co-directeur de thèse*

David MENIER
Maître de conférences HDR, Université de Bretagne Sud (France) / *Directeur de thèse*

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ABSTRACT

A geochemical survey of the Quiberon bay and gulf of Morbihan surficial sediments located in south Brittany was investigated in order to define the distribution and concentration patterns of selected metallic trace elements (Cr, Mn, Fe, Co, Cu, Zn, As, Cd, Hg and Pb), sedimentary facies and total organic carbon contents. These elements were surveyed twice, Dec 2009 and Oct 2010 at 103 sites in the Quiberon bay and 121 sites in the gulf of Morbihan. The temporal and spatial distribution maps of the concentrations of all the studied elements were produced as a contour plot based on geography information system technology. Meanwhile, the correlation between these studied elements with types of sediment and total organic carbon contents was also investigated. The level of pollution attributed to these metallic trace elements was evaluated using several pollution indicators to determine anthropogenically derived sediment contaminations. Enrichment factors, index of geoaccumulation index and pollution load index were used to assess and visualize using ArcGIS software. Association with adverse effects to aquatic organisms was determined, using the classification of the sediments according to the sediment quality guidelines. With the aim of understanding the sedimentation patterns in gulf of Morbihan, a total of ten cores were collected in the gulf and analyzed for $^{210}Pb_{excess}$ activities to calculate the sedimentation rate. On the other hand, levels of Cu, Zn, Cd, Pb, As and Hg were determined in marine oysters, *C. gigas* and *O. edulis* collected from the Quiberon bay and the gulf of Morbihan. Oyster fleshes (in-toto) were analyzed with the purpose of the degree accumulation of these metallic trace elements. To safeguard public health, metallic trace elements studied in the flesh were assessed for human consumption according to provisional tolerable weekly intake and provisional tolerable daily intake. Further to gather the status of contamination, the levels of each chemical element in sediments and oysters were compared with levels found by other investigators from European and Asian regions.

Keywords : *Quiberon bay, gulf of Morbihan, surficial sediments, metallic trace elements, pollution indicators, sedimentation, oysters, public health*

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LIST OF SYMBOLS

µm	micrometer
mm	milimeter
cm	centimeter
m	meter
km	kilometer
ppm	part per million
g	gram
mL	mililiter
ha	hectare
km^2	square kilometre
^{o}C	degrees Celcius
%	percentage
Ø	phi
µg g^{-1}	microgram per gram
µg g^{-1} *dw.*	microgram per gram dry weight
mg kg^{-1} *dw*.	milligram per kilogram dry weight
mg kg^{-1} *ww*.	milligram per kilogram wet weight
mg kg^{-1} body weight	milligram per kilogram body weight
m/s	meter per second
mm/year	millimetre per year
cm/year	centimetre per year
g/week	gram per week
Bq kg^{-1} dry *wt*.	Becquerel per kilogram dry weight

LIST OF ACRONYMS

Oct	October
Dec	December
MTEs	metallic trace elements
ICP-MS	inductively coupled plasma mass spectrometer
GIS	geography information system
GPS	global positioning system
TOC	total organic carbon
O. edulis	*Ostrea edulis*
C. gigas	*Crassostrea gigas*
As	arsenic
Cd	cadmium
Co	cobalt
Cr	chromium
Cu	copper
Fe	iron
Hg	mercury
Mn	manganese
Pb	lead
Zn	zinc
Li	lithium
Al	aluminium
Sc	scandium
Cs	cesium
Th	thorium
UCC	upper continental crust
H_2O_2	hydrogen peroxide
HF	hydrofluoric acid
HCl	hydrochloric acid
$HClO_4$	perchloric acid
H2SO4	sulphuric acid
H3PO4	phosphoric acid
$K_2Cr_2O_7$	potassium dichromate
$FeSO_4$	ferrous sulphate
EF	enrichment factor
*I*geo	index of geoaccumulation
PLI	pollution load index

SQGs	sediment quality guidelines
ERL	effect range low
ERM	effect range median
TEL	threshold effect level
PEL	probable effect level
M–ERM–Q	mean–ERM–quotient
PTWI	provisional tolerable weekly intake
PMTDI	provisional maximum tolerable daily intake

INTRODUCTION

Metallic trace elements (MTE) pollution has drawn increasing attention worldwide due to a dramatic increase of anthropogenic contaminants to the ecosystems through air, water and soils (Santos *et al*., 2002; Woitke *et al*., 2003). Pollution of the natural environment by MTE is a worldwide problem because these chemical elements are indestructible and most of them have toxic effects on living organisms, when they exceed a certain concentration (Schuurmann and Market, 1998; MacFarlane and Burchett, 2000). Most MTEs contaminants are, however, adsorbed to or occluded within the hydrogenous and biogenic phases, which coat natural particle (Thomas and Bendell–Young, 1999). MTEs accumulated in this way may be subsequently released to the overlying water column as a result of either physical disturbance or digenesis and the sediments may persist as a source of pollutant long after the cessation of direct discharges.

Nowadays, estuarine and coastal environments are contaminated by waste by human activities containing elevated concentrations of nutrients, organic pollutants, trace metals, and radionuclide (Clark *et al*., 2000; Kennish, 2002). Some chemicals are highly toxic and persistent, and have a strong tendency to become concentrated in marine food webs. The pollution of coastal zones near metropolitan areas, by these anthropogenic wastes is due to the large coastal human population and the enormous amounts of sewage discharged into coastal waters (Bothner *et al*., 2002; Matthai *et al*., 2002; Sadiq, 2002; Bay *et al*., 2003). The addition waste products into rivers and estuaries, especially those in industrial and population centres have led to a significant increase in MTE contamination (Forstner *et al*., 1990; Jayaprakash *et al*., 2005). Accumulation of MTE in surface sediments from industrial effluents and urban sewage discharged into the river without proper cleaning will easily be identified through MTE spatial variations in sediments (Baptista Neto *et al*., 2000; Dauvalter and Rognerud, 2001).

Rivers transport MTEs into the marine environment, and the magnitude of the chemical elements input to the oceans depends on their levels in the river sediments, water, suspended particulate matter, and the exchange processes that take place in the estuaries (Chester *et al.*, 1985). With the rapid industrialization and economic development in the coastal region, these MTEs are continuing to be introduced to estuarine and coastal environment through rivers, runoff and land–based point sources where the chemical elements are produced as a result of metal refinishing by products. MTEs concentrations in harbour or estuarine sediments usually are quite high due to significant anthropogenic contaminants loading carried by the upstream of tributary rivers (Paetzel *et al.*, 2003; Muniz *et al.*, 2004). The sediments serve as a metal pool that can release metals to the overlying water via natural or anthropogenic processes, causing potential adverse health effects to the ecosystems (Fatoki and Mathabatha, 2001; McCready *et al.*, 2006). Moreover, marine organisms or biota can uptake these chemical elements, which in turn enhances the potential of some elements entering into the food chain. Therefore, MTEs contaminations are still an environmental problem today in both developing and developed countries throughout the world (Zhang *et al.*, 2007).

MTEs accumulate in the sediments through complex physical and chemical adsorption mechanisms depending on the nature of the sediment matrix and the properties of the adsorbed compounds (Ankley *et al.*, 1992; Leivouri, 1998). Several processes lead to the association of MTE with solid phases, such as the direct adsorption by fine–grained inorganic particles of clays; adsorption of hydrous ferric and manganic oxides which may in turn be associated with clay; adsorption on or complexion with natural organic substances, which may also be associated with inorganic particle, and direct precipitation as new solid phases (Gibbs, 1973; Wen and Allen, 1999). Therefore, they are widely used as geo–markers for monitoring and identifying the possible sources of pollution in the coastal environments. Sediment analysis is a sound tool for the assessment of marine pollution as settled particles on the seafloor with different chemical constituents reflects long–term changes in the marine ecosystems. In addition, the sediment act as a useful indicator of long and medium term MTEs flux in industrialized estuaries and rivers, and they help to improve management strategies as well as to assess the success of recent pollution controls (Ravichandran *et al*., 1995).

More than 90 % of the MTEs load in marine aquatic systems is bound to suspended particulate matter and sediments (Calmano *et al*., 1993). Therefore, sediments serve as a pool of MTE that could be released to the overlying water from natural and anthropogenic processes such as bioturbation and dredging, resulting in potential adverse health effects (Daskalakis and O'Connor, 1995; Long *et al*., 1995; Argese and Bettiol, 2001). Because estuaries are among the most productive marine ecosystems in the world, serving as feeding, migration routes, and nursery grounds of many marine and freshwater organisms, it is important that sediment contamination by MTEs be evaluated, and that natural versus anthropogenic contribution be distinguished for effective remedial actions against MTEs pollution (Din, 1992; Balls *et al*., 1997; Chapman and Wang, 2001).

Lying in the second trophic level in the marine aquatic ecosystem, mollusc species have long been known to accumulate both essential and non–essential MTEs in the ecosystems (Dallinger and Rainbow, 1993). Many researchers have reported the potentiality of using molluscs, especially mussel and oyster species, as bio–indicators or biomarkers for monitoring the MTEs contamination of the aquatic system (Bryan *et al*., 1985; Cossa, 1988; Philips and Rainbow, 1993; Andersen *et al*., 1996; Scanes, 1996; Claisse *et al*., 2001; de Astudillo *et al*., 2002; Szefer *et al*., 2002; Liang *et al*., 2004). Studies on the aquatic pollution in French coast (Claisse *et al*., 2001; Bustamante and Miramand, 2004; Amiard *et al*., 2008; Sirot *et al*., 2009), Spain coast (Suner *et al*., 1999; Besada *et al*., 2002; Franco *et al*., 2002), Mediterranean coast (Gundacker, 2000; Szefer *et al*., 2002;

El–Sikaily *et al*., 2003; Locatelli, 2003; Kalpaxis *et al*., 2004;), Arabian coast (Al–Sayed *et al*., 1994; Hamed and Emara, 2006; Mostafa *et al*., 2009), Taiwan coast (Lee *et al*., 1996; Lin and Hsieh, 1999), Hong Kong coast (Wong *et al*., 1981; Liu and Kueh, 2005; Amiard *et al*., 2008) and Malaysia coast (Alkarkhi *et al*., 2008; Yap *et al*., 2004) had used these bio–markers to monitor the MTEs pollution in aquatic systems and the results showed that various degrees of MTEs pollution existed in molluscs. Beside as a bio–marker for marine pollution studies, oyster species also been used in ecotoxicology and toxicity studies by several investigators (Geffard *et al*., 2002; Geffard *et al*., 2003; Losso *et al*., 2007; Money *et al*., 2011).

Oyster mariculture activities are the primary aquaculture in France with a production of 130 000 tonnes/year (Bragigand *et al*., 2004). Thus, France is the principal oyster producer in the European region and among the top five oyster producing countries in the world (Comité National de la conchyliculture, 2002) which contribute about 460 million Euros each year (IFREMER, 2002). In this case, the safety of food to the consumer is a major concern to ensure the safety of consumers of MTEs particularly in the oyster species. Therefore, MTEs analyses of the aquatic organisms of the study area can provide important information on the degree of environmental contamination, and potential impact of seafood, especially oyster and mussel consumption.

Maintaining good marine environmental quality is crucial for several socio–economic reasons. The seafood, notably oysters and mussels, is of value for both local consumption and export revenue. In addition, the MTE compositions of aquatic organisms may further assist the identification of possible sources of contamination and biological pathways. However, the purpose of our study is to understand the current environmental status and the extent of MTE contamination with respect to the natural environment.

The assessment of impacts of man–related activities on the marine environments, especially on enclosed systems such as Quiberon bay and the Gulf of Morbihan can be achieved by measuring various chemical markers including nutrients, organic compounds and toxic MTE in the water column, biota and sediments (Alley, 2000; Simeonov *et al*., 2000). This work is part of a project intended to study the sources and distribution of MTEs in the surficial sediment, water and biota, sedimentation rate and organic pollutants. Therefore, the goals of the present study are:

(1) to assess and to illustrate the degree of MTEs contamination in surficial sediments and their distribution in the coastal water of South Brittany.

The first objective was intended to determine the distribution of MTEs (Cr, Mn, Fe, Co, Cu, Zn, As, Cd, Hg and Pb) concentration in Quiberon bay and gulf of Morbihan surficial sediments followed by analysis of geochemical maps using ArcGIS software to show the hotspot of MTEs contamination. The MTEs concentrations were compared with both sampling periods, Dec 2009 and Oct 2010; and then a comparison between the Quiberon bay and gulf of Morbihan ecosystem.

(2) to determine total organic carbon and sediment grain size in surficial sediments and to further evaluate relationships between MTE concentration.

The second objective was evaluated the total organic carbon content and sediment grain size in Quiberon bay and gulf of Morbihan surficial sediments followed by analysis of ArcGIS software to develop the concentration map. These contours or isopleth maps representations used to illustrate spatial variations among all the sampling locations and comparison between two sampling periods, Dec 2009 and Oct 2010 dataset as the interpolation method. This objective involved the establishment of the relationship that may exist between MTE levels and TOC contents and sedimentary facies.

(3) To compare the sediment quality and pollution status using several approaches.

The third objective was assessed the recent pollution levels in the Quiberon bay and gulf of Morbihan surficial sediments. Several approaches were used to assess the degree of contamination and the potential toxicity of the Quiberon bay and gulf of Morbihan sediments, namely (1) comparison of the MTEs concentration to the upper continental crust and French limits for sediment dredging; (2) calculation of MTE enrichment factors (EF), index of geoaccumulation (*I*geo), pollution load index (PLI); (3) ecotoxicological assessment of MTEs by sediment quality guidelines (SQG).

(4) to estimate the recent sedimentation rate and age of sediment cores from the gulf of Morbihan.

The fourth objective was analyzed the activity of $^{210}Pb_{excess}$ to calculate the sedimentation rate in gulf of Morbihan sediment cores. With the sedimentation rate value, the age of sediment can be estimated.

(5) and to evaluate MTE levels in oyster flesh and further to explore the human intake and health risk associated by consuming these oysters.

The last objective was determined the MTEs (Cu, Zn, Cd, Pb, As and Hg) levels in whole soft part of the oyster (in–toto) followed by tolerable intake of MTE for human consumption. Two main mariculture oyster species were chosen, *C. gigas* and *O. edulis* for this purpose.

A range of studies have been conducted on MTEs distribution in estuarine and plain sediments throughout the world. The majority of these studies, however have concentrated on polluted areas with the objective of describing MTEs concentration and identify the sources of the pollutants (Owen and Sandhu, 2000; Chen *et al*., 2001; de Carlo and Anthony, 2002). The environmental pollution with the MTEs in the Quiberon bay and gulf of Morbihan has not been previously well assessed or investigated, to the best of the author's knowledge. Few studies on the MTEs distribution in bottom sediments in the adjacent sea, bay of Biscay, coastal area of northern and western France and coastal area of Mediterranean sea have been documented by local investigators (*Figure 1*).

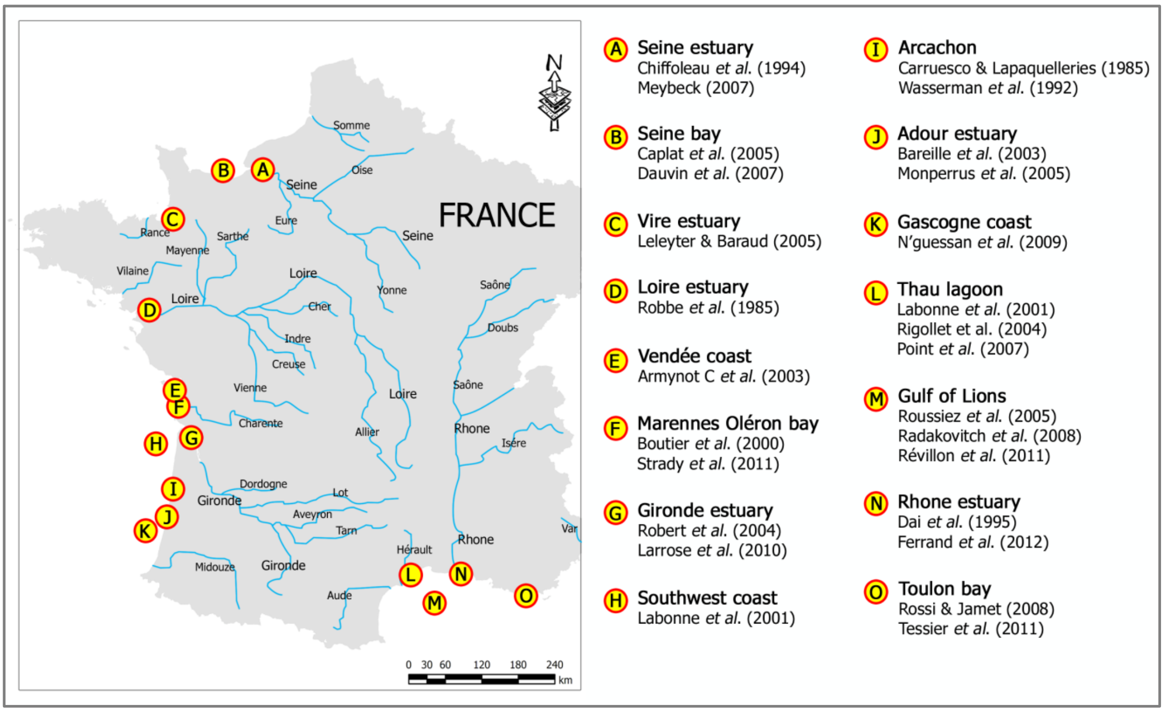

Figure I–1. *Metallic trace elements studies conducted by other researchers in France region.*

Coastal areas are sensitive to both climate changes and human impacts, which make such areas ideal for studying environmental changes, and coastal sediments sequence have become attractive targets to document the paleoenvironmental changes. Quiberon bay and gulf of Morbihan is an excellent example of coastal sea with high terrestrial influence, which is a semi–enclosed bay, surrounded by densely populated areas and mariculture activities (*Figure 2*). Such an investigation is required if the environmental impacts in the region are to be understood quantitatively and qualitatively.

In this exploration, surficial spatial distributions of ten MTEs; Cr, Cu, Zn, As, Cd, Hg, Pb (identified as priority contaminants in aquatic systems by the European Community Water Framework Directive 2000/60/EC; Anonymous, 2000; Tessier *et al*., 2011), Fe, Mn and Co were characterized in the surficial sediments which reflects the recent input to evaluate the contamination level resulting from anthropogenic input. This EC work recommends monitoring of fluvial MTEs loads as a tool for a sustainable management in the aquatic ecosystem (Masson *et al*., 2006).

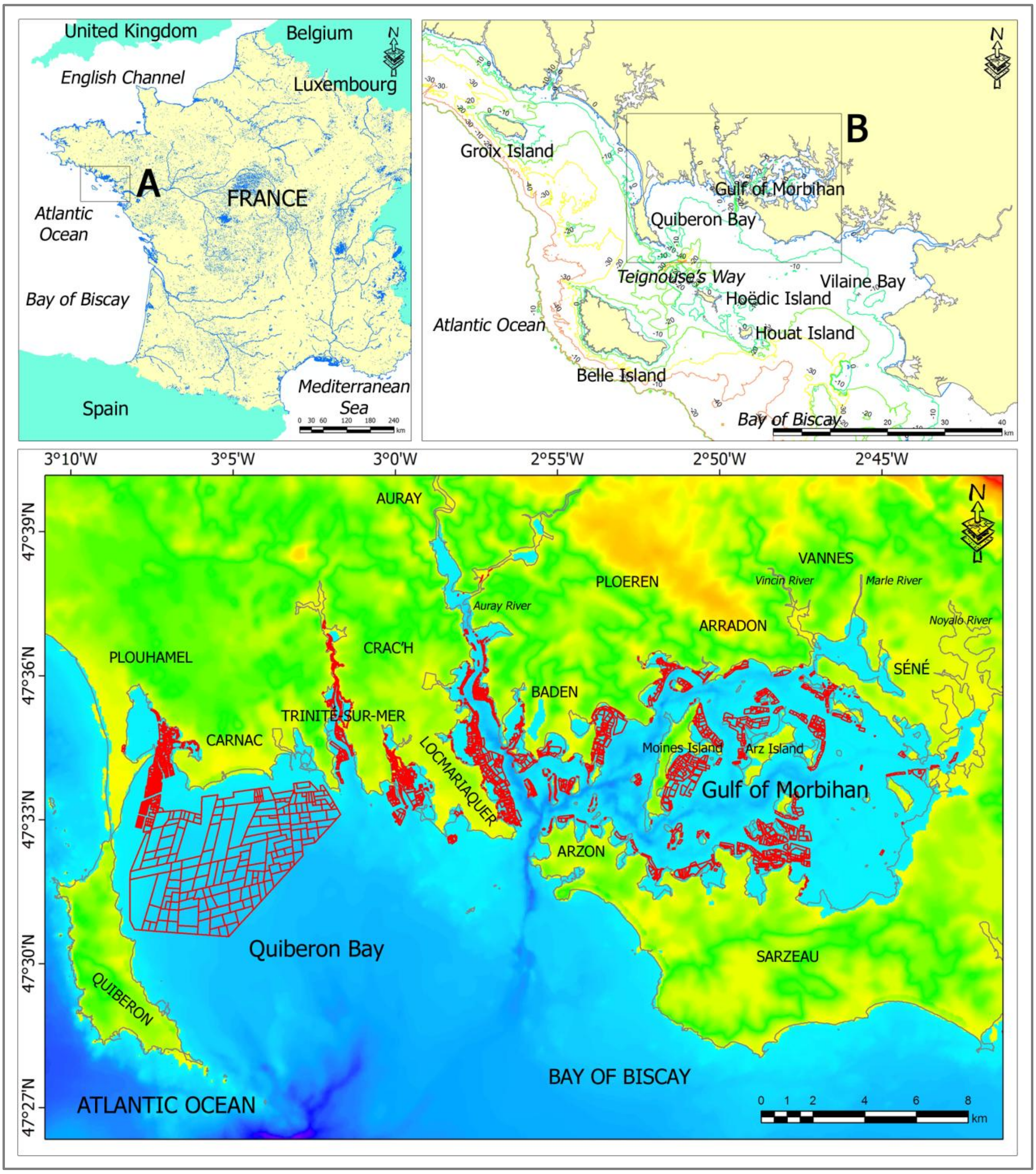

Figure I–2. *Zone of study area, Quiberon bay and gulf of Morbihan at South Brittany region.*

The layout of this dissertation is divided into several chapters, each one developing a different topic.

Chapter 1 represents of the *Literature review* on page **11** summarizes the description of the literature relevant to a geochemistry study.

Chapter 2 correspond of the *Materials and Methods* on page **31** present all the methodologies that used in the field and laboratory to complete this study. This chapter includes the geographical location of Quiberon bay and gulf of Morbihan in south Brittany waters, how the surficial sediments and oysters were collected and laboratory analyses used to analyse all the obtained samples (*Figure 3*).

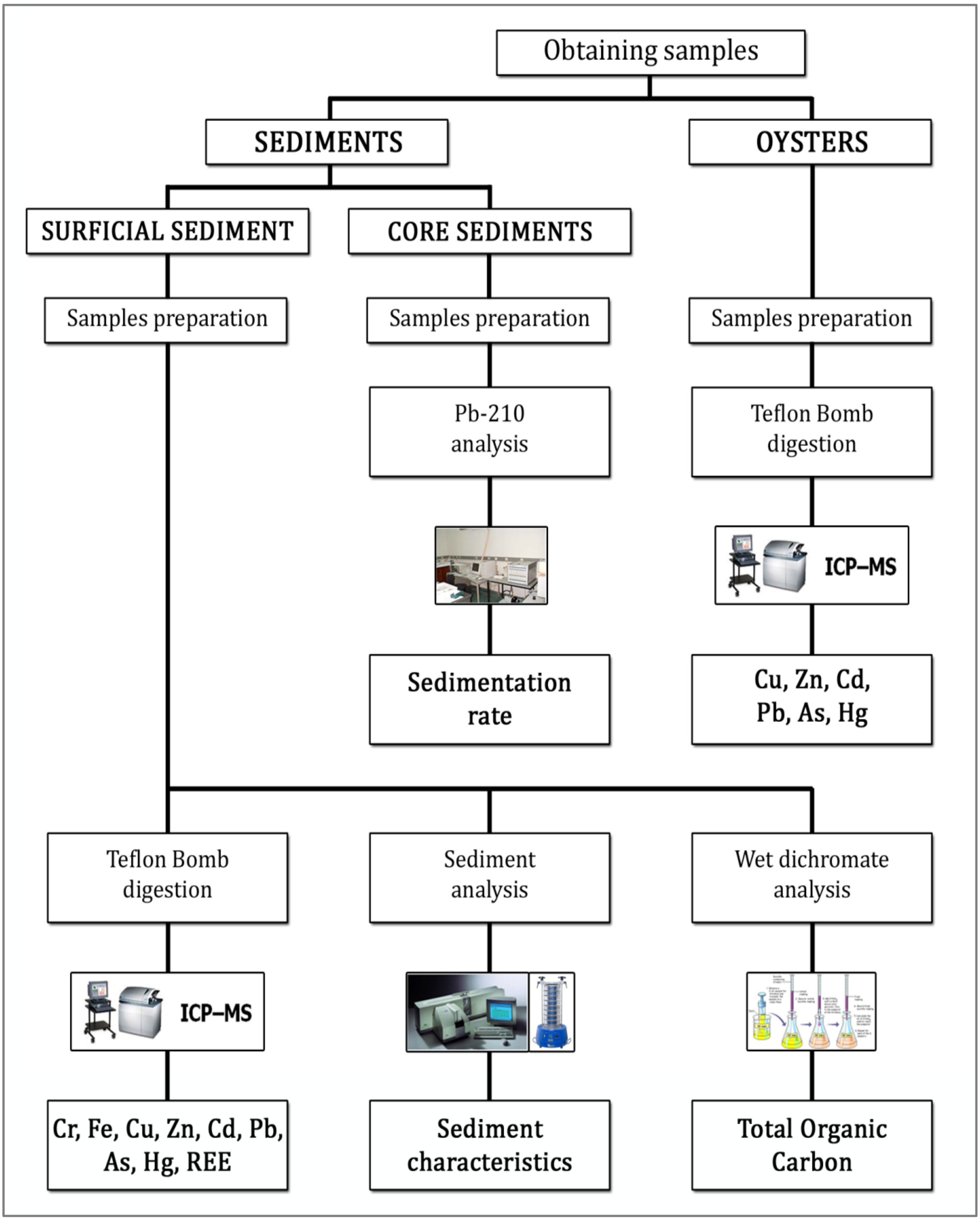

Figure I–3. *Process of laboratory analyses conducted in this study to achieve the study objectives.*

Chapter 3 represents of the *Result / Findings* on page **65** displays all the results in this study which are divided into several sub–chapter, namely; sediment characteristics, total organic carbon (TOC) contents and total metallic trace elements (MTEs) in the topmost/surficial sediments, sedimentation rate in core sediments and total MTEs in oyster samples.

Chapter 4 corresponds of the data interpretation and discussion on page **107** elaborate the several factors that may contribute to the distribution of MTEs concentration such as the relationship between the types of sediment and TOC contents that may influence the concentration and also the co–association among all the studied elements. In this chapter, four assessments and calculation namely (1) enrichment factors, (2) index of geoaccumulation, (3) pollution load index, and (4) sediment quality guidelines are used to determine the level of pollution is discussed. Besides that, the factors that may control the sedimentation rate also were discussed. On the other hand, for oyster studies, pollution load index calculation is used to evaluate the oysters quality. Finally, the estimated tolerable intake for human consumption was calculated before to reach the maximum levels set by the World Health Organization. At the end of each sub–chapter, the levels of MTEs in sediments and oysters, TOC and sedimentation rate were compared with results obtained by other scientists from European and Asian regions to gather the status of contamination in Quiberon bay and gulf of Morbihan environment.

The last part of this dissertation consists of a general conclusion of results obtained. This chapter finishes with recommendations for future investigations in this field.

CHAPTER 1

LITERATURE REVIEW

1.1 Marine sediments

Marine sediments, including materials originating from the terrestrial inputs, as well as atmospheric deposition and autogenetic matter from the ocean itself, preserve a continuous record of regional and even global environmental changes, which can be employed in reconstructing environmental evolution (Wan *et al*., 2003; Song, 2004). To some extent, sediment is the mirror of sedimentary environmental changes, which can reflect the biological, geodynamic and geochemical process of former conditions (Dai *et al*., 2007). 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 led to eutrophication process in coastal zone and offshore and the interaction of the natural force and human activities have exerted great effects on the whole environmental system.

Marine sediments are important shipping agents of trace elements in the hydrological cycle and because elements are partitioned with the surrounding waters and they can display the sediment quality of a marine aquatic system (Singh *et al*., 2005). Coastal and estuarine regions are the important sinks for many persistent contaminants or pollutants and they accumulate in bottom sediments through particulate settled down and marine organisms through bio–accumulation processes (Szefer *et al*., 1995). Thus, the geochemical characteristics study of the sediments can be used to infer the weathering trends and the sources of pollution (Förstner and Salomons, 1980; Fedo *et al*., 1996; Nesbitt *et al*., 1996; Nath *et al*., 2000).

Furthermore, while marine sediment data are useful for describing trace elements occurrence and assessing their distribution in the coastal plains, in spatial or vertical trend studies such as the present investigation, errors associated with sampling and analysis can make it difficult to detect differences between sites (Kelly *et al*., 1994; Liaghati *et al*., 2003; Celino *et al*., 2008). Marine sediments are considered a suitable medium to study the contamination of marine aquatic environments because they represent the sink of multiple contamination sources (Casado–Martìnez *et al*., 2006; Sprovieri *et al*., 2007).

1.2 Sediment characteristics

Analyses of grain size distribution have been widely used by sedimentologist to classify sedimentary environments and elucidate transport dynamics. Grain sizes of the sediment are also an important abiotic component of the dune ecosystem (Abuodha, 2003). The grain sizes of sediments provide an indication of the shear stress that must be applied by the medium to initiate and sustain particle movement (Farahi and Mohammadi, 2012). Grain size distribution is affected by other factors such as distance from the shoreline, distance from the source (river), source material, topography and transport mechanisms (Passega *et al*., 1967).

The system for size classification is based on the log normal model (Krumbein and Pettijohn, 1938). The resulting measures are easily plotted on cumulative frequency curves from which ad hoc graphic measures are determined (Trask, 1932; Inman, 1952; Folk and Ward, 1957; Friedman and Sanders, 1978). Graphic measures derived from the cumulative frequency curve are the mean, sorting, skewness and kurtosis, which provide the descriptive statistics of the particle size distribution. According to Fuechtbauer and Mueller (1977), the Folk and Ward (1957) indices enable a more precise characterization of grain size distributions and also approximate the arithmetic moments.

Sediments can be classified into six different classes according to their particle size; gravelly sand, sand gravel, sand, clayly silt, silty clay and clay (Hassan, 1978). These classes are an important texture parameter as it can provide information on the condition of sediment transportation, sorting and the sediment deposition. It is also vial in controlling the contents of elements such as MTEs and TOC contents. Generally, the content of both chemical elements increases when the sediment grain size is decreased.

The dry and wet methods are the most widely used by sedimentologist to determine the grain sizes. Wentworth (1922) proposed that sediment could be referred to as size grade. Mod, mean, median, standard deviation is the statistical data obtained after the particle size analysis. However, Krumbein (1934) suggested that a logarithmic transformation of the Udden–Wentworth grade scale (*Figure 1–1*) which characterize grain size in phi (∅) by using this formula;

$$\varnothing = -log_2 D$$

where, D is the sediment diameter in mm unit.

The moment method is used to obtain statistical information about the sediment population. It characterizes the grain size data into mean, sorting, skewness and kurtosis. The mean is an index of grain size measurement due to its weight. The increment of the mean value indicates a decrease of grain size; where coarse sediments have a low mean value compared to fine sediments.

1.3 Total organic carbon contents

Total organic carbon (TOC) is one of the elements in organic matter and can be defined as particles that are derived from living organisms that contain chemical compound according to the carbon and hydrogen chain, or without oxygen, nitrogen and other elements (Stevenson and Cole, 1999). Neilson and Sommers (1982) proposed that organic carbon component include cells of microorganism, plant and animal at various stages of decomposition, humic substance and graphite.

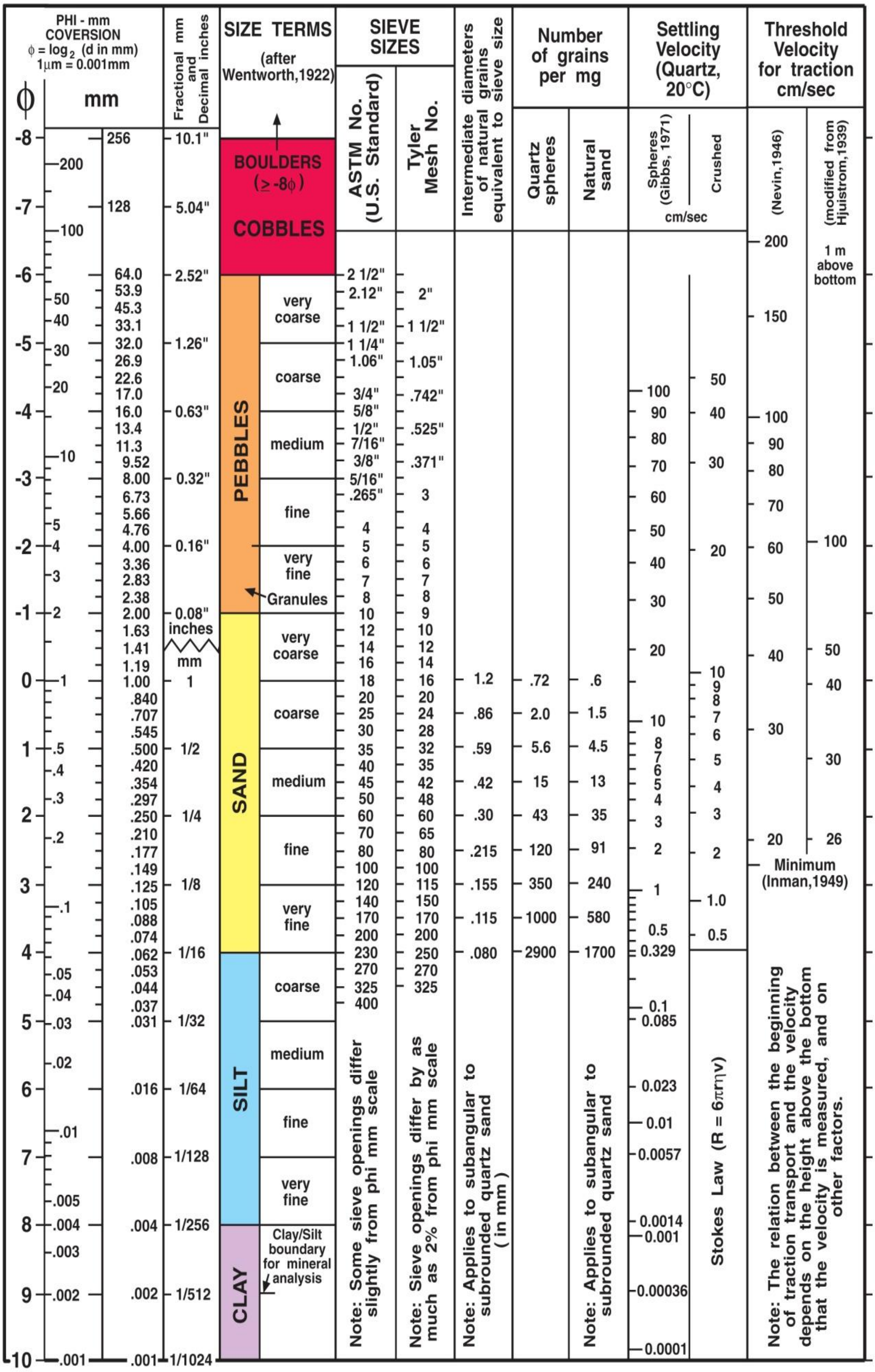

Figure 1–1 *Udden–Wentworth grain sizes classification scale (Wentworth, 1922)*

TOC compound is vital to a marine ecosystem as it provides energy and food for marine bacteria, microorganisms and plants. Most of the organic carbon in seawater is derived from a photosynthetic process in the euphotic layer. The photosynthetic sources include phytoplankton, seaweeds and microscopic pelagic algae (Ichikawa *et al*., 1987). In marine sediment, these organic carbons usually originate from the atmosphere and riverine introduction of pollutant such as industrial and domestic or urban waste, agricultural and mining runoff, accidental spillages by shipping activities and decomposition debris from marine organism.

TOC compounds play an important role in determining some of the MTEs concentrations in sediments. This is due to linkages between reactive functional group site (organic matter) and inorganic cations (MTEs). The exchange capacity of sediments depends on the organic component of the sediment. These MTEs complexes could further coordinate anions such as sulphate, chloride and phosphate. Thus, marine sediments regulate the transportation of these elements, which are essential for marine life. Some organic and inorganic pollutant could be adsorbed, fractioned, precipitated, eluted or desorbed when in contact with inorganic component is sediment. Due to the exchange reaction, MTEs can also be liberated from sediments to the marine environment.

1.4 Metallic trace elements

The ocean burden of metallic trace elements (MTE) and different kinds of pollution is now a serious environmental concern and public interest regarding this issue has been increasing (Harikumar and Jisha, 2010). Research efforts have focused primarily on salt marshes, estuaries and coastal environments since these highly productive and sensitive areas are often directly and most seriously affected and exposed to this problem because of their proximity to sources of pollution (Arellano *et al*., 1999; Huh and Chen, 1999). Nevertheless, in recent years effluent discharges have been reduced considerably and the main concern has therefore shifted from the impact of direct loading to possible effects of contaminants in the sediment caused by these discharges (Berge and Brevik, 1996).

Trace element of natural and/or anthropogenic origin is transported by rivers and transferred to the coastal marine system through the estuaries (Regnier and Wollast, 1993). MTEs enter the coastal environments and oceans by two means: natural processes (including erosion of ore–bearing rocks, wind–blown dust, volcanic activity and forest fires); and processes derived from human activities by means of atmospheric deposition, rivers, and direct discharges or dumping (Clark *et al*., 1998). There, MTEs are distributed between the dissolved and particulate phase, while their fate and bioavailability strongly depends on the particle chemistry and competition between surface and dissolved forms in terms of complication processes (Poikāne *et al*., 2005). Therefore, the estuaries constitute a natural reactor in which heterogeneous processes at the interface between dissolved phase and suspended particulate matter constitute an important part of the MTEs geochemical cycle (Zhou *et al*., 2003; Landajo *et al*., 2004; Morillo *et al*., 2005).

Marine aquatic organisms can accumulate MTEs from various sources in their surrounding environment. The possible sources these MTEs include sediments and soils erosion (Labonne *et al*., 2001; Goodwin *et al*., 2003), air depositions of dust and aerosol (Gelinas and Schmit, 1997; Labonne *et al*., 2001), discharges of wastewater (Labonne *et al*., 2001; Goodwin *et al*., 2003), and so on (Blackmore *et al*., 1998; Hoven *et al*., 1999; Goodwin *et al*., 2003). The accumulation of MTEs in marine aquatic organisms can pose a long–term burden on biogeochemical cycling in the ecosphere (Ip *et al*., 2005). Once the MTEs enter the food chain, they may accumulate to dangerous levels and be harmful to human health (Manahan, 2000).

MTEs accumulation in marine aquatic organisms depended on several factors, including the environmental concentrations of MTEs in water and sediments; the species of organisms; body size and age of the marine organisms. Different concentrations of MTEs can also be found in different organs (stomach, gill, muscle, tissue) in the same biological sample. However, this study mainly focused on the general MTEs burden in mollusc species (oyster), and the potential major pathways for MTEs contaminant in the coastal environment.

1.4.1 Metallic trace elements pollution in marine environment

Pollution is a negative outcome of rapid development and industrialization. Coastal areas adjacent to metropolitan areas have been strongly polluted by domestic wastewater, factory disposal and other sources, and anthropogenic impacts have seriously influenced the whole marine ecosystem. The distribution of MTEs in sediments adjacent to settlement areas can provide researchers with evidence of the anthropogenic impact on ecosystems and, therefore, aid in assessing the risks associated with discharge human waste (Demirak *et al*., 2006). Sediment MTEs data can be used to uncover the pollution history of aquatic system, because they are widely available and more reliable than the dissolved MTEs concentration in a marine aquatic system (Valdés *et al*., 2005).

Marine sediments can act as a scavenger agent for MTEs and behave as an adsorptive sink in the marine aquatic environment. It is therefore considered to be an appropriate indicator of monitoring the MTEs pollution. MTEs can accumulate in marine sediment from both natural and anthropogenic sources occur in the same manner (Hamed and Emara, 2006), and this makes it difficult to identify and determine the origin of MTEs present in the sediments. In order to overcome this obstacle, it has been proposed to adopt the granulometric normalization method. This method implies the separation of sediment particles into different size fractions (Luoma and Bryan, 1981; Sakai *et al*., 1986; Horowitz *et al*., 1990; Szefer *et al*., 1995). The rationale behind this approach is that MTEs from anthropogenic sources mostly concentrates in the fine grain–size fraction because the larger surface area of the fine grains results in higher cation exchange capacity and subsequent metal adsorption (Yeasts and Bewers, 1982; Horowitz and Elrick, 1986). The very fine sediment, silt/clay fraction in particular grain–size less than 63 μm and is considered the most geochemically active fraction of sediment particles. Therefore, these particles are eminently suitable to gauge potential pollution of sediment by MTEs.

In addition, the spatial distribution of MTEs in marine sediments is impacted by natural and anthropogenic factors, such as parent rock weathering, industrial wastewater, transportation, agriculture and climate (Morillo *et al.*, 2004; El Nemr *et al.*, 2006; Luo *et al.*, 2006). It is essential to distinguish between natural and human impacts on MTEs in marine sediments. An index of geoaccumulation, enrichment factor and pollution load index calculations have been applied to indicate the degree of contamination by MTEs from lithogenic and anthropogenic sources (Rubio *et al.*, 2001; Simeonov *et al.*, 2001; Santos *et al.*, 2005; El Nemr *et al.*, 2006).

In a stable state, MTEs concentration in seawater is very low. According to Perkins *et al.* (1973), these elements can be divided into four major groups according to their pollution potential (*Figure 1–2*):

(a)	Very high pollution potential	Ag, As, Cd, Cr, Cu, Hg, Pb, Sb, Sn, Te, Zn
(b)	High pollution potential	Ba, Bi, Ca, Fe, Mn, Mo, Ti, U
(c)	Moderate pollution potential	Ai, Au, B, Be, Br, Cl, Co, F, Ge, K, Li, Na, Ni
(d)	Low pollution potential	Ga, I, La, Mg, Nb, Si, Sr, Ta, Zr

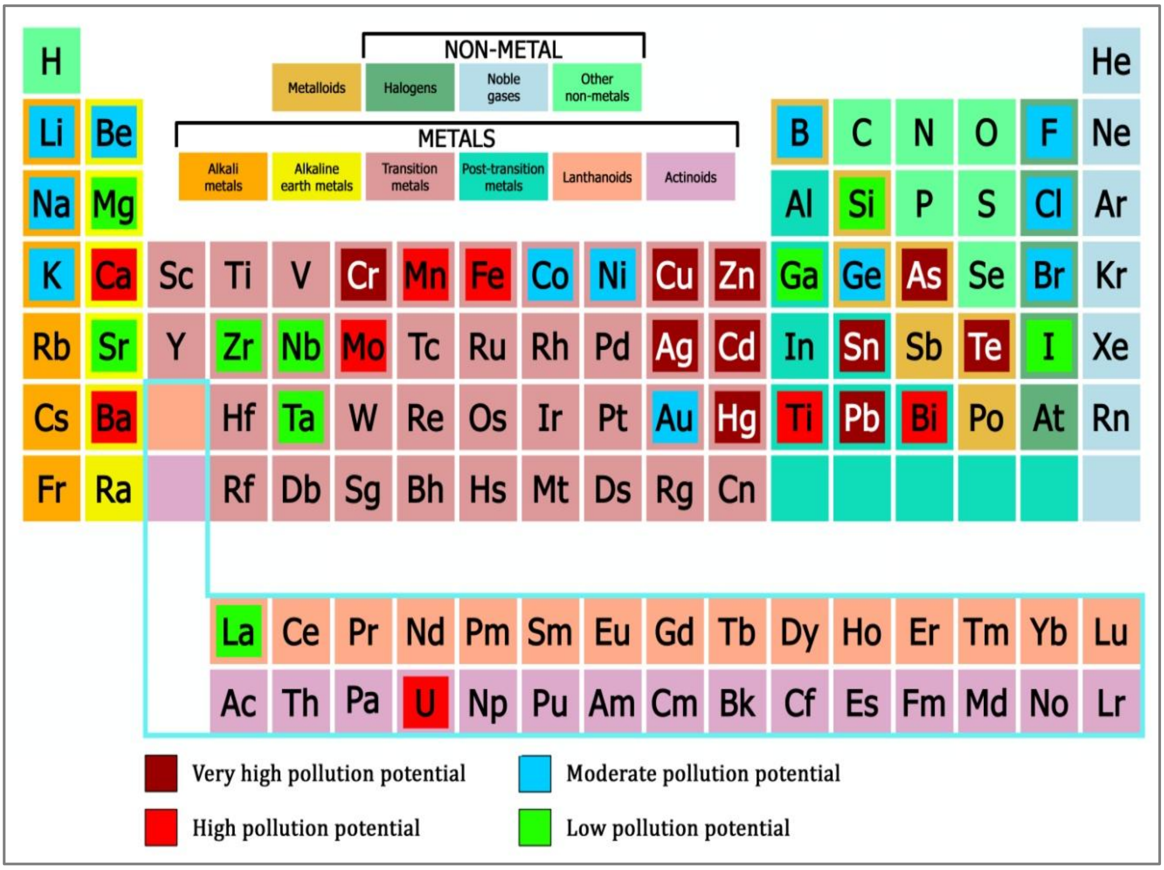

Figure 1–2. *Periodic table of chemical elements which indicate the different pollution potential in an environment.*

1.4.2 Source of metallic trace elements in marine environment

MTEs that enter the aquatic environment can become associated with fine grained particulates, after which they settle and accumulate in the sediments (Murray *et al*. 1999). These contaminated sediments then serve as a contaminant pool that can release the MTEs to the overlying water via natural or anthropogenic processes, thereby posing a potential risk to the health of the marine ecosystems (Dickinson *et al*. 1996). When MTEs are released into the marine environment, they are soon transferred to the surface sediments phase by adsorption on the surface of suspended particulate matter and eventually settle as sediment (Hatji *et al*. 2002). Therefore, sediments are both carriers of MTEs and potential pollution sources in the marine aquatic systems.

MTEs found in coastal sediments may be derived from a variety of natural and anthropogenic sources (Burridge *et al*. 1999). Entry may be a result of direct discharges into both freshwater and marine ecosystems or through indirect routes such as dry and wet deposition and land run–off. Important natural sources are volcanic activity, continental weathering and forest fires. The contribution from volcanoes may occur as large but sporadic emissions due to explosive volcanic activity or as other low continuous emissions, including geothermal activity and magma degassing (Crowe *et al*., 1987; Halmer *et al*., 2002).

In most circumstances, the major part of the MTEs compound in the water and the seabed sediments is anthropogenic and associated with terrestrial sources related to untreated municipal sewage (Shear *et al*. 1996; Isaac *et al*. 1997), industrial wastewaters (Majori *et al*. 1978), intensive aquaculture (Tovar *et al*. 2000), harbour activities (Tanner *et al*. 2000) as well as riverine fluxes loaded with urban and agricultural runoff (Pope *et al*. 1978; Granier *et al*. 1990). However, rivers flowing through urban areas, may bring the pollutants to the downstream estuarine sediments, from where they are incorporated in the mudbank cycle. This process may result downstream such as estuary ecosystem in higher concentrations in MTEs.

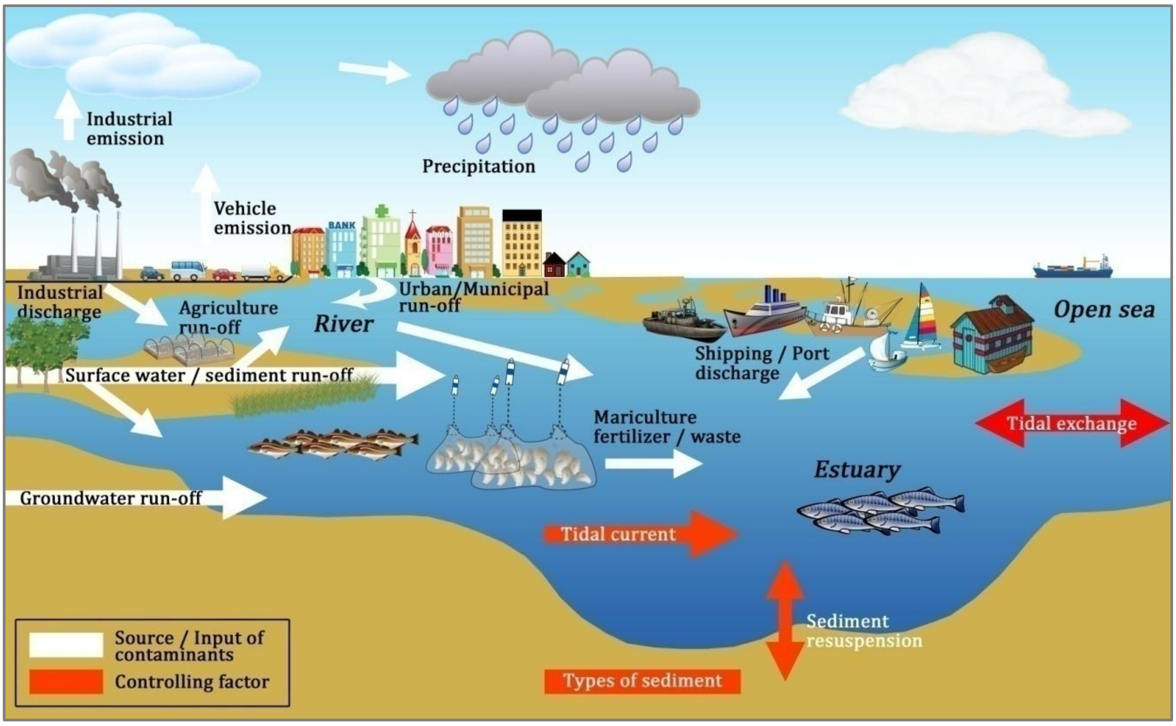

Figure 1–3. *Sources and factors controlling metallic trace elements contaminant of the aquatic environment.*

1.4.3 Marine sediments as a marker for metallic trace elements pollution study

Marine sediments play a key role in the geochemical and biological processes of an estuarine ecosystem. In particular, these sediments act as sinks for toxic metals that enter the estuary. In doing so, they regulate the concentration of these minerals and compounds in the water column (de Groot *et al*. 1976). Marine sediment also plays a very important role in the physicochemical and ecological dynamics of MTEs in marine aquatic ecosystems. The physicochemical nature of sediment bound MTE is important in the bioaccumulation of aquatic organisms.

Sediment quality has been recognized as an important and sensitive indicator or geo–marker of environmental pollution (Larsen and Jensen, 1989; Pekey *et al*., 2004) since sediments are the main sink for various pollutants, including MTEs compound discharged into the environment (Williams *et al*., 1996; Balls *et al*., 1997; Dassenakis *et al*., 1997; Tam and Wong, 2000; Bettinetti *et al*., 2003). Sediments also play a significant role in the remobilization of contaminants in marine aquatic systems under favourable conditions and in interactions between water and surface sediments. Comprehensive methods for identifying and assessing the severity of sediment contamination have been introduced in order to protect the marine aquatic life community (van de Guchte, 1992; Chapman, 2000).

Most MTEs are bound in the fine–grained fraction (<63 μm) mostly because of its high surface area–to–grain size ratio and humic substance content (Horowitz and Elrick, 1987; Moore *et al.*, 1989) where they have a potentially greater biological availability than those in the larger (2 mm – 63 μm) sediment fraction (Brayan and Langston, 1992; Everaat and Fischer, 1992). MTEs may be mobilised as a result of natural processes such as weathering and erosion of geological formation. In the mobilisation process, these elements may be absorbed by clays, can complex with organic compounds or co–precipitate with oxide and hydroxides.

Because of their large adsorption capabilities, fine–grained sediments represent a major repository for MTEs and a record of the temporal changes in contamination. Thus, they can be used for historical reconstruction. As many MTEs occurs naturally in weathered materials and drainage systems due to their presence in local rocks, the relative influence of natural and anthropogenic sources on the geochemistry of coastal sediments is not always clear. Therefore, for a better assessment of MTEs distributions within such environments, it is important to distinguish between metallic elements released by natural processes and those introduced by human–related activities.

1.5 Bio–monitor of metallic trace elements assessment

Individual bio–monitors respond differently to different sources of bioavailable chemical elements for example, in the solution, in sediments or in foods. To gain a complete picture of total MTEs bioavailability in a marine habitat it is necessary, therefore, to use a correct bio–monitor that can reflect the element bioavailability in all available sources (Phillips, 1990). Such comparative use of different bio–monitors should allow identification of the particular source of the contaminant elements (Rainbow, 1997).

Ideally, species to be chosen as bio–monitors should fulfil several criteria (Bryan *et al*., 1980; Phillips and Rainbow, 1993). Ideal bio–monitors should be sedentary, easy to identify, abundant, long lived, available for sampling throughout the year, large enough to provide sufficient tissue for (individual) analysis, resistant to handling stress caused by laboratory studies of metal kinetics and/or field transplantations, tolerant of exposure to environmental variations in physico–chemical parameters such as salinity, and net accumulators of the metal in question with a simple correlation between metal concentration in tissues (body) and average ambient bioavailable metal concentration over a recent time period (Butler *et al*., 1971). Not all marine organisms fulfil these criteria, nor indeed do all species commonly employed as bio–monitors fulfil all the criteria. Most critically, a bio–monitor should be a net accumulator of the relevant chemical elements, preferably a strong net accumulator thus minimizing any danger of significant contamination of a sample during laboratory handling.

Marine organisms fall along a gradient of MTEs accumulation strategies or patterns from body concentration regulators (maintaining a constant body concentration of chemical elements across a wide range of ambient element availabilities), through partial regulators, weak net accumulators to strong net accumulators (Rainbow and White, 1989; Depledge and Rainbow, 1990; Rainbow *et al*., 1990; Phillips and Rainbow, 1993). There is some objection to the term 'accumulation strategy' for there may be implications of teleology and/or anthromorphism in the use of the term; such accumulation patterns are still nevertheless under natural selection. Similarly the term 'regulator' can be criticized (Depledge and Rainbow, 1990), for it is difficult to imagine a physiological feedback process controlling body and MTE concentrations. Such physiological homeostasis is familiar and can be envisaged at a tissue level and therefore the organ level. It follows, nevertheless, that if tissue concentrations of trace metals are regulated (albeit at different levels) throughout an animal, the overall effect will be the regulation of whole body concentrations within relatively narrow limits as the contribution of different tissues to total body weight might vary. It is important to know the MTEs accumulation pattern of a chosen bio–monitor, incorporating an understanding of MTE kinetics including rates of uptake and loss into and from the body. This allows definition of the period over which the bio–monitor reflects the ambient MTE bioavailability.

1.5.1 Choice of bio–monitors for environmental study

Living organisms can transport pollutants and contaminants into, within, and out of the marine aquatic ecosystem. These organisms can ingest the pollutants via water and food, and inhale them as they breathe and feeding (Blais *et al*., 2007). Once in the body, some contaminants pass quickly while others can be retained for long periods and accumulate in body tissues, particularly fatty tissues (Erickson *et al*., 2008). Some of the chemical elements that show the greatest bioaccumulation are those that do not dissolve in water, but instead dissolve in fats and oils (i.e., mercury and PCBs). In some cases, the accumulation of pollutants is intensified in carnivorous animals high in the food chain, ranging from big organism such as fishes and to human (Liu and He, 1987).

The choice of a suitable bio–monitor needs to consider the potential sources of MTEs to the biota. Seagrass not in contact with sediments will take up MTEs from dissolved sources only (Phillips, 1990). Suspension feeders take up MTEs both directly from seawater and from the suspended particles collected during feeding. Thus, mussels, oysters and barnacles are all candidates as suspension feeding bio–monitors, and a careful choice will differentiate between suspended particles of different size ranges. As a generalization, sessile barnacles, but not stalked barnacles, have evolved microfeeding, using the first thoracic legs to filter small suspended particles which would pass through the setae of the expanded cirral net formed by the more posterior thoracic legs (Crisp and Southward, 1961; Anderson, 1999).

Deposit feeding bivalves will reflect the bioavailability of MTEs in the surrounding water via respiratory currents, but also MTEs bioavailability in newly deposited particles, for they suck up such particles via the inhalant siphon during feeding (Bryan *et al*., 1985). Some bivalves are protected by the shell from contact with the interstitial water of the sediment, a protection not offered, for example, to a sediment burrowing polychaete, the soft epidermis of which may be bathed directly by interstitial water with a redox potential possibly very different from that of the overlying water (Rainbow, 1995).

1.6 Assessment of pollution levels

The absolute concentration of MTEs in marine sediments never indicates the degree of contamination coming from either natural or anthropogenic sources because of grain–sizes distribution and mineralogy (Tam and Yao, 1998; Rubio *et al*., 2000; Liu *et al*., 2003). Normalization of MTE concentrations to grain sizes, specific surface area and reactive surface phases such as Li and Al is a common technique to remove artefacts in the data due to differences in depositional environments (Daskalaskis and O'Connor, 1995; Balls *et al*., 1997; Cobelo–Garcìa and Prego, 2004; Santos *et al*., 2005; El Nemr *et al*., 2006). This allows for a direct comparison to be made between contaminant levels of samples taken from different locations. One of the most common normalization techniques is converting trace metal concentrations to enrichment factors (EF) by normalizing metals concentrations to a common element (usually Al or Fe) and index of geoaccumulation (*I*geo) or comparing the normalized concentration to average crustal abundance data (Summer *et al*., 1996; Schiff and Weisberg, 1999 Tanner *et al*., 2000; van der Weijden, 2002; Cobelo–Garcìa and Prego, 2003; El Nemr *et al*., 2007).

To evaluate the MTEs contamination of Quiberon bay and gulf of Morbihan sediments, determined element concentrations were compared with either quality objectives (Gruiz *et al*., 1998; Tarras–Wahlberg *et al*., 2001) or background concentrations (Irabien and Velasco, 1997; Celo *et al*., 1999; Harland *et al*., 2000;

Howari and Banat, 2001). In some cases case, sediment cores or sediments from pristine, non–industrialized regions were analyzed (Kehrig *et al*., 2003; Corredeira *et al*., 2008; Gong *et al*., 2008; Ho *et al*., 2010; Larrose *et al*., 2010, Masoud *et al*., 2011; Strady *et al*., 2011) or literature data on average world shale concentrations of elements (Lopez–Sanchez *et al*., 1996; Jones and Turki, 1997; Sanchez *et al*., 1998; Datta and Subramanian, 1998; Loska and Wiechula, 2003; Cevik *et al*., 2009; Nobi *et al*., 2010) were used to establish an unpolluted MTEs level for suspended solids and sediments.

1.7 Ecological risk assessment by sediment quality guidelines

Over the last two decades a considerable amount of research effort has been put into investigating sediment toxic threshold levels (Long and Morgan, 1990; MacDonald *et al*., 1992; Long *et al*., 1995; Smith *et al*., 1996). As a result there are now a number of international guidelines relating to toxic concentrations as determined by field and laboratory data. The work of Long *et al*. (1995) on sediment quality guidelines (SQGs) provide a useful tool for screening sediment chemical data to identify pollutants of concern and priorities problem sites (Birch and Taylor, 2006). Long *et al*. (1995) defines ranges of chemical concentrations found in bulk estuarine sediments based on toxicity levels estimated from experimental laboratory studies and field observations and measurements. The results of this work provide estimates of two contaminant levels that are likely to produce adverse biological effects in 10 % and 50 % of biota populations.

Using this approach, Long *et al*. (1995) classified the toxicity of contaminants into effect range low (ERL) and effect range median (ERM) concentrations. ERL indicates that below this level, a chemical element or compound is considered to be of low or minimal concern, since adverse effects on organisms are infrequently observed (i.e. in <10 % of biota) when the concentration falls below the ERL value. ERM indicate that at and above this level harmful effects are likely to be observed in 50 % or more of the biota population and this concentration is considered to be toxic and of significant concern. Concentrations between the ERL and ERM values represent an intermediate range within which effects occur in 10–50 % of biota populations.

The development and implementation of SQGs reflect the recognition by regulatory authorities of the importance of contaminated sediments as a possible cause for adverse environmental effects. SQGs are tools to aid the interpretation through the comparison with sediment contaminant concentrations. One of the numerous SQGs types, the National Oceanic Atmospheric Administration (NOAA) SQG for the biological effect of MTE concentrations were developed from a chemical and biological effects database, BEDS (Long *et al*., 1995) and classify the metal concentrations relative to ERL and ERM, representing the 10th and 50th percentiles of the dataset for each component. However, the boundaries that define concentrations at which adverse biological effects can occur are based upon strictly empirical arguments since chemical measurement do not directly correspond to sediment toxicity (O'Connor and Paul, 2000).

1.8 Radionuclide

Fallout radionuclide (^{137}Cs, ^{210}Pb, ^{230}Th) has been used with success to investigate lacustrine and floodplain sedimentation (Robbins and Edgington, 1975; Walling and He, 1999) and soil erosion processes (Branca and Voltaggio, 1993; Zhang *et al*., 1998). Lithogenic radionuclide in the ^{238}U and ^{232}Th decay series have also been used to address a range of problems in geology and geomorphology, including provenance determination of coastal sediment; resolution of sedimentation rates of fluvial sands (Murray *et al*., 1995) and resolving fluvial sediment sources (Yeager and Santschi., 2003). These radionuclide have been used solely (Olley *et al*., 1990) and together with fallout radionuclide (He and Owens, 1995) to address fluvial sources and transport questions.

1.8.1 Lead–210

Lead–210 (^{210}Pb) is one of the radionuclide natural occurs in environment from decay of ^{238}U series (*Figure 1–4*). It utilized the accumulation of ^{210}Pb from the decay of ^{232}Rn ($T_{1/2}$ = 3.8 days) in the air (Cochran *et al.*, 1998). ^{210}Pb have half–life 22.3 years and it decays to ^{210}Bi with beta rays in energy, E_{max} = 0.018 MeV. As ^{232}Rn decays, its daughter products settle all over the Earth's surface, quickly decaying to ^{210}Pb. Once other sediment covers a layer of sediment, it is no longer exposed to the settling of these daughter products and ceases to accumulate ^{210}Pb from the air (Nozaki and Tsunogai, 1973). A measurement of the amount of ^{210}Pb remaining in the sample can give the sediment age. The more ^{210}Pb there is, the younger the age.

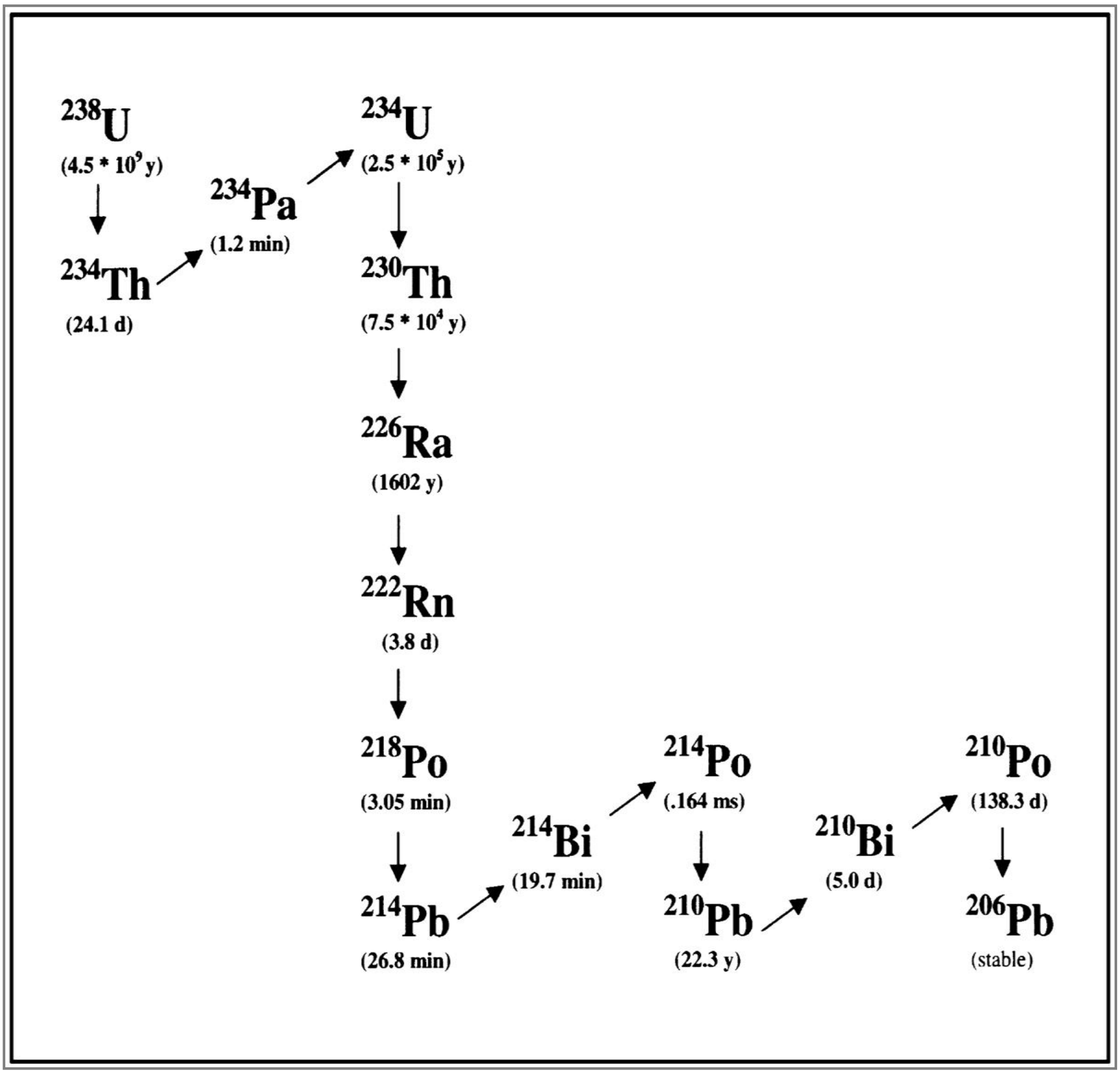

Figure 1–4. *^{210}Pb from ^{238}U decay series.*

Secondary source for ^{210}Pb in column water is from in–situ disintegration of ^{226}Ra into the gas ^{226}Rn, which in turn decays through a series of isotopes to ^{210}Pb. The ^{210}Pb derived from radium ("supported" ^{210}Pb) assumed to be in equilibrium with ^{226}Ra. A portion of the radon formed in the soil escapes into the atmosphere where it decays into ^{210}Pb. This Pb when added back to the earth's surface becomes the "excess" or "unsupported" component that used in sediment dating. It decays exponentially with time in accordance with the half–life of ^{210}Pb. The "supported" Pb can be estimated by assaying ^{226}Ra, or by determining background levels at depth; the "unsupported" ^{210}Pb is determined by subtraction of supported Pb from total ^{210}Pb (Oldfield and Appleby, 1984).

While the sediment no longer accumulates ^{210}Pb from the air once it has been covered, it continues to accumulate ^{210}Pb from the decay of ^{238}U that is everywhere in the rock itself. Thus, a distinction must be drawn between ^{210}Pb from the rock, or supported ^{210}Pb, and that from the air, unsupported ^{210}Pb. In can measure ^{214}Bi as an indicator of supported ^{210}Pb, because it appear before ^{210}Pb in the decay chain and has a very short half–life (about 20 minutes). Any ^{214}Bi in the sample therefore comes from the rock itself, and a measurement can give the amount of supported ^{210}Pb.

^{210}Pb dating is a relatively new and very useful method in radiolimnology. Core chronologies using ^{210}Pb analysis was first suggested by Goldberg (1963) and was first applied to lake sediments by Krishnaswamy *et al*. (1971). It has been applied successfully to sediments from lagoons, estuaries and coastal environments with sedimentation rates ranging from mm/y to cm/y. Lake, mangrove, lagoon and estuarine sediments are favorable for the use of the ^{210}Pb dating method as ^{210}Pb is concentrated in a stratified manner and then decays at a known rate.

^{210}Pb may reach these sediments in two forms, a 'supported' component and an 'unsupported' (or excess) component. A 'supported' component derived directly from eroded soil in the estuary's catchments. 'Supported' ^{210}Pb has not been in the atmosphere and emanates from its parent isotope, ^{226}Ra, which is present in the eroded sediment (Hakanson and Jansson, 1983). An 'unsupported' component from the atmosphere deposited either directly onto the estuarine surface or deposited within the estuary's catchments and reaching the estuary via the drainage network (Oldfield and Appleby, 1984).

To determine sedimentation rate using ^{210}Pb both total ^{210}Pb and 'supported' ^{210}Pb activity must be established. Total ^{210}Pb activity is therefore determined indirectly by measurement of its alpha–emitting grand–daughter nuclide, ^{210}Po (Beks, 1998). Measurement of ^{226}Ra activity will provide an adequate figure of 'supported' ^{210}Pb, as these two elements are assumed to be in equilibrium (Gale *et al*., 1995). Subtracting of 'supported' ^{210}Pb will determine 'unsupported' ^{210}Pb (Hakanson and Jansson, 1983).

1.9 Geographical information system application

Nowadays, the rapid developments of computer technology, geographical information system (GIS) are receiving increasing interest in environmental geochemistry study (Munafò *et al*., 2005; Schaffner *et al*., 2009). It is becoming increasingly popular to incorporate digitized and computerized technologies in studies of marine environmental pollution. These technologies may include GIS and global positioning system (GPS) in the interpretation and presentation of data and in geochemical modelling (*Figure 1–5*).

Thus, there have been few studies that have made use of GIS to graphically and digitally present the distribution of MTEs in marine environments (O'Regan, 1996). The spatial interpolation methods of geometrical interpolation, trend surface analysis and Kriging method are commonly used (Davis *et al*., 2009). These base chemometric approach was applied to investigate the spatial distribution patterns of MTEs in marine sediment and to identify spatial human impacts on global and local scale (Nasr *et al*., 1997; Zhou *et al*., 2007a; Zhou *et al*., 2007b; Poggio *et al*., 2009).

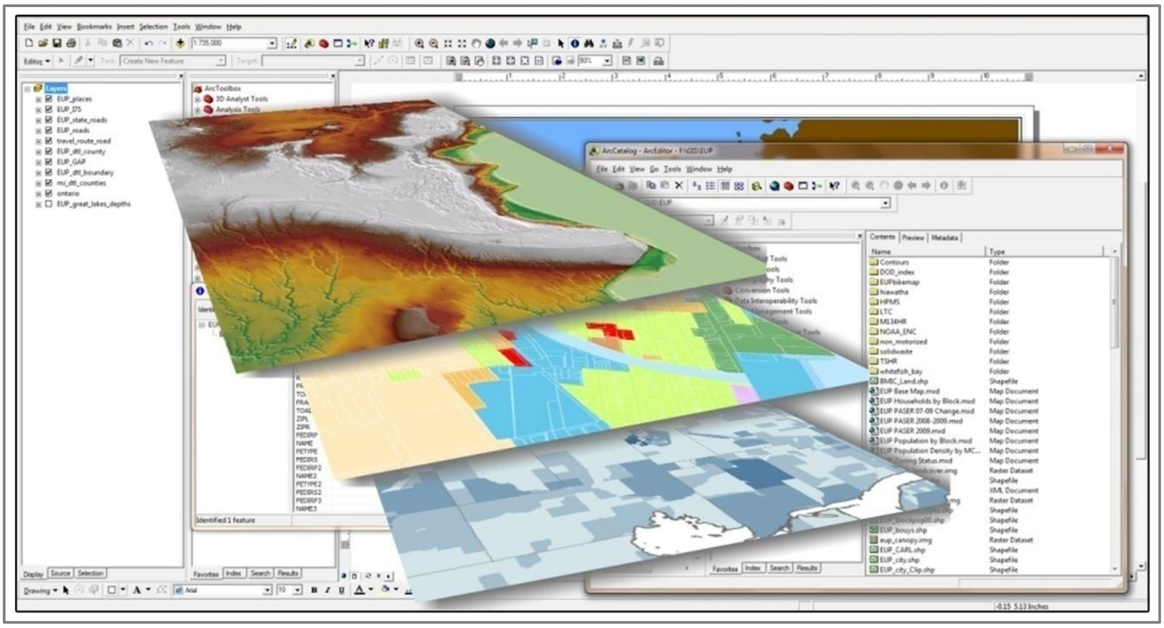

Figure 1–5. *GIS application of ArcGIS software for environmental geochemistry studies.*

GIS is a tool for decision making, using information stored in a geographical form. Some researcher defined major requirements and function of GIS and mentioned spatial data handling tool for solving complex geographical problems (Bloemer *et al*., 1986; Carrara, 1989; Langran, 1989). Besides, GIS is increasingly used in environmental pollution studies because of its ability in spatial analysis and interpolation, and spatial interpolation utilizes measured points with known values to estimate an unknown value and to visualize the spatial patterns (Facchinelli *et al*., 2001; Wang, 2006). On the regional and national scales, the geochemical mapping of MTEs can be used as a tool for visualization which enhanced by computer–aided modelling using GIS to make it easier to identify the possible locations of contaminated area. At present, joint using of GIS and chemometric approach mainly focuses on river estuary (Yin *et al*., 2004), soil (Lee *et al*., 2006; Zhang, 2006) and non–point source identification (Corwin and Wagenet, 1996; Chowdary *et al*., 2005).

CHAPTER 2

MATERIALS AND METHODS

2.1 Description of study area – South Brittany waters

The fine–sediment fluxes from the remaining small rivers of south Brittany are poorly known but fluxes can be estimated to be very low (Sorrel *et al*., 2010). According to Proust *et al*. (2001), the sediment filling of incised valleys in southern Brittany is generally composed of two sedimentary sequences. The basal sequence appears to correspond to braided–river sediments deposited during Saalian and/or Elsterian sea–level lowstands, or even older (Menier *et al*., 2006). This basal sequence is capped by a second depositional sequence related to meandering and estuarine fluvial environments, of unknown age, evolving later into open marine facies. Therefore, it seems that incised valleys of south Brittany waters are characterized by a compound infilling whose preservation is interpreted as resulting from recent tectonic reactivation of the South Armorican block (Proust *et al*., 2001).

South Brittany waters have experienced a very low average rate of subsidence over the last 40 Ma, and, except over short periods, the shoreline might have remained at its present–day location (Guillocheau *et al*., 2003). The rivers in this area have a graded depositional profile (Bonnet *et al*., 2000). They supply a small amount of sediment to the shelf which is mostly by passed to the outer shelf margin and deep sea during lowstands.

In this region, the tide is semi–diurnal with a mean spring tidal range of 4.5 m. Associated tidal currents are weak (maximum: 0.25–0.4 m/s during spring tides) and strongly gyratory on the continental shelf (S.H.O.M., 1993). However, they become much stronger in the vicinity of the coasts and especially in the passages between the Quiberon peninsula and neighboring Houat and Hoëdic islands, and are amplified in shallower water depths (Pinot, 1974; Vanney, 1977). Hence, during mean spring tide at the passage of la Teignouse, the current reaches a velocity of 0.9 m/s at flood and 1 m/s at ebb tides (S.H.O.M., 1990).

Many areas along the coast are used as recreation areas by the public. A numbers of port for shipping as for recreational purposes and fishing activities are located in this region. Furthermore, surrounding coast is successfully used for commercial shellfish (oyster and mussel) mariculture activities with a significant market around this region (*Figure 2–1*).

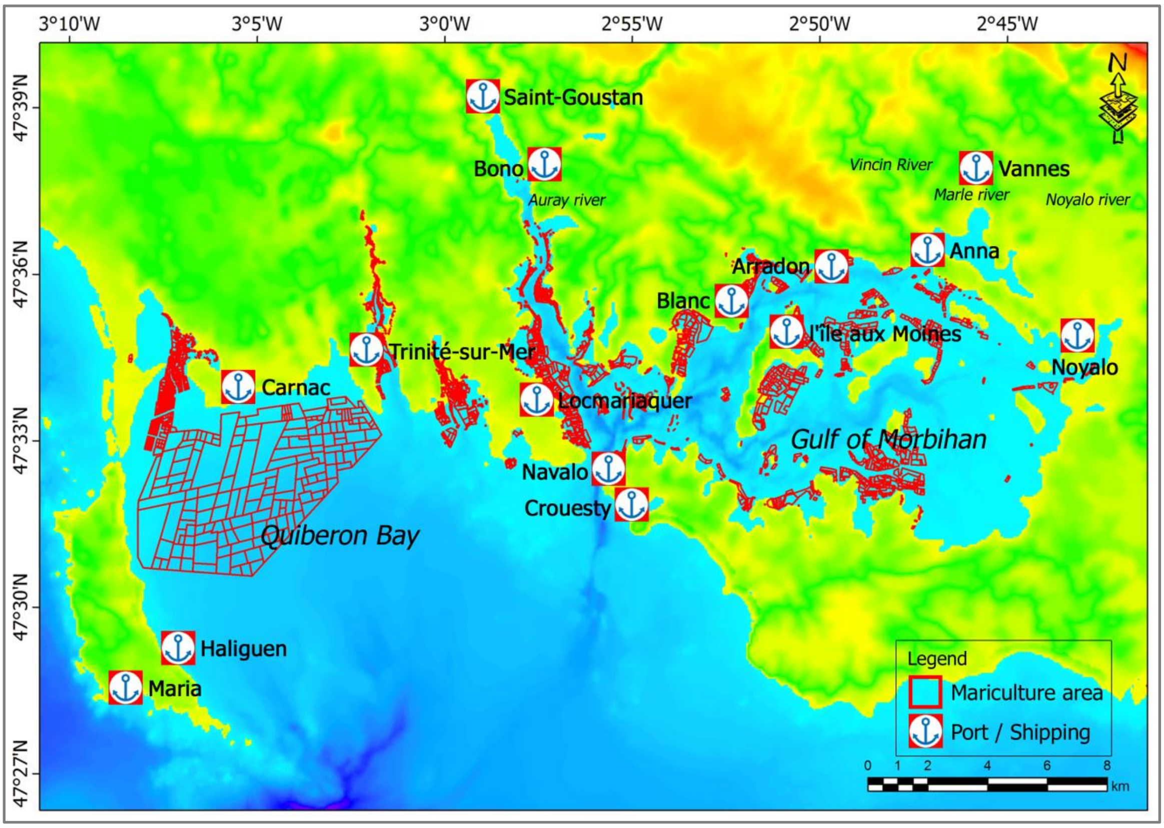

Figure 2–1. *Mariculture and shipping activities in south Brittany waters.*

2.1.1 Study area 1 – Quiberon bay

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 km^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 peninsula of Quiberon provides protection from the Atlantic Ocean to the west (Proust *et al.*, 2001; Chaumillon *et al.*, 2008). The Belle, Houat and Hœdic islands add to the bay's protection (Guillaud *et al.*, 2008).

Sediment facies in the Quiberon bay is primarily sandy fraction. Grain–sizes and chemical analyses of the deposits reveal two sectors within the bay (Vanney, 1977). One sector is located west of the longitude of Houat Island, where the muddy sediment supply is associated with abundant quantities of sands with shell fragment. Sand–dominated raised areas border channels that are richer in mud. The seafloor becomes more regular towards the east, forming the muddy floor of Houat Island.

In order to have a better understanding about the geochemistry distribution, Quiberon bay was divided into six zones of study (*Figure 2–2*) based on criteria such as geographical location, geomorphology and hydrography characteristics. Five zones are located within the bay area and one zone from Crac'h river run–off area. Descriptions of each zone are shown in *Table 2–1*.

Table 2–1. *Sampling zone in Quiberon bay and its description.*

Zone	Mean depth	Sediment types	Physical characteristic
Southern (A)	8 m	Mixed sediments (sand dominated)	▪ Very strong water current and tidal wave Outer bay
Western (B)	6 m	Mixed sediments (sand dominated)	▪ Moderate water current and tidal wave Outer bay
Centre (C)	10 m	Mixed sediments (sand and mud)	▪ Strong water current and tidal wave
Eastern (D)	9 m	Mixed sediments (sand dominated)	▪ Very strong water current and tidal wav Inner bay
Northern (E)	5 m	Sandy sediments	▪ Weak water current and tidal wave Inner bay
Trinité–sur–Mer (F)	3 m	Muddy sediments	▪ Very weak water current and tidal wave

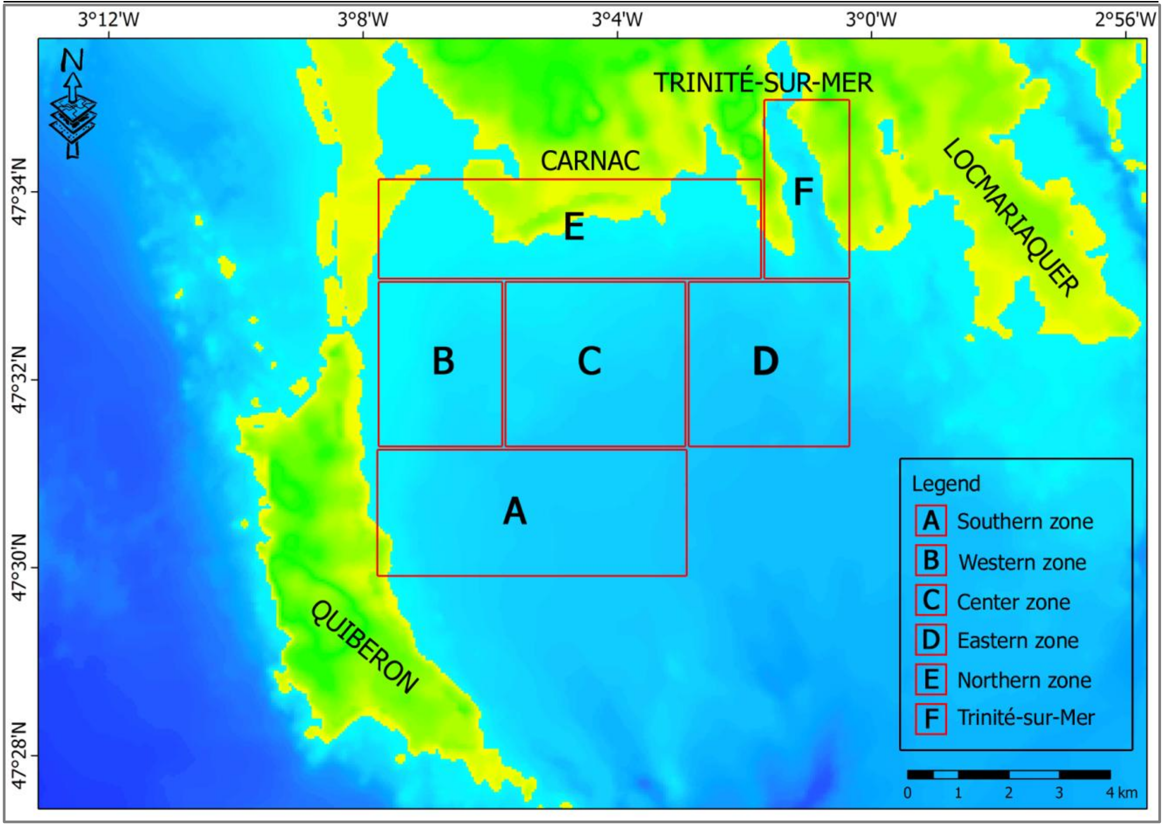

Figure 2–2. *Division in zone of study (A–F) in Quiberon bay.*

2.1.2 Study area 2 – Gulf of Morbihan

Gulf of Morbihan ("Mor–bihan" = "little sea" in Breton) is a natural harbor located in South Brittany, in the north of the Loire river, northwest France. It is a close sea body (11 500 ha) and a shoreline of 250 km (Menier *et al.*, 2011). It is a shallow basin with a maximum water depth value of 30 m and is connected to the sea by a 900 m wide and 30 m deep tidal inlet at Port Novalo (Rossi *et al.*, 2011). *Institut Géographique National* recorded that there are 37 islands located in the gulf where the two largest islands are the Moine Island and Arz Island. 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 fresh water input from Auray, La Marle and Noyalo rivers. The further from the entrance, the lower tidal range; 3 m at the eastern zone, 4 m at the center zone and 5 m at the gulf entrance. Hence, tides are hypersynchronous, a characteristic feature of tide–dominated environments (Dalrymple and Choi, 2006), while the attenuation of the tidal pause is due to the local geomorphology itself (Marcaillou *et al*., 1996).

Similar to that described in the Quiberon bay sampling area, gulf of Morbihan is also divided into several zones of study. Due to the different and complex topography, this study area is divided into 8 zones (*Figure 2–3*); where one zone for the entrance of the gulf area, three zones for each river (Auray, Marle and Noyalo rivers) and four zones within the gulf area. Descriptions of each zone are shown in *Table 2–2*.

Table 2–2. *Sampling zone in gulf of Morbihan and its description.*

Zone	Mean depth	Sediment types	Physical characteristic
Gulf entrance (A)	10 m	Sandy sediments and rocky	▪ Very high hydrodynamic process and wave action Entrance of the gulf
Auray river (B)	5 m	Mixed sediments (mud dominated)	▪ High hydrodynamic process and wave action at downstream; Hydrodynamic process decreasing towards the upstream
Marle river (C)	3 m	Muddy sediments	▪ Very low hydrodynamic process and wave action River pass through Vannes city
Noyalo river (D)	2 m	Muddy sediments	▪ Very low hydrodynamic process and wave action
Western (E)	8 m	Sandy sediments	▪ High hydrodynamic process and wave action
Northern (F)	6 m	Mixed sediments (sand dominated)	▪ Moderate hydrodynamic process and wave action
Southern (G)	5 m	Mixed sediments (sand dominated)	▪ Moderate hydrodynamic process and wave action
Eastern (H)	3 m	Muddy sediments	▪ Low hydrodynamic process and wave action Innermost gulf

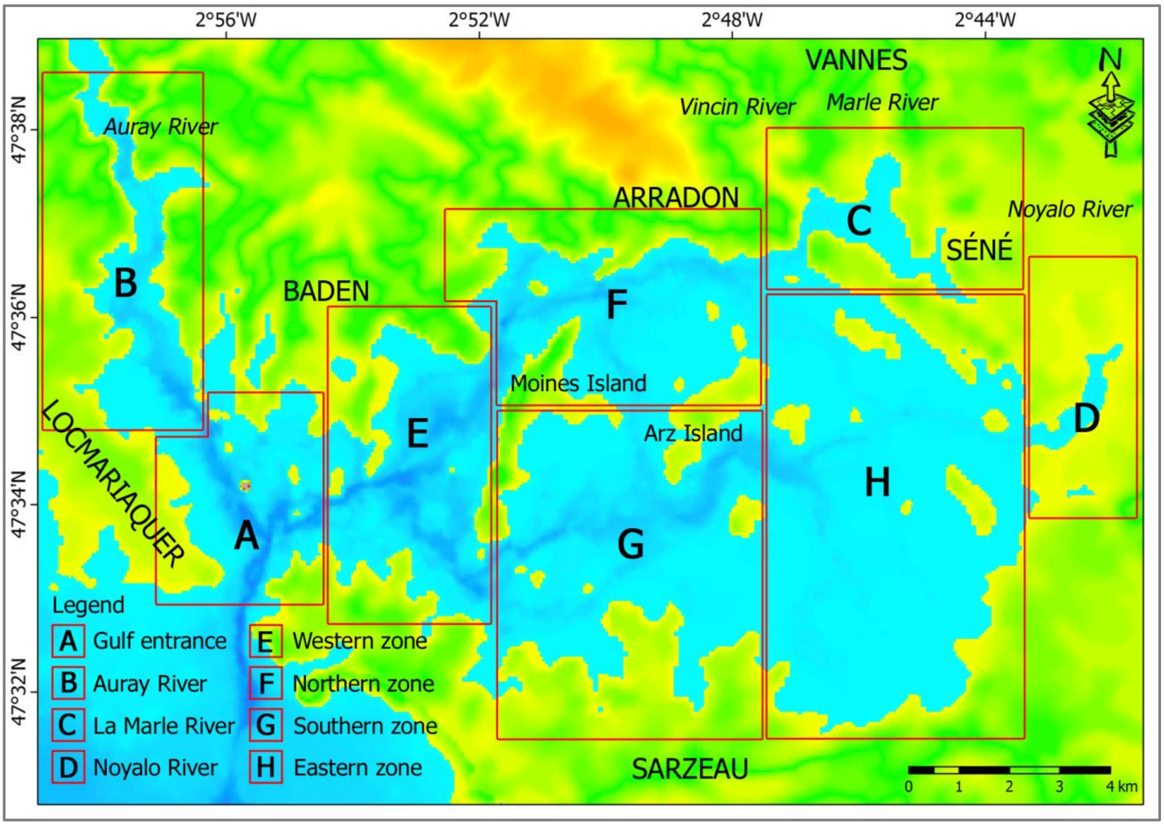

Figure 2–3. *Division in zone of study (A–H) in gulf of Morbihan.*

2.2 Sampling methodology

2.2.1 Surficial sediments collection

The sampling locations, symbols map with the sampling locations and distribution maps were prepared with the aid of geographical information system (GIS). Geographic coordinates of sampling sites were recorded by the aid of a global positioning system (GPS) derived from the boat and cross check with a handheld GPS.

In this study, two sampling periods were completed both in the Quiberon bay and gulf of Morbihan during winter season, Dec 2009 and autumn season, Oct 2010. In the Quiberon bay, a total of 95 surficial sediment samples was collected during Dec 2009 sampling meanwhile, 103 surficial sediment samples were collected during Oct 2010 sampling (*Figure 2–4*; *Table 2–3*). Meanwhile, a total of 101 sediments were sampled during Dec 2009 sampling in gulf of Morbihan, and the addition of 20 surficial sediment samples during Oct 2010 (*Figure 2–11*; *Table 2–4*).

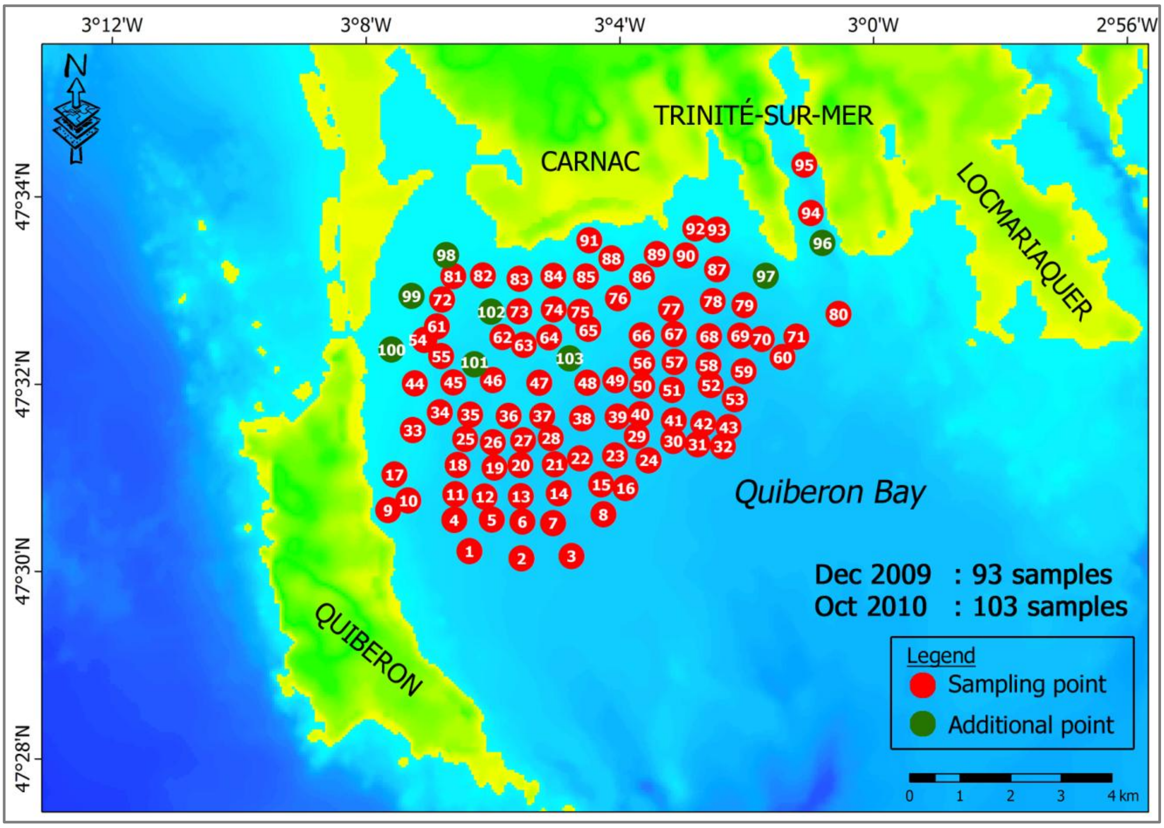

Figure 2–4. *Sampling points in Quiberon bay surficial sediments for both sampling periods.*

Table 2–3. *GPS coordinate of surficial sediment sampling locations at Quiberon bay.*

Station ID	Latitude (° N)	Longitude (° W)	Site Description
BQ 01	47.509	3.097	Zone A Southern area
BQ 02	47.509	3.083	
BQ 03	47.510	3.070	
BQ 04	47.514	3.103	
BQ 05	47.514	3.092	
BQ 06	47.514	3.083	
BQ 07	47.515	3.075	
BQ 08	47.517	3.063	
BQ 09	47.515	3.120	
BQ 10	47.517	3.115	
BQ 11	47.518	3.102	
BQ 12	47.519	3.095	
BQ 13	47.519	3.085	
BQ 14	47.521	3.075	
BQ 15	47.522	3.065	
BQ 16	47.522	3.057	
BQ 17	47.522	3.119	

Table 2–3. *Continued.*

Station ID	Latitude (° N)	Longitude (° W)	Site Description
BQ 18	47.525	3.102	Zone B Western area
BQ 19	47.524	3.092	
BQ 25	47.528	3.100	
BQ 35	47.533	3.099	
BQ 44	47.539	3.114	
BQ 45	47.539	3.104	
BQ 46	47.540	3.095	
BQ 100	47.544	3.121	
BQ 54	47.546	3.114	
BQ 55	47.543	3.109	
BQ 101	47.542	3.099	
BQ 61	47.548	3.111	
BQ 62	47.548	3.092	
BQ 99	47.554	3.117	
BQ 72	47.553	3.109	
BQ 102	47.552	3.096	
BQ 20	47.525	3.086	Zone C Center area
BQ 21	47.525	3.077	
BQ 22	47.527	3.071	
BQ 23	47.528	3.060	
BQ 24	47.528	3.053	
BQ 27	47.530	3.085	
BQ 28	47.530	3.078	
BQ 29	47.532	3.056	
BQ 36	47.534	3.090	
BQ 37	47.534	3.081	
BQ 38	47.534	3.070	Zone C Center area
BQ 39	47.535	3.060	
BQ 40	47.536	3.056	
BQ 47	47.539	3.082	
BQ 48	47.541	3.068	
BQ 49	47.541	3.063	
BQ 50	47.541	3.054	
BQ 103	47.544	3.074	
BQ 56	47.545	3.056	
BQ 63	47.547	3.087	
BQ 64	47.548	3.080	
BQ 65	47.550	3.071	
BQ 66	47.550	3.057	
BQ 73	47.552	3.089	
BQ 74	47.554	3.080	
BQ 75	47.554	3.072	
BQ 76	47.555	3.063	

Table 2–3. *Continued.*

Station ID	Latitude (° N)	Longitude (° W)	Site Description
BQ 30	47.532	3.046	Zone D Eastern area
BQ 31	47.531	3.039	
BQ 32	47.530	3.033	
BQ 41	47.534	3.046	
BQ 42	47.534	3.038	
BQ 43	47.534	3.032	
BQ 51	47.540	3.047	
BQ 52	47.542	3.037	
BQ 53	47.539	3.031	
BQ 57	47.545	3.048	
BQ 58	47.545	3.038	
BQ 59	47.545	3.029	
BQ 60	47.547	3.019	
BQ 67	47.550	3.047	
BQ 68	47.550	3.038	
BQ 69	47.550	3.030	
BQ 70	47.550	3.025	
BQ 71	47.551	3.016	
BQ 77	47.554	3.049	
BQ 78	47.557	3.038	
BQ 79	47.556	3.029	
BQ 80	47.556	3.005	
BQ 81	47.557	3.106	Zone E Northern area
BQ 82	47.558	3.098	
BQ 83	47.557	3.088	
BQ 84	47.558	3.080	
BQ 85	47.559	3.072	
BQ 86	47.560	3.056	
BQ 87	47.562	3.038	Zone E Northern area
BQ 97	47.562	3.024	
BQ 88	47.563	3.065	
BQ 89	47.564	3.052	
BQ 90	47.564	3.045	
BQ 91	47.566	3.071	
BQ 92	47.569	3.044	
BQ 93	47.569	3.038	
BQ 98	47.561	3.108	
BQ 94	47.573	3.013	Zone F Trinité–sur–Mer
BQ 95	47.581	3.016	
BQ 96	47.568	3.010	

Figure 2–5. *Zone A, southern area.*

Figure 2–6. *Zone B, western area.*

Figure 2–7. *Zone C, center area.*

Figure 2–8. *Zone D, eastern area.*

Figure 2–9. *Zone E, northern area.*

Figure 2–10. *Zone F, Trinité–sur–Mer area.*

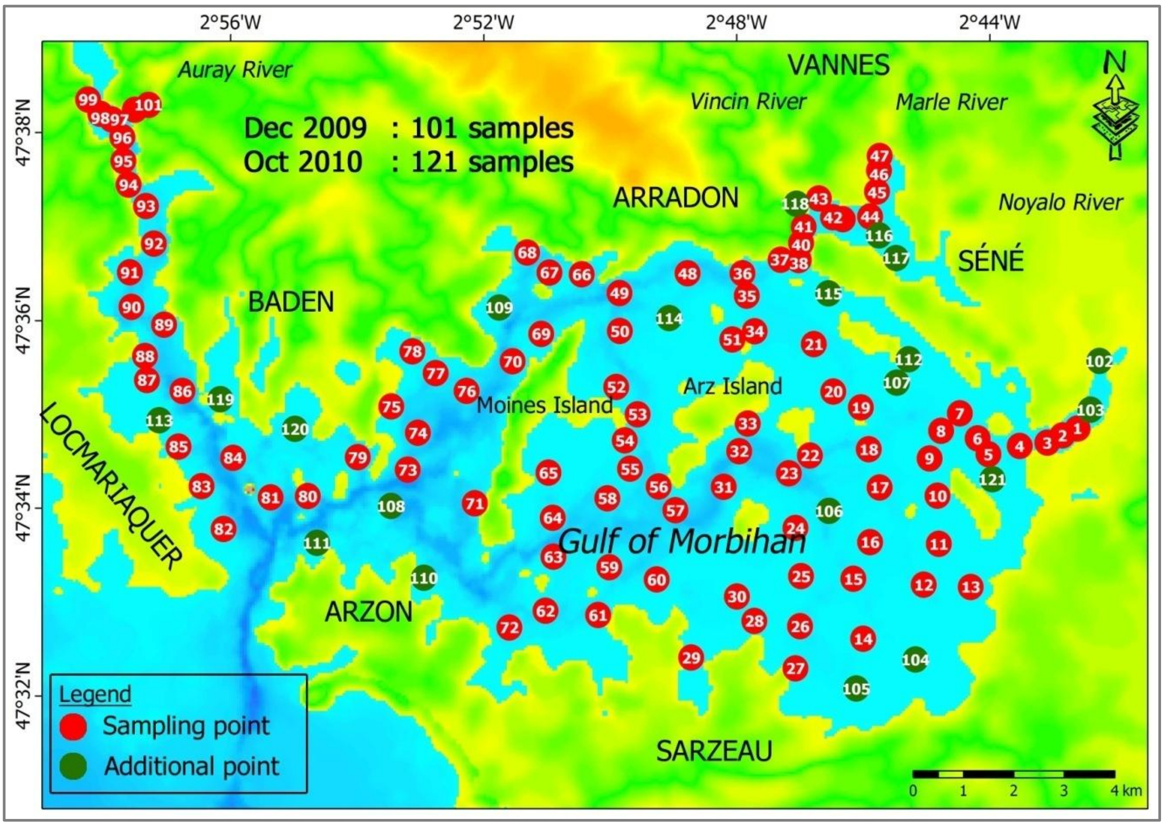

Figure 2–11. *Sampling points in gulf of Morbihan surficial sediments for both samplings.*

Table 2–4. *GPS coordinate of surficial sediment sampling locations at gulf of Morbihan.*

Station ID	Latitude (° N)	Longitude (° W)	Site description
GM 80	47.572	2.905	Zone A Gulf entrance area
GM 111	47.564	2.902	
GM 81	47.571	2.915	
GM 82	47.565	2.927	
GM 83	47.572	2.933	
GM 84	47.578	2.925	
GM 120	47.584	2.910	
GM 85	47.579	2.940	Zone B Auray river
GM 119	47.588	2.930	
GM 113	47.584	2.945	
GM 86	47.589	2.940	
GM 87	47.591	2.949	
GM 88	47.595	2.950	
GM 89	47.601	2.946	
GM 90	47.603	2.955	
GM 91	47.610	2.956	
GM 92	47.615	2.950	
GM 93	47.622	2.953	
GM 94	47.625	2.958	
GM 95	47.629	2.960	
GM 96	47.633	2.960	
GM 97	47.637	2.963	
GM 98	47.637	2.966	
GM 99	47.640	2.970	
GM 100	47.638	2.957	
GM 101	47.640	2.954	
GM 37	47.619	2.785	Zone C Marle river
GM 38	47.620	2.780	
GM 39	47.627	2.769	
GM 40	47.622	2.780	
GM 41	47.626	2.779	
GM 118	47.630	2.781	
GM 42	47.627	2.772	
GM 43	47.627	2.775	
GM 44	47.628	2.762	
GM 116	47.625	2.759	
GM 117	47.621	2.754	
GM 45	47.633	2.761	
GM 46	47.636	2.761	
GM 47	47.639	2.760	

Table 2–1. *Continued.*

Station ID	Latitude (° N)	Longitude (° W)	Site description
GM 102	47.605	2.699	Zone D Noyalo river
GM 103	47.596	2.701	
GM 01	47.593	2.704	
GM 02	47.591	2.708	
GM 03	47.590	2.712	
GM 04	47.589	2.719	
GM 71	47.573	2.861	Zone E Western area
GM 72	47.551	2.850	
GM 110	47.559	2.873	
GM 108	47.571	2.883	
GM 73	47.578	2.879	
GM 74	47.585	2.877	
GM 75	47.589	2.885	
GM 76	47.592	2.865	
GM 77	47.595	2.874	
GM 78	47.599	2.880	
GM 79	47.580	2.893	
GM 34	47.607	2.790	Zone F Northern area
GM 35	47.613	2.793	
GM 36	47.617	2.795	
GM 48	47.616	2.809	
GM 114	47.608	2.813	
GM 49	47.612	2.827	
GM 50	47.605	2.826	
GM 51	47.605	2.798	
GM 52	47.595	2.826	
GM 53	47.590	2.820	
GM 66	47.615	2.837	
GM 67	47.615	2.845	
GM 68	47.618	2.852	
GM 109	47.608	2.858	
GM 69	47.603	2.846	
GM 70	47.598	2.853	
GM 28	47.555	2.785	Zone G Southern area
GM 29	47.548	2.802	
GM 30	47.559	2.791	
GM 31	47.578	2.796	
GM 32	47.585	2.792	
GM 33	47.590	2.791	
GM 54	47.586	2.823	
GM 55	47.581	2.821	
GM 56	47.578	2.813	
GM 57	47.574	2.808	

Station ID	Latitude (° N)	Longitude (° W)	Site description
GM 58	47.575	2.826	Zone G Southern area
GM 59	47.563	2.824	
GM 60	47.561	2.811	
GM 61	47.554	2.826	
GM 62	47.555	2.841	
GM 63	47.564	2.839	
GM 64	47.571	2.840	
GM 65	47.579	2.842	
GM 121	47.583	2.725	Zone H Eastern area
GM 05	47.587	2.727	
GM 06	47.590	2.730	
GM 07	47.594	2.735	
GM 08	47.591	2.740	
GM 09	47.586	2.742	
GM 10	47.579	2.739	
GM 11	47.571	2.738	
GM 12	47.563	2.742	
GM 13	47.564	2.729	
GM 14	47.553	2.757	
GM 104	47.550	2.742	
GM 105	47.544	2.757	
GM 15	47.564	2.760	
GM 16	47.570	2.756	
GM 17	47.580	2.755	
GM 18	47.587	2.759	
GM 19	47.594	2.761	
GM 107	47.599	2.752	
GM 112	47.603	2.749	
GM 20	47.597	2.769	
GM 115	47.614	2.772	
GM 21	47.605	2.775	
GM 22	47.585	2.774	
GM 23	47.582	2.779	
GM 106	47.575	2.768	
GM 24	47.572	2.777	
GM 25	47.564	2.773	
GM 26	47.554	2.774	
GM 27	47.547	2.773	

Figure 2–12. *Zone A, gulf of Morbihan entrance area.*

Figure 2–13. *Zone B, Auray river.*

Figure 2–14. *Zone C, Marle river.*

Figure 2–15. *Zone D, Noyalo river.*

Figure 2–16. *Zone E, western area.*

Figure 2–17. *Zone F, northern area.*

Figure 2–18. *Zone G, southern area.*

Figure 2–19. *Zone H, eastern area.*

Surficial sediment samples were collected with an Orange Peel grab (*Figure 2–20; Figure 2–21*). The top 0.5–1 cm of the sediment was removed with an acid washed plastic spoon to prevent sediment contamination. In addition to avoid the contamination from grab's wall, the outer part of the sediment sample was removed and only the inner part was further processed. So, even if removal of fine material had occurred, this would affect only the outer part of the sediment sample and not the sub–sample used for the analysis and no contact with the edge of grab happened during the sub sampling procedure (Pekey, 2006). Any foreign objects such as leaves, snails or shells were discarded in the field. Immediately after collection, samples were bagged in self–sealed acid pre–cleaned polyethylene bags, rinsed with metal–free water and preserved at a low temperature and transport to the laboratory.

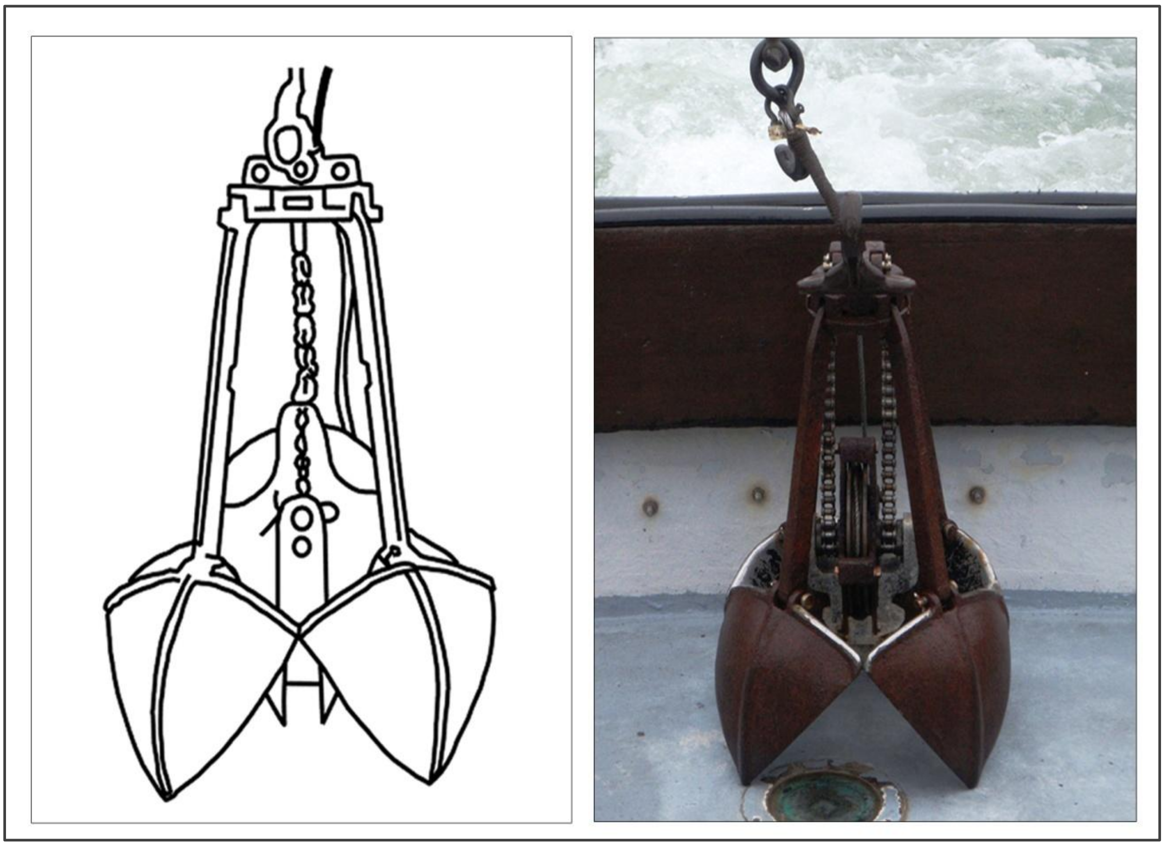

Figure 2–20. *Sediment samplers to obtain the surficial sediments, Orange Peel grab.*

During sampling, precautions were taken to minimize any disturbance in the grain–size distribution of the original sediments. The sediment sample was taken only when the grab was firmly closed on the arrival of the boat, so as to avoid any leaks of fine material withdrawn by water. Special care was taken to avoid leakage of fine–grained materials during retrieval. Prior to sediment sample collection, all the apparatus for the collection and storage of sediment samples were thoroughly cleaned with acid (10 % HNO_3) and then rinsed with deionized water (Mili–Q) before each use.

Figure 2–21. *Processes obtaining surficial sediments by Orange Peel grab.*

2.2.2 Core sediments collection

Ten (10) core sediments were collected in gulf of Morbihan (*Figure 2–22*). Sediment core was obtained by using the D–section corer (*Figure 2–23*). The corer was pushed slowly into the sediment up to its maximum depth of 50 m and turned 180^o before being lifted up from the substratum (*Figure 2–24*). Upon its collection, the core sample was placed in the PVC tube and wrapped with a plastic wrapper to prevent contamination and preserved at a low temperature. The cores were transported in a vertical position to the laboratory for further analysis (Hung and Hsu, 2004; Sirinawin and Sompongchaiyakul, 2005).

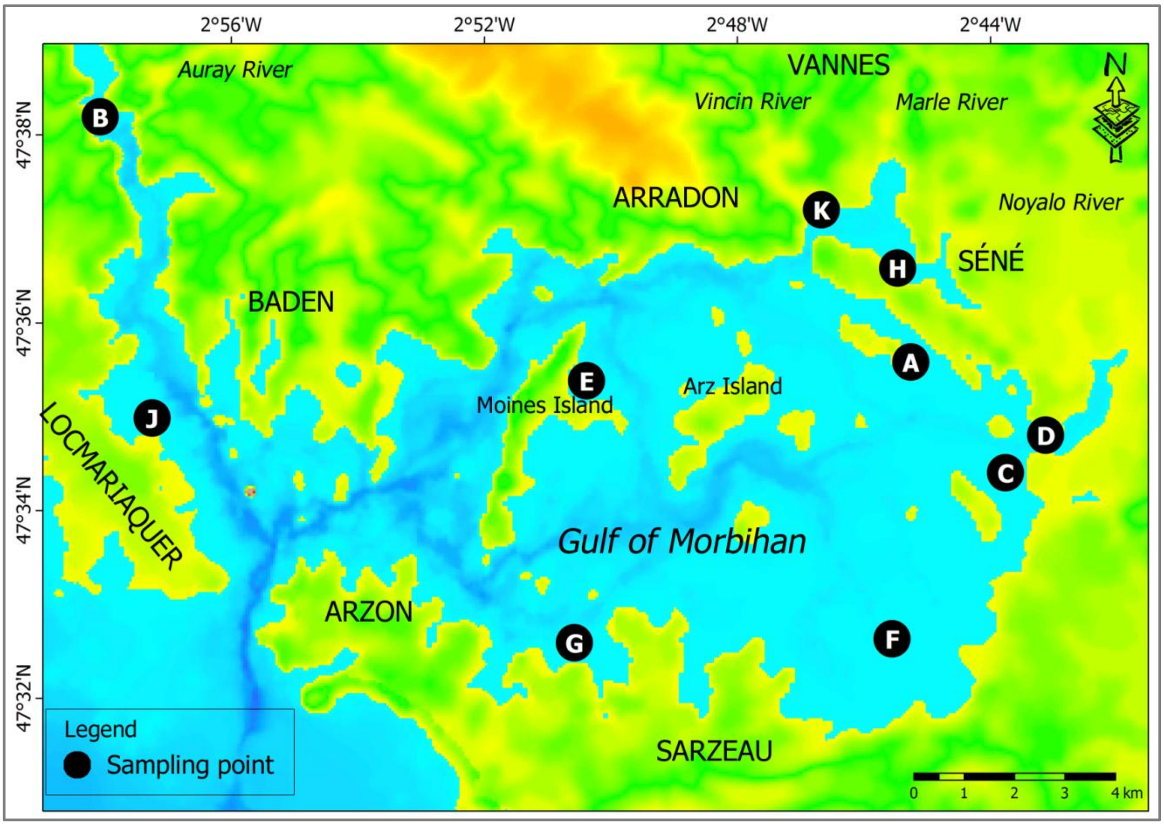

Figure 2–22. *Sampling points for core sediments in gulf of Morbihan.*

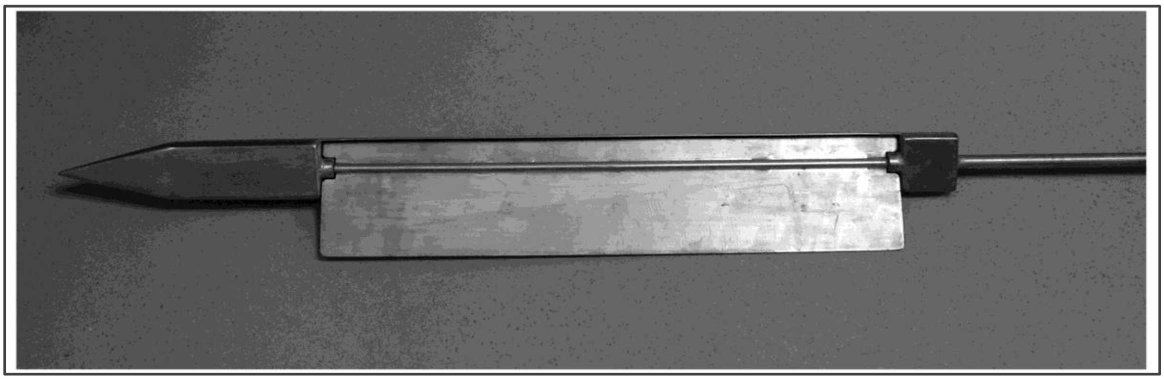

Figure 2–23. *Sediment sampler to obtain the core sediment, D–section corer.*

Figure 2–24. *Processes obtaining the core sediment by D–section corer.*

2.2.3 Oyster samples collection

Oyster samples were collected from the oyster mariculture farming racks and river bed (*Figure 2–25*). Cultivated oysters were collected from the farming racks help from the Regional Committee of South Brittany Shellfish *(Comité Régional de la Conchyliculture Bretagne–Sud; CRC)* (*Figure 2–26*). On the other hand, some wild oysters were collected by hand during low tide in the river bed (*Figure 2–27*). Sediment adhering to the oyster shell was washed thoroughly in the field with in–situ seawater. The collected oyster samples were preserved in pre–cleaned polyethylene bags, and packed in an ice–chest at 4°C while being shipped back to the laboratory. The organisms covering a wide size–range was chosen taking into account their different feeding habits, as well as their distribution along the gulf and bay (Baudrimont *et al.*, 2005; Blasco *et al.*, 1999). *Table 2–5* shows the oyster species with their size and weight used in this study.

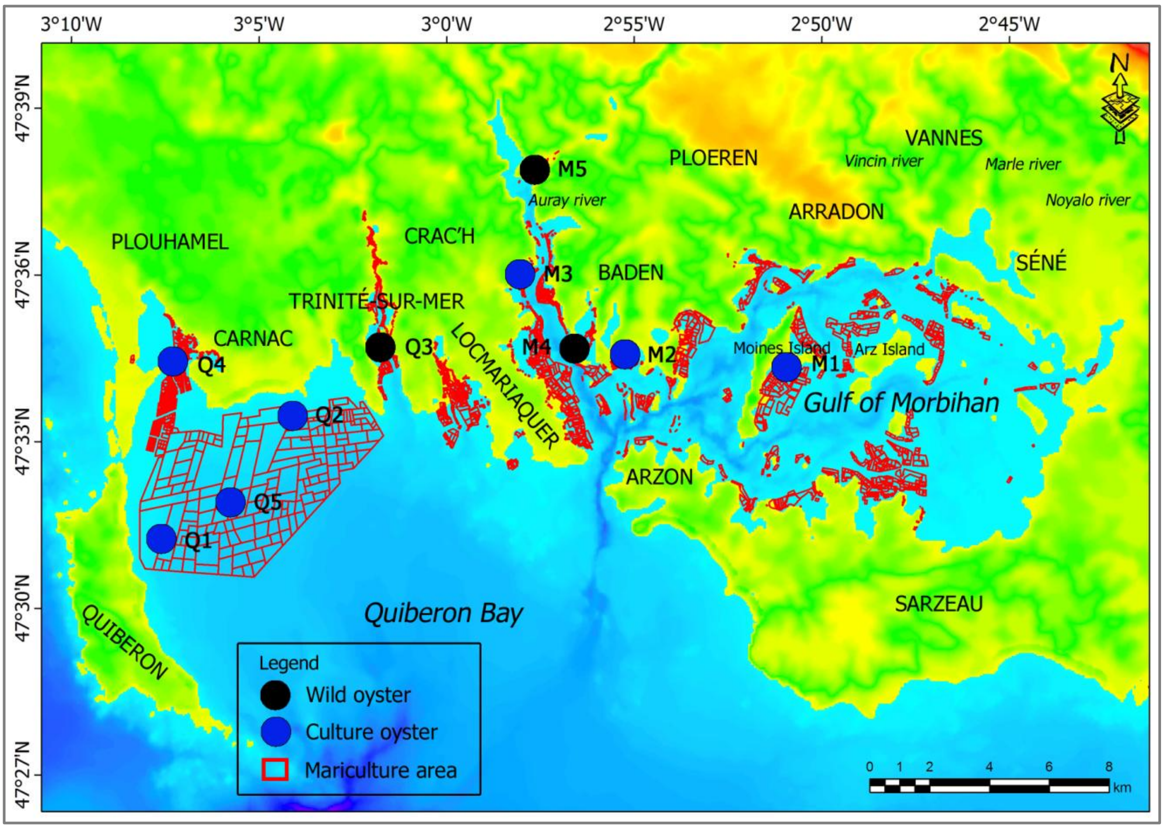

Figure 2–25. *Oyster collection locations in Quiberon bay and gulf of Morbihan.*

Table 2–5. *Oyster samples characteristic collected in Quiberon bay and gulf of Morbihan.*

Station ID	Species	Length (mm)	Weight (g)	Wet weight, in-toto (g)	Type of oyster
Q1 (n = 40)	*C. gigas*	93.3 (79.0–119)	75.6 (44.1–125)	13.3 (7.4–20.4)	Cultivated
Q2 (n = 37)	*C. gigas*	94.1 (67.3–113)	83.0 (44.3–160)	14.8 (8.4–21.7)	Cultivated
Q3 (n = 45)	*C. gigas*	142 (114–181)	241 (143–380)	16.3 (8.2–27.2)	Wild
Q4 (n = 49)	*C. gigas*	101 (73.7–130)	101 (63.7–167)	9.80 (4.2–20.1)	Cultivated
Q5 (n = 41)	*O. edulis*	63.3 (53.2–71.5)	51.4 (33.0–81.3)	6.4 (3.7–8.7)	Cultivated
M1 (n = 53)	*C. gigas*	100 (58.9–145)	65.8 (37.9–104)	6.80 (3.37–13.3)	Cultivated
M2 (n = 47)	*C. gigas*	105 (90.8–126)	106 (72.6–153)	10.5 (7.58–15.2)	Cultivated
M3 (n = 51)	*C. gigas*	93.0 (70.2–119)	80.3 (54.0–123)	7.42 (3.16–12.4)	Cultivated
M4 (n = 16)	*C. gigas*	112 (27.2–196)	209 (50.3–401)	21.0 (6.74–39.4)	Wild
M5 (n = 10)	*C. gigas*	69.7 (37.3–121)	129 (69.0–224)	15.9 (8.33–26.6)	Wild

Figure 2–26. *Cultivated oyster samples from the mariculture farm.*

Figure 2–27. *Wild oyster samples from the river bed.*

The kind of oyster species, the specific way of food intake and the shell lengths of oyster are as follows according to the reference book in conjunction with a catalogue of marine molluscs (Zhao *et al*., 1982; Liang *et al*., 2004):

1. *Ostrea edulis*, Common name: European Flat Oyster, Mollusca (Bivalvia), Family: Ostreidae, tropical type: herbivorous (grazing), with the typical shell length of 53.2–71.5 mm (*Figure 2–28*) .
2. *Crassostrea gigas*, Common name: Pacific Oyster, Mollusca (Bivalvia), Family: Ostreidae, tropical type: herbivorous (grazing), with the typical shell length of 67.3–180.8 mm (*Figure 2–29*).

Figure 2–28. *Oyster species 1– European flat oyster, Ostrea edulis.*

Figure 2–29. *Oyster species 2– Pacific oyster, Crassostrea gigas.*

2.2.4 Mapping application by Geographical Information System software

For a better interpretation, the concentration distribution maps were analyzed using geographical information system (GIS) method and overlaid on a background map. The MTEs concentration was used as the input data for a grid–base contouring map, to study the concentration distribution in the surficial sediments. GIS software, ESRI ArcView 9.3 was used for the area digitization in order to display the spatial distribution of the study. GIS software was used in the following aspects:

i. to locate the sampling locations in the study area,
ii. to generate geochemical maps showing hotspots of MTEs contamination in superficial sediment,
iii. to analyze the correlation between the sediment MTE concentration and zone of human activities using GIS spatial analysis techniques.

First, GPS was used to provide the accurate longitude and latitude position of the sampling locations. Digital records of the each coordinate position were transferred and store in a computer, where geochemical maps of MTEs can be made and easily digitalized. Furthermore, give the ease of manipulating and transferring the data, the data can readily be incorporated with other existing GIS information. A better understanding of the interactions between MTEs and the environment can also be obtained by overlaying the MTEs distribution with key features such as topography and zone of activities (Li *et al.*, 2004; Lee *et al.*, 2006)

2.3 Laboratory pre–analysis preparation

2.3.1 Apparatus preparation

All apparatus including glassware and sampling gears were immersed in 5 % nitric acid (HNO_3) for 2–3 days. Then all the apparatus were rinsed with distilled water and dried using the oven. As for the sieve, ethanol was used to clean the surface of the sieve after it has been used in order to clean the debris that might be stuck in between the mesh and could result in samples contamination. Such precaution steps were taken in preparation of apparatus and sampling gears as to ensure a precise and accurate result to minimize the sample contamination. As a conclusion, all apparatus must be free from any metal characteristic when using rubber, glass or which materials can contaminate the samples.

2.3.2 Sediment samples preparation

All the surficial and core sediment samples were transferred to petri disc and were dried in an oven at 60 ^{o}C to a constant weight for one week. The core sediments were sub–sampled at 2 cm interval using a plastic knife and a thin film zone of sediment next to the PVC tube was left in the core itself to avoid contamination. The visible marine organisms and coarse shell fragments, sea grass, leaves and roots were removed manually.

One set of samples was used for the estimation of organic matter and for MTEs analysis by acid digestion in a closed PTPE container. The second set of samples was for the particle size analysis, using the standard Wentworth scale methodology.

To facilitate geochemical analysis, the dried samples were ground into a fine powder using an agate mortar and pestle, sieved through 63 μm sieve and stored in PE vials until analysis. This sediment fraction size was chosen because experience indicated that <63 μm size fractions contains significant organic matter and metals (Morillo *et al.*, 2004).

2.3.3 Oyster samples preparation

Each individual oyster samples were shucked and washed with running distilled water. Prior to analysis, samples were classified, weighed and measured the size and separated into distinct class size; 0–25 mm, 26–45 mm, 46–65 mm and >65 mm for analysis (Hamed and Emara, 2006; Bayen *et al.*, 2007). The samples were occasionally dissected using stainless steel scalpels and forceps in a laminar flow bench where the shells were opened and whole soft tissue (in–toto) were removed from their shells, thoroughly rinsed with distilled water to remove extraneous impurities and transferred in polypropylene vials. The weights of the soft tissue were recorded for each organism and dried in an oven at 60 ^{o}C to a constant weight.

2.4 Laboratory analysis

Table 2–6 shows the summary of laboratory analyses and methodologies conducted on samples obtained to complete this study.

Table 2–6. *Laboratory works in this study and their references.*

Analysis	Methodology	References
Sediment characteristic	Coarse fraction analysis	Wentworth, 1922
	Dry sieving method	McBride, 1971
	Fine fraction analysis	Folk, 1980
	Laser diffraction method	
Total organic carbon	Wet dichromate analysis	Holme and McIntyre, 1984
		Tung and Tanner, 2003
MTE in sediments	Teflon Bomb digestion	Noriki *et al.*, 1980
	ICPMS	Yuan *et al.*, 2004
	Hg Analyzer	
MTE in oysters	Teflon Bomb digestion	Papagiannis *et al.*, 2004
	ICPMS	Agusa *et al.*, 2004
	Hg Analyzer	
Sedimentation rate	Pb–210 Analysis	Carpenter *et al.*, 1981
	Alpha Spectrophotometer	Kato *et al.*, 2003
Data mapping and interpolation	ArcGIS software	Li *et al.*, 2004 Lee *et al.*, 2006

2.5 Laboratory analysis 1 – Sediment characteristics analysis

2.5.1 Coarse fraction analysis by dry sieving method

Dry sieving method was employed when sand particle predominated in sediment samples. For coarser sand, 100–250 g is sufficient, but for finer sand, 10–100 g is considered adequate. Before the process began, all exotic material such as leaves and shell fragments in the samples were removed. The sediment samples were oven dried at 105 ^oC for 24 hours. Each subsample was sieved using a mechanical sieve shaker with mesh sizes arranged consecutively finer downwards of 4000 µm, 2400 µm, 1400 µm, 1000 µm, 710 µm, 500 µm, 355 µm, 250 µm, 200 µm, 125 µm, 90 µm, 63 µm (Folk, 1980). Sample retained in each mesh was accurately weighted and the data processed to obtain moment statistics of mean grain size value (*Figure 2–30*).

Figure 2–30. *Dry sieving procedures for coarse fraction sediments.*

2.5.2 Fine fraction analysis by laser diffraction method

1.5 g sample was placed in a 100 mL glass beaker and diluted with distilled water. Then the sample was heated on the hotplate at the constant temperature of 60 ^oC. Distilled water and a few drops of hydrogen peroxide (H_2O_2) were added into the solution slowly and stir it with a glass rod. This process was continuing until all organic matter in the reaction stops (no formation of bubbles). The aim was to remove all the organic matters in the sediment samples.

Finally, the solution was cooled down to room temperature. The 10 % calgon solution was added into the solution to break down the sediment particles, which are bonded together. The sediment characteristics of the sediments were analyzed using Malvern 2000 Particle Size Analyzer (*Figure 2–31*). This method of analysis utilizes the diffraction properties of laser light when passes through a medium containing suspended particles, and provides a normalized measure of the relative mass of particles in many size fractions of the sample (Syvitski, 1991).

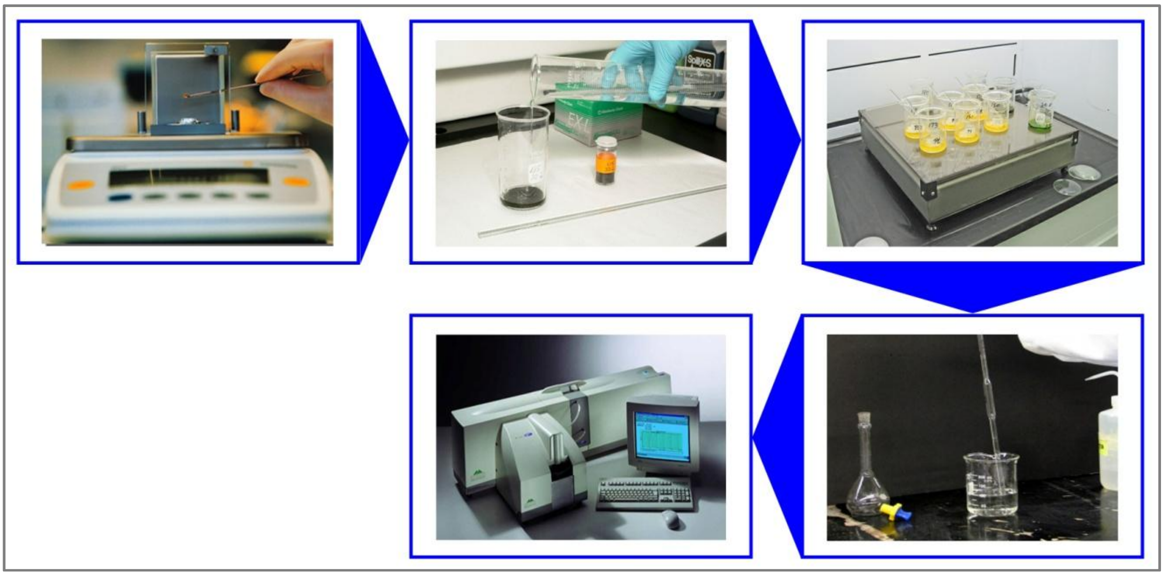

Figure 2–31. *Laser diffraction procedures for fine fraction sediments.*

2.5.3 *Mean grain size calculation*

The result obtained from both laser diffraction and dry sieving method was converted into percentage of weight. All data collected were subjected to statistical analysis by using the Moment method (Griffiths, 1967; McBride, 1971; Folk, 1974). By using this method, the values of mean grain size values were calculated. The formulas are as below:

$$Mean, X = \frac{\Sigma fm}{n}$$

where,

f = percentage weight of each grade of particle size
m = median of each particle size (∅)
n = total number of the particle samples in 100 where f is in percentage (%)
∅ = diameter of the particle in mm

2.6 *Laboratory analysis 2 – Total organic carbon analysis*

Wet dichromate oxidation method (Holme and McIntyre, 1984) was used in the organic carbon analysis (*Figure 2–32*). 0.5 g of sediment sample was weighted and transferred to a test tube followed by the addition of 10 mL of potassium dichromate ($K_2Cr_2O_7$) solution. The mixture was shaken well. Then 20 mL of concentrated sulphuric acid was added and being shaken slowly. If the mixture turned green, additional 5 mL of potassium dichromate was added until the mixture turned dark brown. The total volume of potassium dichromate used was recorded.

Then, the sample was boiled in a water bath for 30 minutes. After that, 200 mL of distilled water was used to rinse the content of the test tube into a 250 mL conical flask. 10 mL of 85 % phosphoric acid (H_3PO_4) was added into the flask followed by 1 mL of diphylamine as an indicator. The flask was shaken well. The solution should turn to blue in color. The process was continued by titration of the sample using ferrous sulphate ($FeSO_4$) solution. Titration was done until the blue color turned into green. The volume of ferrous sulphate used was recorded. The percentage of total organic carbon was calculated by using the following formula:

$$\%\ total\ organic\ carbon = \frac{(V_1 - V_2) \times 0.03 \times 1000}{Sample\ weight\ (g)}$$

where,

V_1 = volume of potassium dichromate used (mL)
V_2 = volume of ferrous sulphate used in titration (mL)

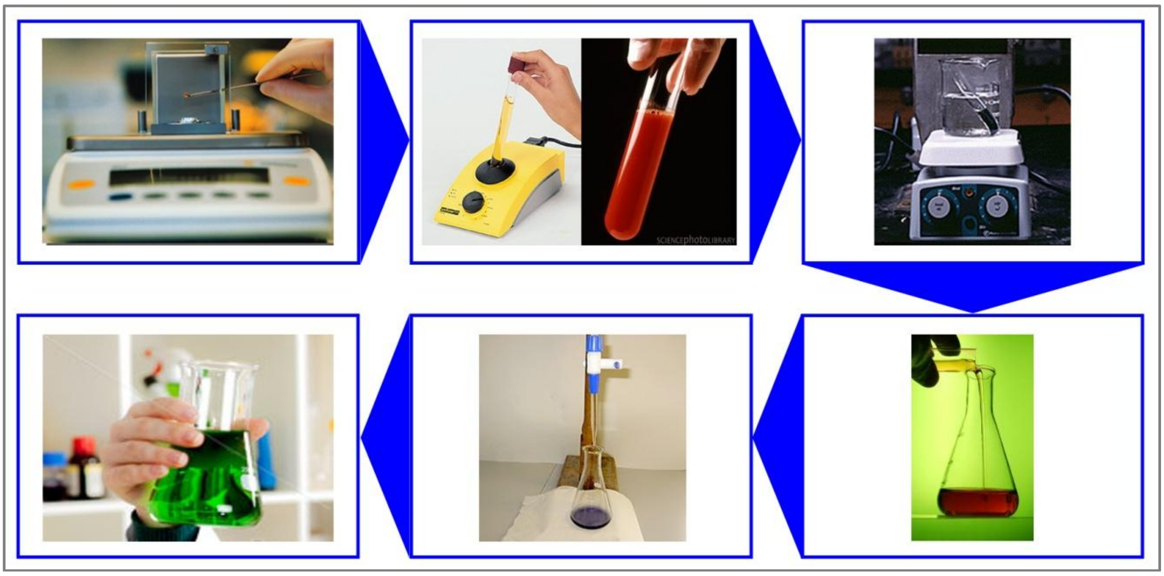

Figure 2–32. *Wet dichromate oxidation procedures for total organic carbon analysis in sediment samples.*

In this analysis, a blank sample and glucose solution was also used. This blank value was deducted from the sample's reading obtained through analysis. Whereas for the glucose solution, it was a standard sample for this analysis as the percentage organic carbon content is known, 36 %. If this organic carbon differed a lot, there might be an error occurring during chemical solution preparation or the chemical had been kept for too long and not suitable to use in this analysis.

2.7 Laboratory analysis 3 – Metallic trace elements analysis

2.7.1 Elements analysis accuracy and precision

All solution of samples was added in 5 % HNO_3. Internal standard such as gallium (Ga) and bismuth (Bi) also were added to control the drift count in samples. The technique of standard addition calibration can be utilized to minimize errors of this analysis precision also can be improved by this technique of internal standards.

All reagents used to prepare the extracts were of analytical–grade quality. Multi–element standard solutions (Merck) were used for the inductively coupled plasma mass spectrometry (ICP–MS) calibrations. Diluted standard working solutions were prepared daily using deionized water. All samples treated with the aqua reagent method were analyzed using an ICP–MS (Perkin Elmer Elan 6000) for determining the element content (Cr^{52}, Mn^{55}, Fe^{57}, Co^{59}, Cu^{63}, Zn^{64}, As^{75}, Cd^{114}, Hg^{201} and Pb^{208}. All data are expressed on a dry weight basis ($\mu g\ g^{-1}$ *dw.*) except for Fe in %.

To evaluate the reproducibility and the accuracy of the method, the analytical method was monitored by analyzing standard reference materials, SRM1646a Estuarine sediment and SRM1566a Oyster Tissue. To check the accuracy of the sequential extraction, the sum of all the extraction steps for each element was compared with that found using direct digestion according to the USEPA standard 3050B method. These data gave satisfactory results with analytical value within 5 % of the certified ones. Our procedures were also checked through repeated analyses of the standard reference materials with ICP–MS. The precision of the analyses was checked by triplicate analysis of standard materials. Calculated coefficients of variation were within 3 % for all elements.

Table 2–7 and *Table 2–8* show the recovery analysis by SRM1646a Estuarine Sediment and SRM1566a Oyster Tissue. The recovery values of element analysis were between 96.3 % and 102.6 % for the sediment analysis and 96.5 % to 103.6 % for the oyster analysis.

Table 2–7. *Recovery of elements in Standard Reference Material 1646a Estuarine Sediment for sediment chemical analysis.*

MTEs	Certified value (μg/g)	Measured value (μg/g)	Recovery value (%)
Cr	40.9±1.9	40.67	99.4
Mn	234.5±2.8	235.1	100
Fe	2.008±0.039	2.011	100.1
Co	5	4.97	99.4
Cu	10.01±0.34	9.64	96.3
Zn	48.9±1.6	48.76	99.7
Cd	0.148±0.007	0.151	102.0
Pb	11.7±1.2	12.01	102.6
As	6.23±0.21	6.02	96.6
Hg	0.04	0.041	102.5

Table 2–7. *Recovery of elements in Standard Reference Material 1566a Oyster Tissue for oyster chemical analysis.*

MTEs	Certified value (μg/g)	Measured value (μg/g)	Recovery value (%)
Cu	66.3±4.3	65.92	99.4
Zn	830±57	802	96.6
Cd	4.15±0.38	4.23	101.9
Pb	0.371±0.014	0.358	96.5
As	14.0±1.2	14.5	103.6
Hg	0.0642±0.0067	0.0639	99.5

2.7.2 Metallic trace elements extraction in sediments

Constant weights of 5 mL acid–cleaned glass beaker was obtained before 50 mg of sediment sample was transferred into glass beakers and stored in an oven at 60 °C. A desiccator was used to transfer the glass beakers inside for it to cool down, before measuring the sample weight. After the constant weight of the sediment was obtained, the sample was transferred into a Teflon beaker for digestion (Noriki *et al.*, 1980). 1.5 mL of mixed acids (2.0 HF : 3.5 HNO_3 : 3.5 HCl) was added into each of the Teflon Bomb and screwed tight before transferring into the oven at 150 °C for six hours. After that, the sample was cooled down to room temperature for 24 hours. Finally, the sample was transferred into 10 mL test tube and 5 % HNO_3 was added to 10 mL of volume. A clear solution with no residue was obtained at this stage. The digestion content was then being analyzed using a multi element technique, ICP–MS, Inductively Coupled Plasma–Mass Spectrometry (Munksgaard *et al.*, 1998; Yuan *et al.*, 2004)(*Figure 2–33*).

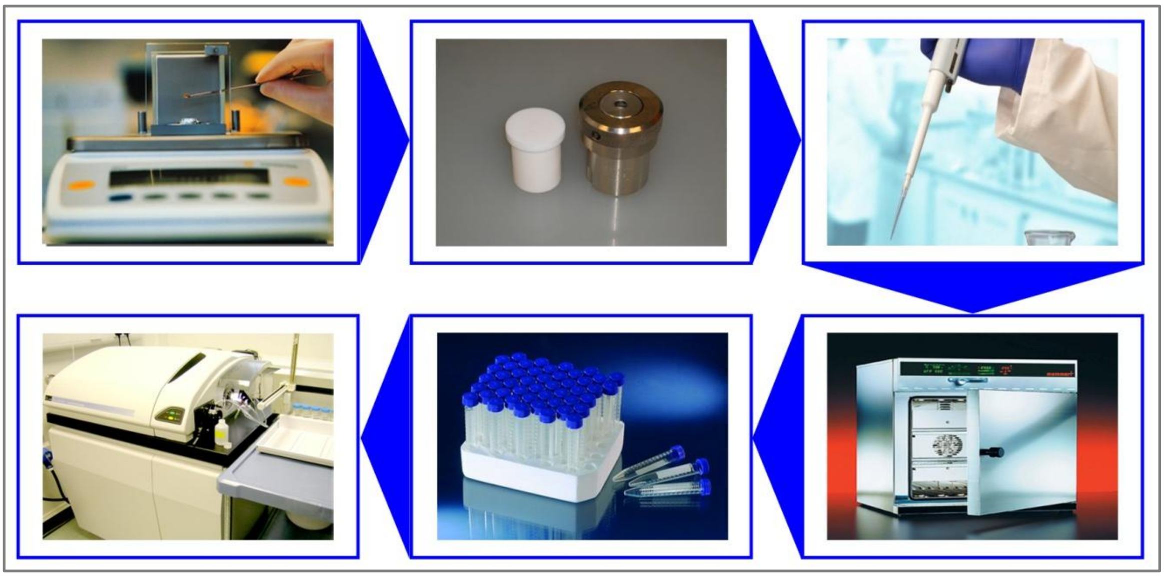

Figure 2–33. *Metallic trace elements extraction procedures in sediment samples.*

2.7.3 Heavy metals extraction in oyster flesh

The soft tissue was weighted to approximately of 0.5 g (dry weights) in a PTFE digestion container. 3 mL HNO_3, 2 mL HCl and 2 mL H_2O_2 was added to each sample and left to predigest. Reagent blank and standard were processed simultaneously. Thereafter, the container was covered and placed in a stainless steel bomb, which was then sealed with a screw closure to avoid any acid leakage and placed in an oven. The oven temperature was kept for six hours at 150 °C. After cooling, the solution was transferred into a polypropylene tube and diluted with 5 % HNO_3. An ICP–MS, inductively coupled plasma mass spectrometry was used (Karadede and Unlü, 2000; Agusa *et al.*, 2004), for the quick and precise determination of MTEs in the tissue samples (*Figure 2–34*).

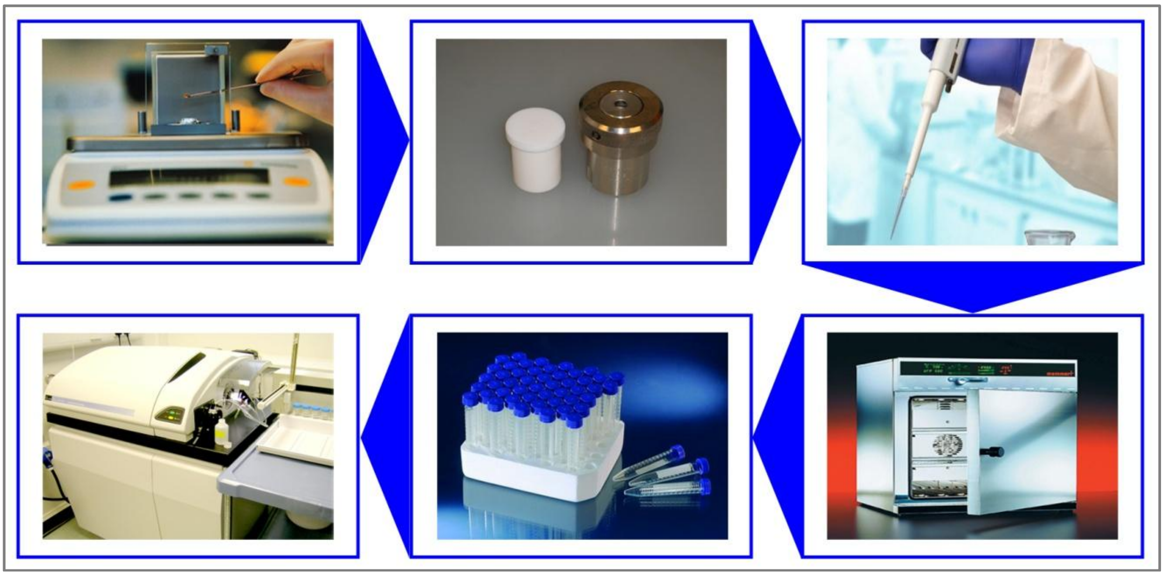

Figure 2–34. *Metallic trace elements extraction procedures in oyster samples.*

2.8 Laboratory analysis 4 – $^{210}Pb_{ex}$ dating analysis

The process was divided into two processes, digestion process and Po platting process (Carpenter *et al.*, 1981; Carpenter *et al.*, 1982). For the first process, 2 g sample was weighted and transferred into 200 mL beaker. Then the weight of the beaker with the sediment sample was obtained. 0.275 mL ^{210}Pb tracer was pipette into the sample and the total weight was recorded. The sediment sample in the beaker was mixed thoroughly and evaporates on the hotplate at temperature not more than 100 ^{o}C to dryness. 30 mL of HNO_3 was then added and heated to dryness. The temperature must not be too high to prevent Po fume coming out from the sample.

After 24 hours (until sample is dried), the sample was cooled down in room temperature. Then 30 mL of $HClO_4$ was added into the sample and heat for 24 hours until the sample dried. After that, 30 mL HCl was added into the sample and heat for 24 hours until it dried again. After 24 hours, the sample was let down to cool at room temperature. 30 mL 6M HCl was added into sample to soften the dried sediment and leave for 24 hours again. Then, the sample solution was transferred into the centrifuge and centrifuges the sample for 15 minutes. After centrifuge, the aqueous was transferred into 120 mL tall bottle for platting and added with 120 mL 0.1 M HCl.

The second process is Po platting. A silver foil with 2 cm x 2 cm four–sided figure was measured. At one side of the silver foil, thin layer of shellac was painted and dry in oven for 5 minutes. Then the silver foil was labeled with the reference station number. On the other side of the silver foil was polished by using Autosol to remove the oxidized silver. A glass hook was used to hook the silver foil and immersed into the sample solution bottle. For the sample, the sample solution was warmed on the hotplate and stirs the solution by using a magnetic stirrer. When the solution is warm enough, half spatula of ascorbic acid was added and the hotplate turned off whiles the stirrer still on. Then the silver foil was immersed into the solution and platting for 24 hours. After 24 hours, the silver foil was taken out and air dry after rinsed it with distilled water. Finally, ^{210}Pb activities were determined by Alpha Spectrometry via the granddaughter nuclides ^{210}Po (*Figure 2–35*).

Figure 2–35. *^{210}Pb extraction procedures in sediment samples.*

To obtain the activity of ^{210}Po and ^{210}Pb in study area, the calculation formula was using as below:

^{209}Po, ^{210}Po and ^{210}Pb from counting and background, cps

$$= \frac{Gross\ counting}{Live\ time} \pm \frac{(\ Gross\ counting\ )^{1/2}}{Live\ time}$$

Actual ^{210}Po (^{210}Pb), cps = [^{210}Po (^{210}Pb) from counting – ^{210}Po (^{210}Pb) background]
Actual ^{209}Po, cps = [^{209}Po from counting – ^{209}Po background]

Activity ^{210}Po (^{210}Pb) when study in laboratory (A), dpm/g

$$= \frac{Actual\ ^{210}Po\ (^{210}Pb)}{Actual\ ^{209}Po} \times {}^{209}Po\ (24.74\ dpm/g) \times \frac{Tracer\ weight\ ^{209}Po}{Sample\ weight}$$

Activity ^{210}Po (^{210}Pb) at study area (A_o), Bq/kg

A = $A_o\ e^{-\lambda t}$, which is cumulative residual unsupported ^{210}Pb activity below sediment of age *t*.
A_o = A / $e^{-\lambda t}$, which is the total residual unsupported lead in the sediment column.
λ = 0.639 / $t_{1/2}$ ^{210}Po (^{210}Pb), which is decay constant of ^{210}Pb (0.03114 per year
t = Depth (cm) / sedimentation rate in years

Activities for A_o and A are in Bq/kg and *t* is in years.

CHAPTER 3

RESULTS / FINDINGS

Chapter 3 represents all the results obtained in this study. Therefore, this chapter is divided into several sub–chapters, namely:

- *3.1* sedimentological characteristics in surficial sediments
- *3.2* total organic carbon contents in surficial sediments
- *3.3* assessment of metallic trace elements in surficial sediments
- *3.4* sedimentation rate by ^{210}Pb dating technique in core sediments from gulf of Morbihan
- *3.5* concentration of metallic trace elements in oyster in–toto

All data were analyzed using Microsoft Excel and SPSS software. Then, the analyzed data were visualized using ArcGIS software and presented in the form of concentrations isopleth map to identify the hotspot of sediment geochemistry concentrations.

3.1 Sedimentological characteristics in surficial sediments

Surficial sediments were analyzed for their grain size distribution using dry sieving and laser particle counter. The continuous spectrum of differential volume fraction for each size range combined into four size classification, namely clay (<4 µm), fine silt (4–32 µm), coarse silt (32–64 µm) and sand (>64 µm). For a better understanding, sedimentary facies map of Quiberon bay and gulf of Morbihan surficial sediment for two seasons (Dec 2009 and Oct 2010) were visualized by ArcGIS 9.3 software. Two types of sediment are recognized in the study area; sand and silt, where sand fraction dominates Quiberon bay sediments while gulf of Morbihan sedimentary is more dominated by silt content.

3.1.1 *Quiberon bay sediments*

From the grain size distribution, Quiberon bay can be divided into two distinctive zones (*Figure 3–1*). Sediments in this area ranged from the medium silt to coarse sand. From both seasons, northern zone sediments were markedly by medium and coarse sand but toward the southern zone, the surficial sediments were dominated by very fine sediments. This may due to the northern zone is strongly influenced by influxes of sediment from the slopes of the Carnac and Quiberon beach, while sediments from open sea supply the fine sediments to the southern zone. From statistical analysis, *t*–Test, there is a significant difference in types of sediment between Dec 2009 and Oct 2010 sampling periods as the *p* value less than 0.05.

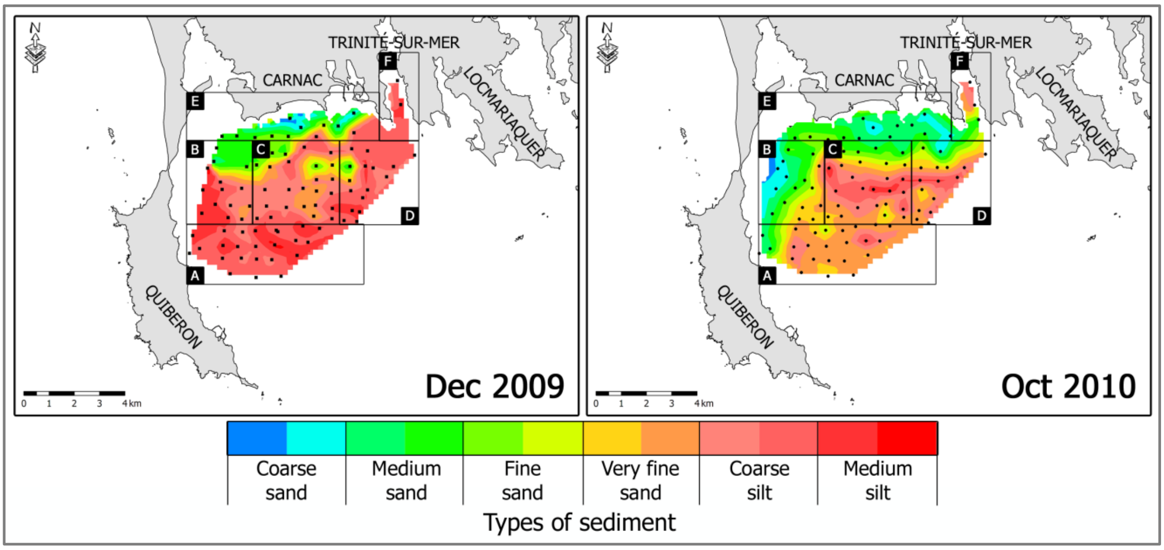

Figure 3–1. *Isopleth maps of sediment characteristics in Quiberon bay surficial sediments for both samplings.*

3.1.2 *Gulf of Morbihan sediments*

Sediment characteristics indicate distinct differences in the sedimentary dynamics of the gulf surficial sediment, which can be divided it into four distinct zones (*Figure 3–2*). Two similar sedimentary facies maps were obtained in Dec 2009 and

Oct 2010, however from the statistical analysis, *t*–Test, there is a significant difference in types of sediment between Dec 2009 and Oct 2009 sampling periods as the p value less than 0.05. Sediments in this area ranged from the fine silt to coarse sand. The entrance of the gulf area was dominant by medium and coarse sands. The lack of fine sediment deposits near the entrance of the gulf could be explained by the high action of waves and tidal currents. The central part of the gulf is a transition between the external and internal zones and characterized by mixture sediments dominated by fine sand. The eastern part of the gulf is protected from wave and tidal current action and is an area of very low–energy hydrodynamics characterised mainly by silt and clay sediments.

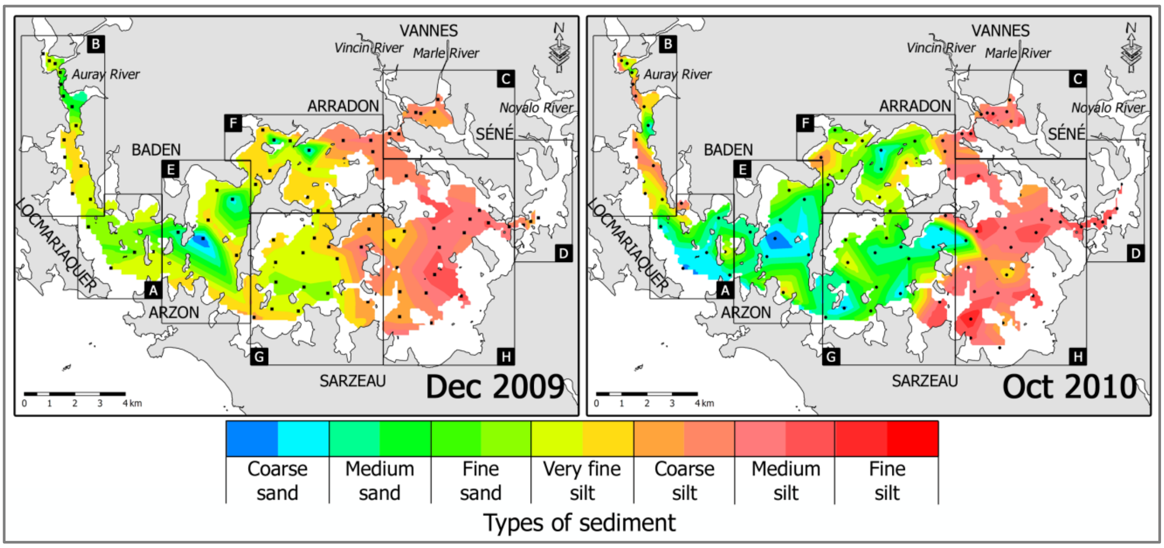

Figure 3–2. *Isopleth maps of sediment characteristics in gulf of Morbihan surficial sediments for both samplings.*

3.2 Total organic carbon contents in surficial sediments

3.2.1 Quiberon bay sediments

For a better interpretation about the concentrations of total organic carbon (TOC) in Quiberon bay surficial sediments, distribution graph for all sampling points are shown in *Figure 3–3* and interpolation analysis using ArcGIS software was used and shown in *Figure 3–4*. From both isopleth maps, TOC contents in surficial sediments were fairly constant over the study area and the TOC contents decrease towards the southern zone of the bay.

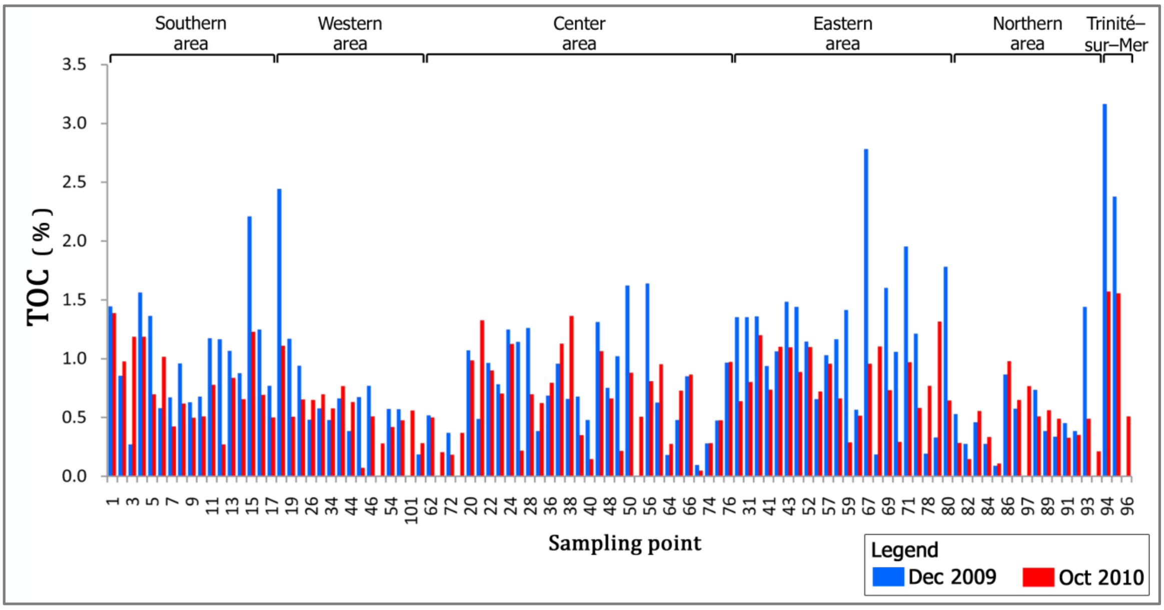

Figure 3–3. *TOC contents based on different zone in Quiberon bay surficial sediments for both samplings.*

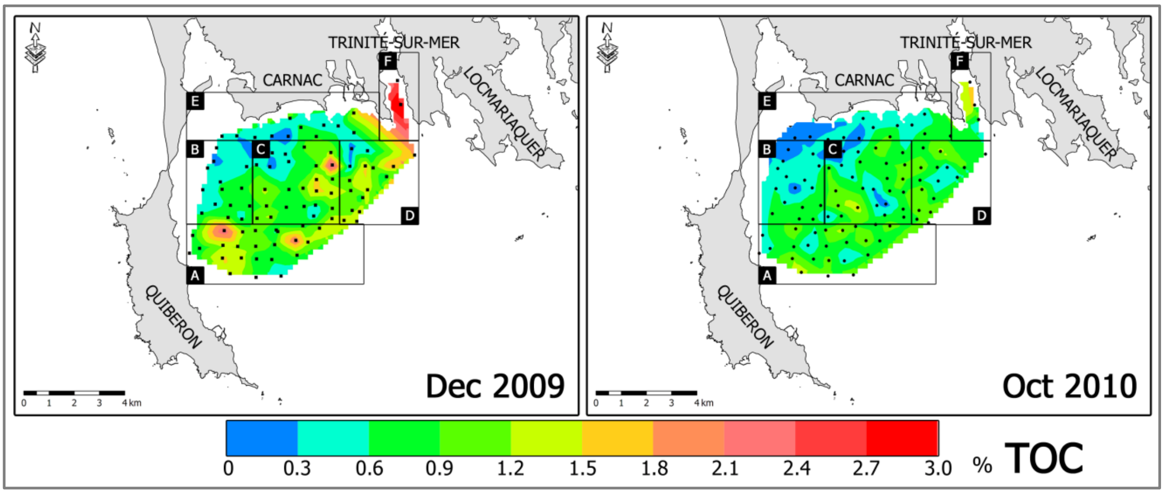

Figure 3–4. *Isopleth maps of TOC contents in Quiberon bay surficial sediments for both samplings.*

The average TOC contents in Dec 2009 sampling was 0.93 % which higher compared to Oct 2010 sampling, 0.69 %. The distribution of TOC content shows highest contents up to 3.16 % and 1.57 % in Trinité–sur–Mer area for two sampling periods, Dec 2009 and Oct 2010, respectively. While the northern zone had the lowest TOC contents, 0.09 % and 0.05 % for both sampling periods. From statistical analysis, *t*–Test, TOC contents in Dec 2009 and Oct 2010 samplings differed significantly with a *p* value smaller than 0.05.

3.2.2 Gulf of Morbihan sediments

The TOC contents of each station in the gulf of Morbihan surficial sediments are expressed in *Figure 3–5* and to be more particular, interpolation analysis from ArcGIS software shows the distribution map of TOC contents (*Figure 3–6*). The TOC contents varied from 0.41 % to 5.39 %, an average of 2.82 % during Dec 2009 sampling, whereas during Oct 2010 sampling, lower TOC contents was found with an average of 2.71 %, ranged from 0.20 % to 5.24 %. The *p* value calculated from statistical analysis, *t*–Test shows that there were no significant differences in TOC contents during Dec 2009 and Oct 2010 sampling period with a *p* value greater than 0.05.

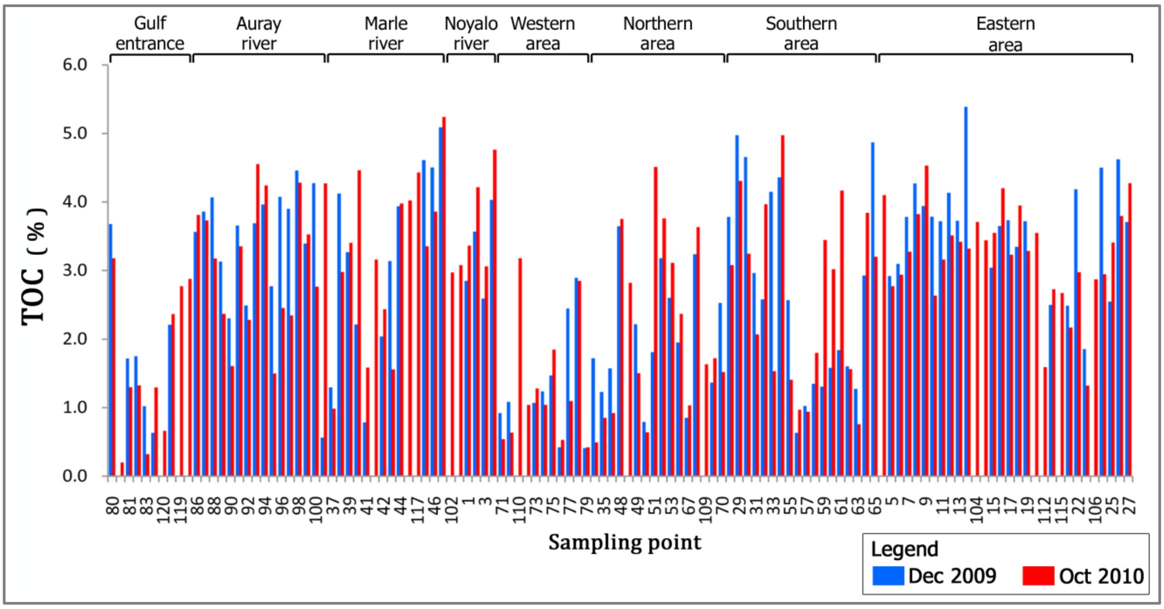

Figure 3–5. *TOC contents based on different zone in gulf of Morbihan surficial sediments for both samplings.*

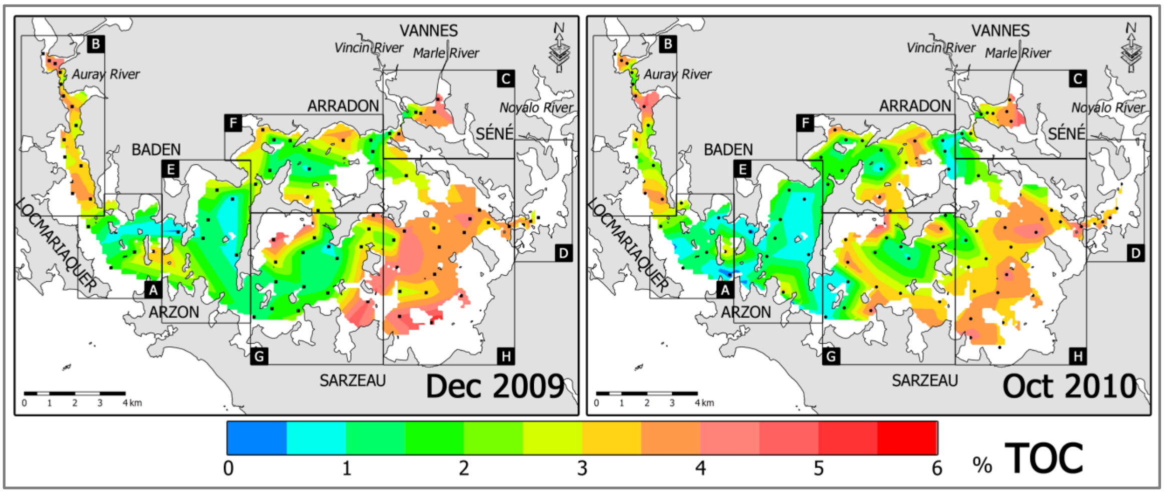

Figure 3–6. *Isopleth maps of TOC contents in gulf of Morbihan surficial sediments for both samplings.*

From the interpolation map, the TOC contents in gulf of Morbihan were divided into three groups. The highest TOC contents were found around the stations located at the rivers run–off zone (Auray, Marle and Noyalo rivers) and eastern zone of the gulf while lower TOC content recorded at western zone and stations near the entrance of the gulf. TOC contents were found to increase towards the eastern zone from gulf entrance.

3.3 Assessment of metallic trace elements in surficial sediments

We analyzed total chromium (Cr^{52}), manganese (Mn^{55}), iron (Fe^{57}), cobalt (Co^{59}), copper (Cu^{63}), zinc (Zn^{64}), arsenic (As^{75}), cadmium (Cd^{114}), mercury (Hg^{201}) and lead (Pb^{208}). The concentrations in all surficial sediment samples collected in two sampling periods, Dec 2009 and Oct 2010 were determined by Inductively Coupled Plasma Mass Spectrometry (ICP–MS) after digesting with mixed acid. All the concentrations data were converted to $\mu g\ g^{-1}$ or part per million (ppm) based on the following calculation:

$$MTE\ concentration\ (\mu g\ g^{-1}) = \frac{\left(\frac{Concentration}{Sediment\ weight}\right) \times Dilution\ factor}{1000}$$

All metallic trace elements (MTEs) concentration were quoted in $\mu g\ g^{-1}$ dry weight basis ($\mu g\ g^{-1}$ *dw.*), except Fe which expressed in percentage (%). Moreover, analytical results have been visualized by using Geographical Information System (GIS) ArcGIS 9.3 software for the area digitization to show the MTEs accumulation areas. ESRI Spatial Analyst extension provided a series of GIS maps, which offer an overview of the surficial sediment MTEs concentration and their spatial variability. These multivariate statistical analyses were evaluated the possibility to distinguish sampling stations, in relation to their geographical location (Guillen *et al*., 2004).

A summary of these MTEs concentrations (average, minimum–maximum and median values) detected during the two sampling campaigns in surficial sediment samples from the Quiberon bay and the gulf of Morbihan are presented in *Table 3–1* and *Table 3–2*, respectively. Generally, the sequence contamination of MTEs studied follows the decreasing order: Fe>Mn>Zn>Cr>Pb>Cu>Co>As>Cd>Hg, for both Quiberon bay and gulf of Morbihan areas.

Table 3-1. *Summary of MTEs concentration in Quiberon bay surficial sediments for both samplings.*

MTEs	**1st sampling (Dec 2009) (n = 93)**			**2nd sampling (Oct 2010) (n = 103)**		
	Average	**Min – Max**	**Median**	**Average**	**Min – Max**	**Median**
Cr	27.6±10.0	8.52 – 61.9	24.8	21.8±12.3	2.94 – 68.9	20.5
Mn	356±101	117 – 669	356	301±154	25.7 – 781	283
Fe	1.50±0.94	0.18 – 4.57	1.62	1.48±0.76	0.09 – 3.92	1.45
Co	11.7±4.94	2.12 – 19.7	13.1	9.22±5.75	1.11 – 23.0	8.34
Cu	14.1±7.24	3.45 – 40.9	13.7	14.7±8.52	2.56 – 37.7	13.2
Zn	42.7±18.2	8.96 – 87.1	44.4	38.9±21.1	4.60 – 98.9	37.1
As	2.77±1.39	0.16 – 5.98	2.64	2.02±1.64	0.12 – 6.80	1.42
Cd	0.08±0.02	0.02 – 0.15	0.08	0.06±0.04	0.01 – 0.19	0.06
Hg	0.025±0.016	0.001 – 0.060	0.02	0.019±0.007	0.005 – 0.033	0.02
Pb	17.9±3.61	8.88 – 28.0	17.5	12.3±3.96	3.61 – 24.1	12.2

*All elements are expressed in µg g^{-1} *dw.* except Fe in %

Table 3-2. *Summary of MTEs concentration in gulf of Morbihan surficial sediment for both samplings.*

MTEs	**1st sampling (Dec 2009) (n = 101)**			**2nd sampling (Oct 2010) (n = 121)**		
	Average	**Min – Max**	**Median**	**Average**	**Min – Max**	**Median**
Cr	36.2±23.9	5.43 – 112	30.2	38.4±18.5	6.73 – 71.1	41.2
Mn	278±140	16.6 – 732	266	380±107	128 – 652	374
Fe	2.40±1.29	0.05 – 5.47	2.52	3.01±1.17	0.50 – 5.10	3.12
Co	14.4±5.31	4.71 – 31.4	14.3	10.9±3.06	3.75 – 18.4	11.1
Cu	16.4±10.3	1.20 – 48.4	14.5	26.5±8.49	8.10 – 47.0	26.0
Zn	38.1±19.1	4.78 – 85.4	34.6	38.7±15.9	9.18 – 90.0	37.4
As	4.30±2.22	0.19 – 6.16	4.40	3.69±1.26	1.27 – 6.30	3.68
Cd	0.11±0.06	0.02 – 0.30	0.11	0.10±0.05	0.01 – 0.23	0.10
Hg	0.026±0.013	0.006 – 0.053	0.02	0.030±0.013	0.011 – 0.060	0.03
Pb	24.9±9.99	2.43 – 42.7	25.4	31.6±6.30	12.8 – 52.4	3.68

* All elements are expressed in µg g^{-1} *dw.* except Fe in %

3.3.1 Quiberon bay case study

3.3.1.1 Levels of chromium in sediments

Figure 3–7 and *Figure 3–8* shows the spatial and temporal distributions of chromium (Cr) concentrations in Quiberon bay surficial sediments in bar graph and isopleth maps, respectively. As shown in both figures, elevated concentrations of Cr occurred in the Trinité–sur–Mer area, with the concentrations increasing toward the southern zone of the bay.

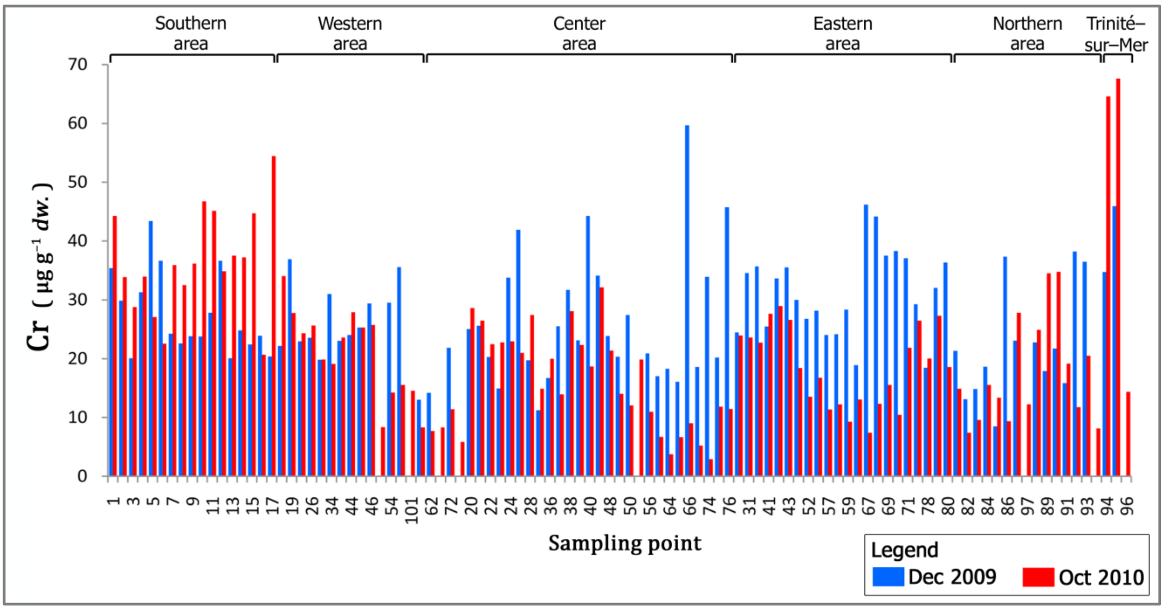

Figure 3–7. *Distribution of Cr based on different zone in Quiberon bay surficial sediments for both samplings.*

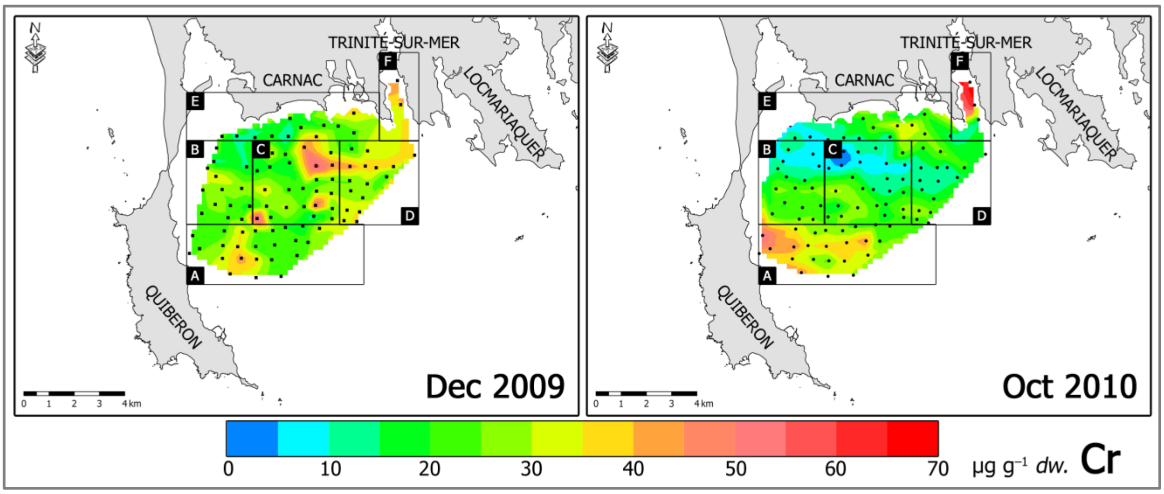

Figure 3–8. *Isopleth maps of Cr accumulation in Quiberon bay surficial sediments for both samplings.*

Concentration of Cr ranged globally 8.52 to 61.9 µg g^{-1} *dw.*, an average of 27.6±10.0 µg g^{-1} *dw.* for Dec 2009 sampling. The average concentrations during Oct 2010 sampling were lower, 21.8±12.3 µg g^{-1} *dw.*, ranged from 2.94 to 6.89 µg g^{-1} *dw.* The statistical analysis, *t*–Test analysis shows that there is significantly different in the concentrations between the two sampling periods with a *p* value less than 0.05.

3.3.1.2 Levels of manganese in sediments

Figure 3–9 and *Figure 3–10* presents the bar graph and isopleths maps of manganese (Mn) concentrations, in Quiberon bay surficial sediments. During Dec 2009 sampling, the western zone of the bay exhibited the high concentrations, while during Dec 2010 sampling, the inner zone and Trinité–sur–Mer area had higher concentrations of Mn. During this period, low concentrations were observed in the outer bay.

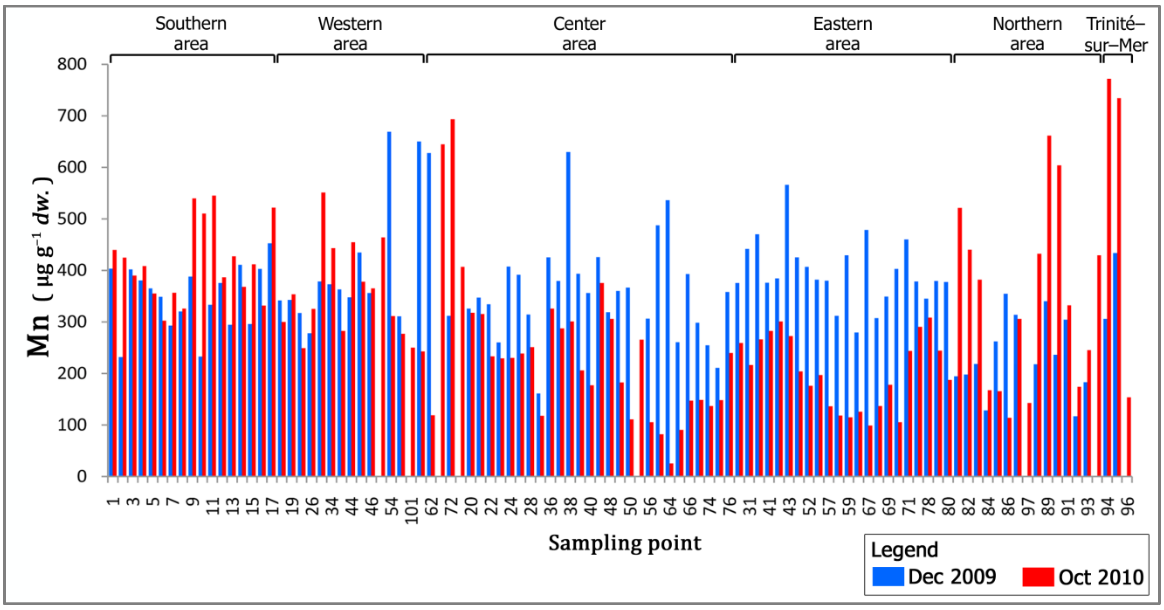

Figure 3–9. *Distribution of Mn based on different zone in Quiberon bay surficial sediments for both samplings.*

The concentrations of Mn in Quiberon bay varied from 117 to 669 µg g^{-1} *dw.* and 25.7 to 781 µg g^{-1} *dw.* for Dec 2009 and Oct 2010 sampling periods, respectively. The mean concentrations were 356±101 µg g^{-1} *dw.* for Dec 2009 sampling and the lower mean concentrations were recorded during Oct 2010, 301±154 µg g^{-1} *dw*. The statistical analysis, *t*–Test shows that the concentrations between Dec 2009 and Oct 2010 sampling periods were significantly different with a *p* value smaller than 0.05.

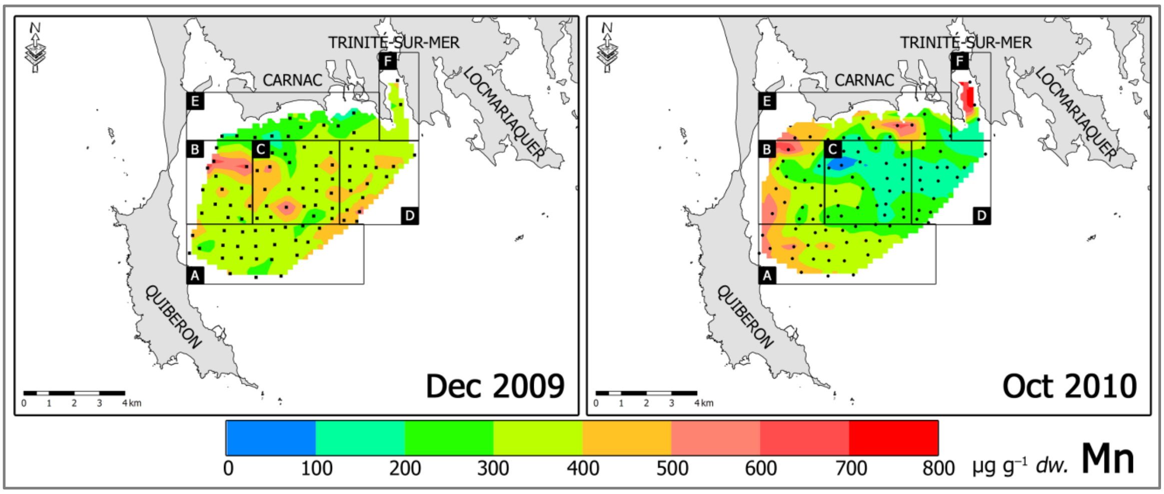

Figure 3–10. *Isopleth maps of Mn accumulation in Quiberon bay surficial sediments for both samplings.*

3.3.1.3 Levels of iron in sediments

Low concentrations of iron (Fe) occurred in the northern zone surficial sediments of the bay, and increasing towards the southern zone (*Figure 3–11; Figure 3–12*). High concentrations were measured at the Trinité–sur–Mer samples for both sampling periods, Dec 2009 and Oct 2010.

The concentrations of Fe were ranged from 0.18 % to 4.57 % in Dec 2009, while in Oct 2010, the concentration ranged from 0.09 % to 3.92 %. Generally, higher concentrations were founded in Dec 2009 sampling compared to Oct 2010 sampling, although the average concentrations did not differ greatly, 1.50±0.94 % and 1.48±0.76 %, respectively. From statistical analysis, *t*–Test, the concentrations for Dec 2009 and Oct 2010 sampling periods were not significantly different with a *p* value greater than 0.05.

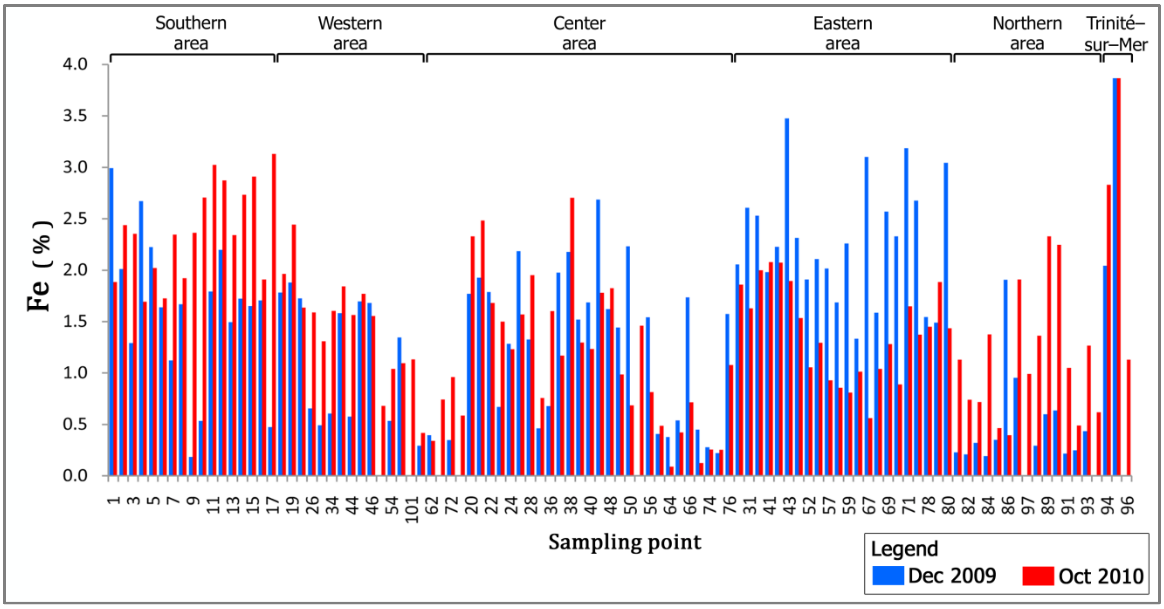

Figure 3–11. *Distribution of Fe based on different zone in Quiberon bay surficial sediments for both samplings.*

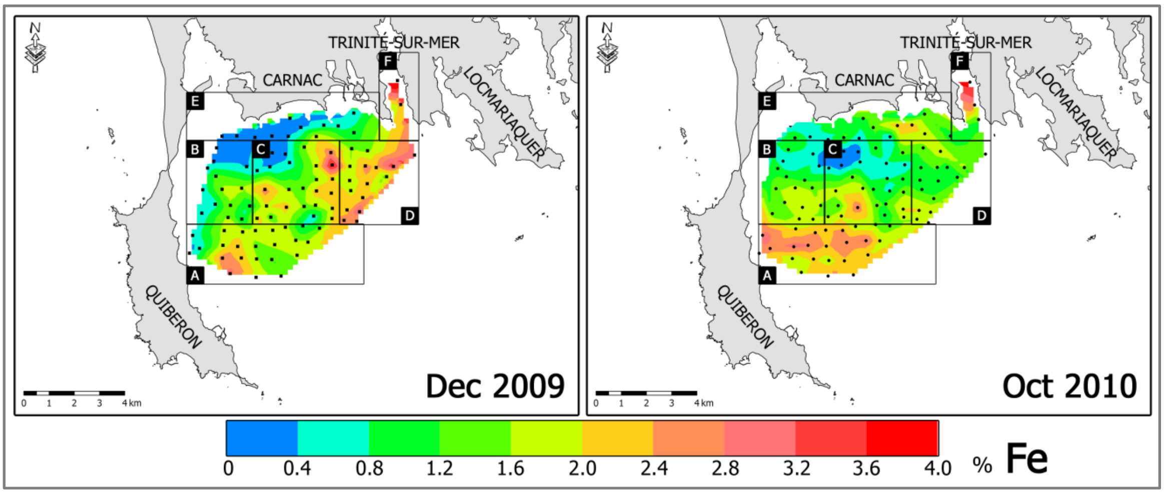

Figure 3–12. *Isopleth maps of Fe accumulation in Quiberon bay surficial sediments for both samplings.*

3.3.1.4 Levels of cobalt in sediments

Figure 3–13 and *Figure 3–14* shows the spatial and temporal distribution and isopleth maps of cobalt (Co) concentrations in Quiberon bay surficial sediments. As shown in the geochemical maps, the innermost zone exhibits a lower concentration while the higher concentration occurred in the outer bay zone.

The mean values for Dec 2009 sampling was 11.7±4.94 µg g^{-1} *dw.*, and the mean value decrease to 9.22±5.75 µg g^{-1} *dw.* for Oct 2010 sampling. Considering the levels of Co in more detail, the concentrations ranging from 2.12 to 19.7 µg g^{-1} *dw.* for Dec 2009 sampling and 1.11 to 23.0 µg g^{-1} *dw.* for Oct 2010 sampling. The *p* value lesser than 0.05 calculated from statistical analysis, *t*–Test shows that there are significant differences in the concentrations for Dec 2009 and Oct 2010 sampling periods.

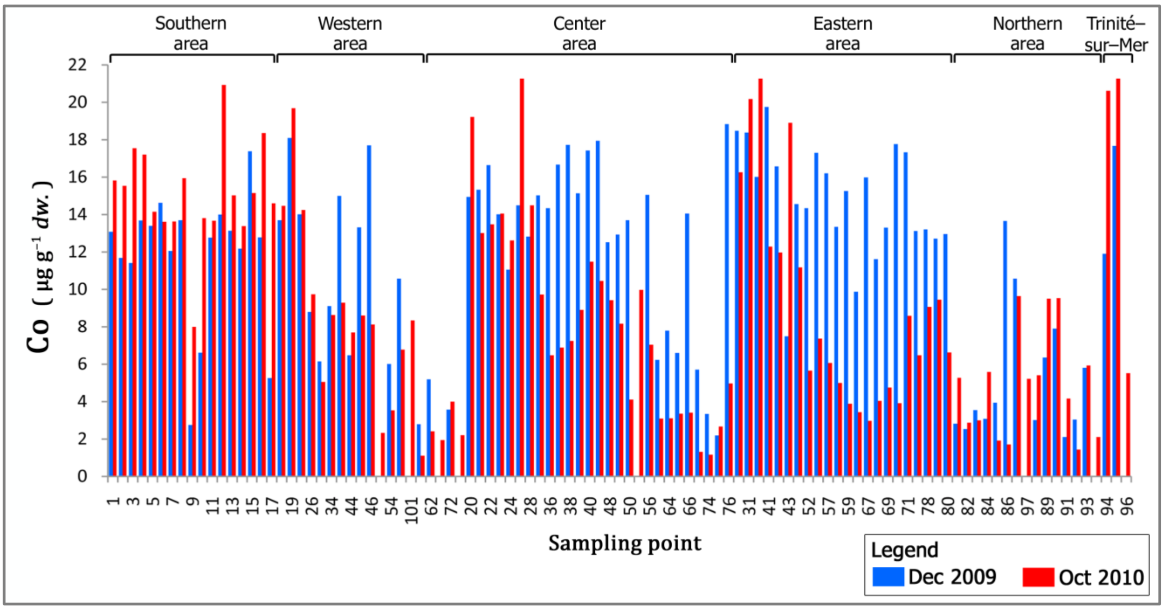

Figure 3–11. *Distribution of Co based on different zone in Quiberon bay surficial sediments for both samplings.*

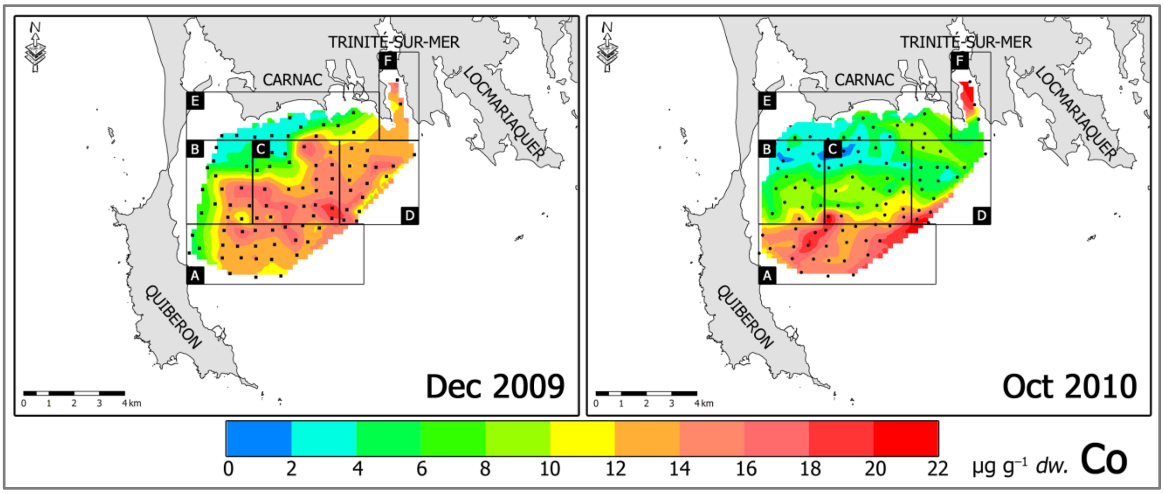

Figure 3–12. *Isopleth maps of Co accumulation in Quiberon bay surficial sediments for both samplings.*

3.3.1.5 *Levels of copper in sediments*

Temporal and spatial distribution and isopleth maps of copper (Cu) concentrations in Quiberon bay surficial sediments are shown in *Figure 3–15* and *Figure 3–16*, respectively. Lower concentrations were observed in the innermost part of the bay while higher concentration occurred in the southern part of the bay and Trinité–sur–Mer area.

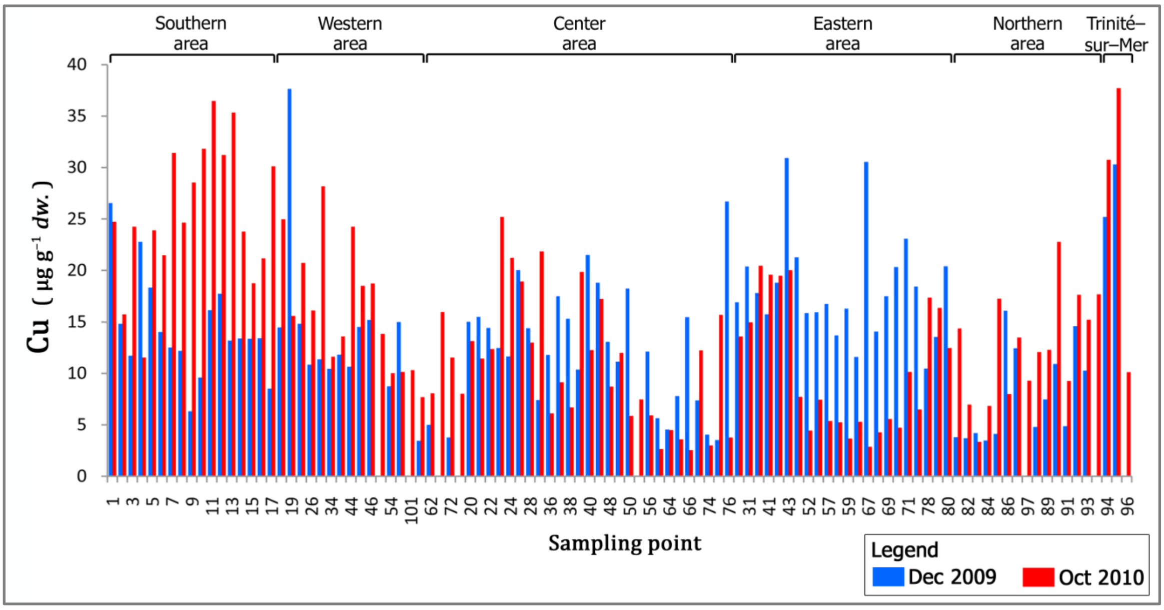

Figure 3–15. *Distribution of Cu based on different zone in Quiberon bay surficial sediments for both samplings.*

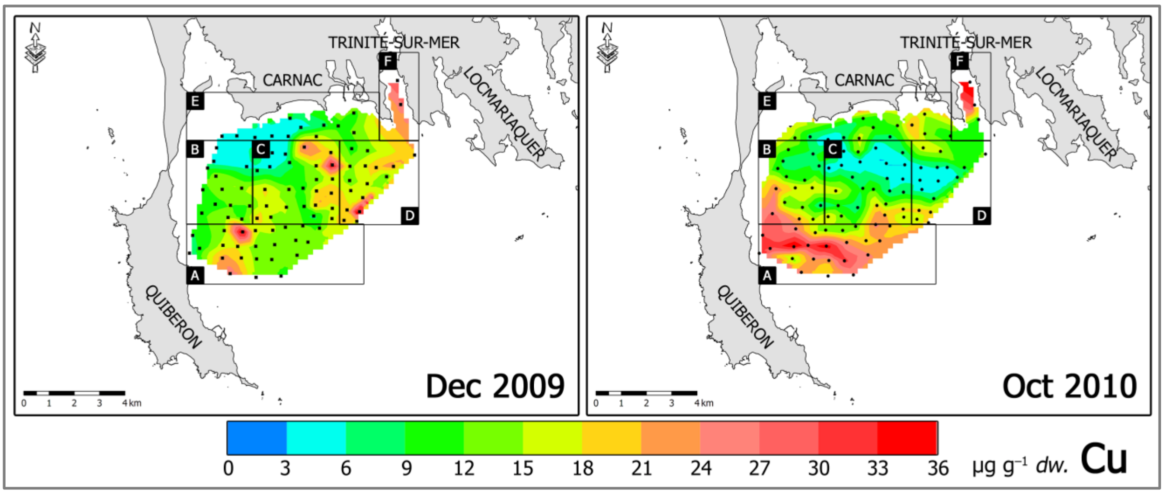

Figure 3–16. *Isopleth maps of Cu accumulation in Quiberon bay surficial sediments for both samplings.*

The mean concentrations of Cu were nearly similar between Dec 2009 and Oct 2010 sampling periods, 14.1±7.24 and 14.7±8.52 µg g^{-1} *dw.*, respectively and this was proven by the statistical analysis, *t*–Test where the calculated value of the *p* value greater than 0.05. The concentrations ranged from 3.45 to 40.9 µg g^{-1} *dw.* during Dec 2009 sampling, while during Oct 2010 sampling, the recorded values were ranged from 2.56 to 37.7 µg g^{-1} *dw*.

3.3.1.6 Levels of zinc in sediments

The spatial and temporal distribution patterns of zinc (Zn) concentration in Dec 2009 and Oct 2010 sampling periods are shown in *Figure 3–17* and *Figure 3–18*, respectively. Higher concentrations were observed in the southern zone and Trinité–sur–Mer area, while the lower concentrations occurred in the innermost part of the bay. The concentrations were ranged from 8.96 to 87.1 µg g^{-1} *dw.* for Dec 2009 sampling and 4.60 to 98.9 µg g^{-1} *dw.* for Oct 2010 sampling. The mean concentrations for Dec 2009 sampling, 42.7 µg g^{-1} *dw.* and this mean value was higher compared to Oct 2010 sampling, 38.9 µg g^{-1} *dw*. From the statistical analysis, *t*–Test, the variance between Dec 2009 and Oct 2010 sampling periods were not significantly different with the *p* value more than 0.05.

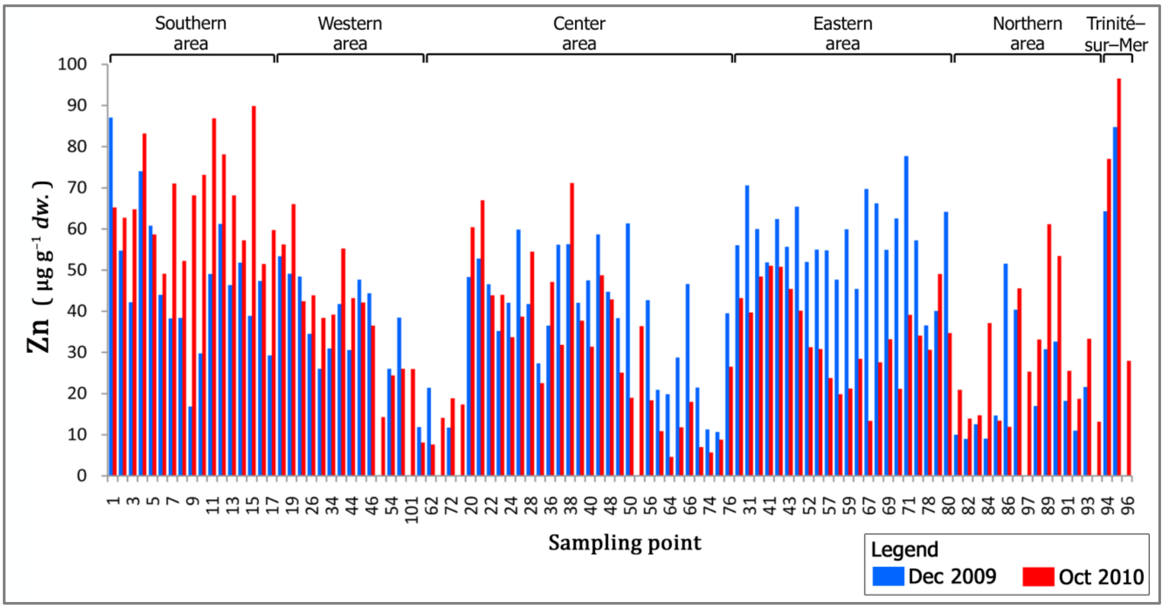

Figure 3–17. *Distribution of Zn based on different zone in Quiberon bay surficial sediments for both samplings.*

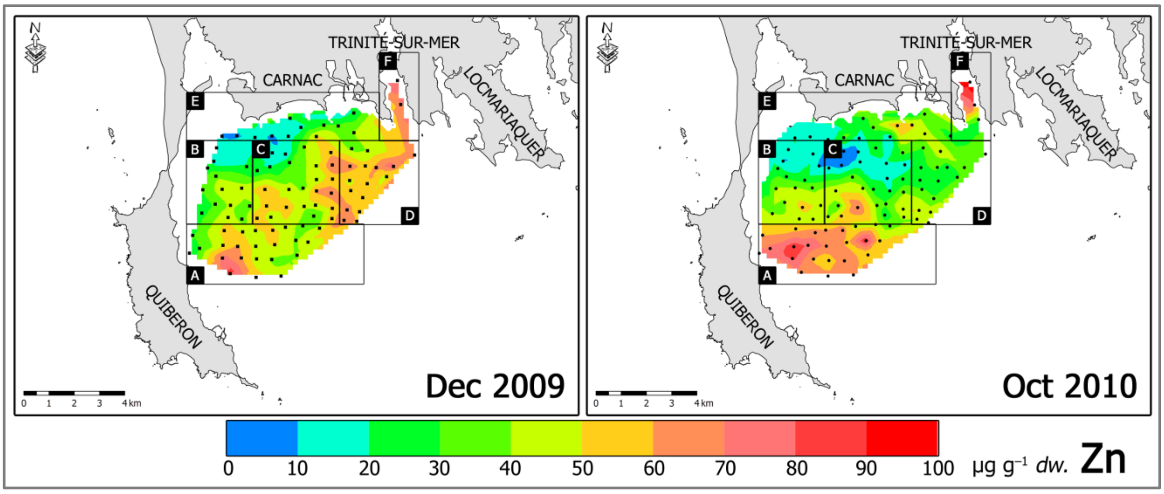

Figure 3–18. *Isopleth maps of Zn accumulation in Quiberon bay surficial sediments for both samplings.*

3.3.1.7 Levels of arsenic in sediments

Figure 3–19 and *Figure 3–20* presents the bar graph and isopleths maps of arsenic (As) concentrations, respectively in Quiberon bay surficial sediments. During Dec 2009 sampling, the innermost part of the bay exhibited a higher concentration compared to the southern part, however during Dec 2010 sampling, an opposite pattern occurred where the innermost part had the low concentration. During this period, high concentrations were observed in the outer bay and Trinité–sur–Mer area.

The concentrations of As in the Quiberon bay surficial sediments varied from 0.16 to 5.98 µg g^{-1} *dw.* and 0.12 to 6.80 µg g^{-1} *dw.* for Dec 2009 and Oct 2010 sampling periods, respectively. The mean concentrations were 2.77 µg g^{-1} *dw.* for Dec 2009 sampling and the lower mean concentrations were recorded during Oct 2010, 2.02 µg g^{-1} *dw*. The statistical analysis, *t*–Test shows that the concentrations between Dec 2009 and Oct 2010 sampling periods were significantly different with a *p* value less than 0.05.

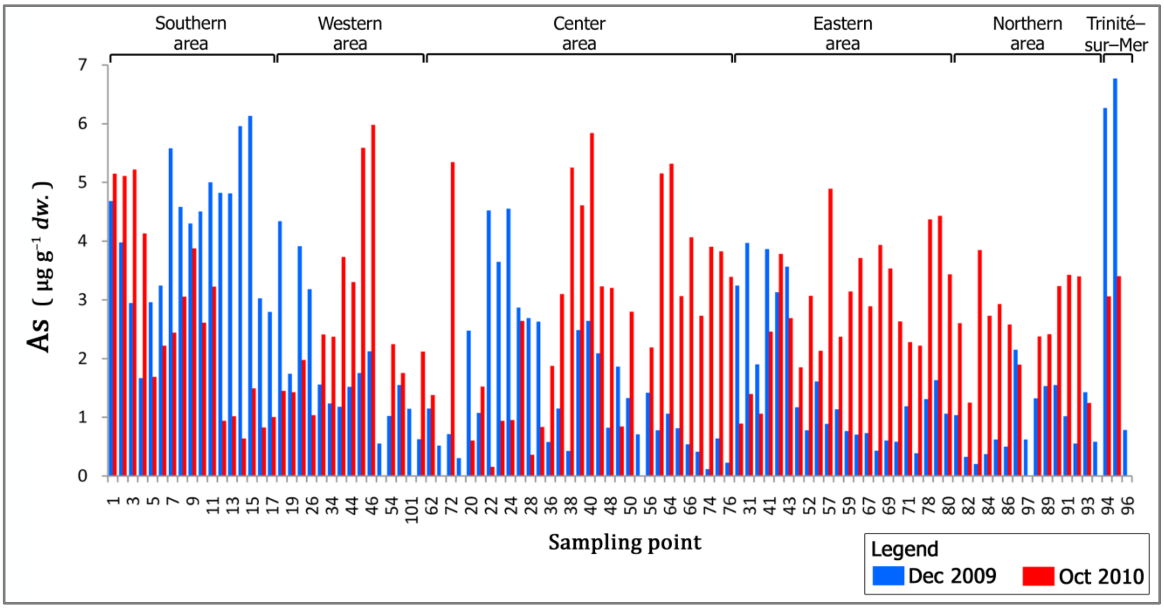

Figure 3–19. *Distribution of As based on different zone in Quiberon bay surficial sediments for both samplings.*

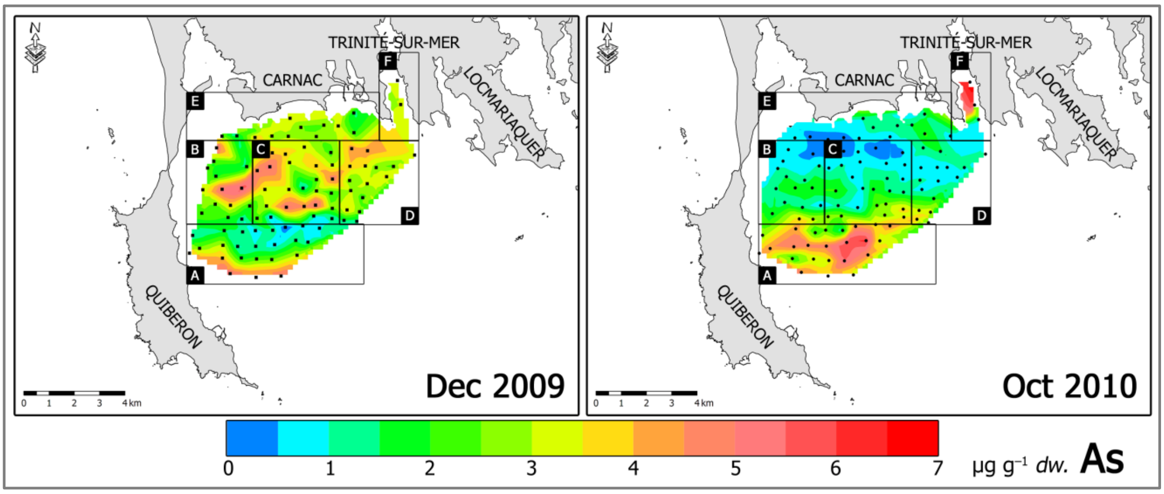

Figure 3–20. *Isopleth maps of As accumulation in Quiberon bay surficial sediments for both samplings.*

3.3.1.8 Levels of cadmium in sediments

This spatial and temporal distribution patterns of cadmium (Cd) concentration are shown in bar graph (*Figure 3–21*) and isopleth maps (*Figure 3–22*). The average concentrations during Dec 2009 was 0.08±0.02 µg g^{-1} *dw.* and drop to 0.06±0.04 µg g^{-1} *dw.* during Oct 2010 sampling. Both highest concentrations, 0.15 µg g^{-1} *dw.* during Dec 2009 sampling and 0.19 µg g^{-1} *dw.* during Oct 2010 sampling were observed at Trinité–sur–Mer area. Meanwhile the lowest concentrations of Cd, 0.02 µg g^{-1} *dw.* and 0.01 µg g^{-1} *dw.* for Dec 2009 and Oct 2010 sampling periods, respectively occurred in the innermost zone of the bay and the concentrations increase towards the outer bay zone. The statistical analysis, *t*–Test shows that there was a significant difference the concentrations for Dec 2009 and Oct 2010 sampling periods with the *p* value less than 0.05.

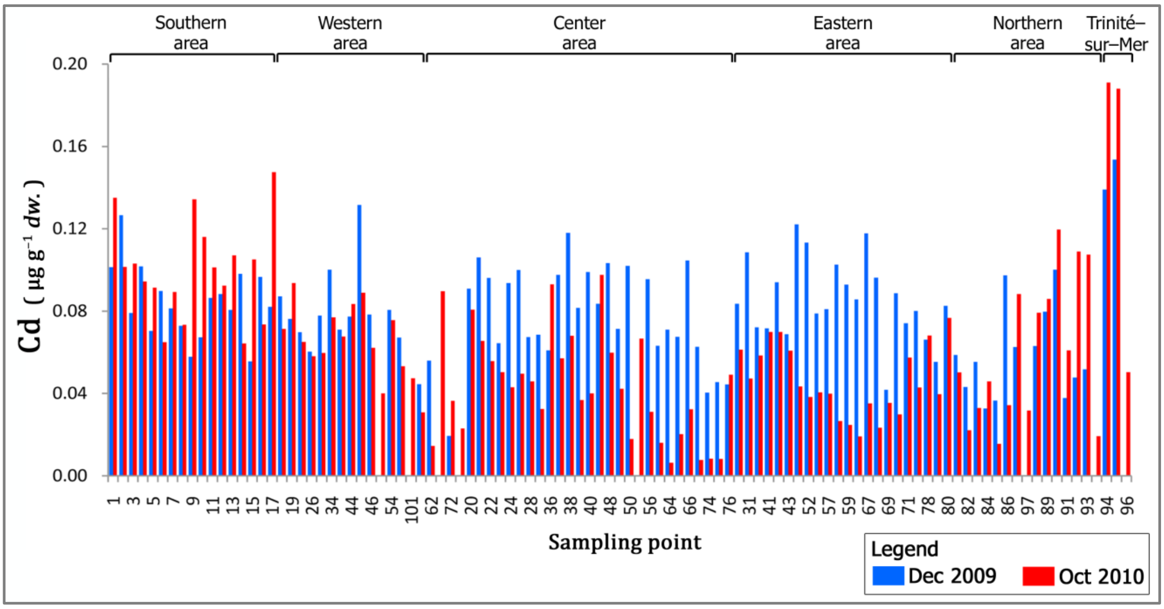

Figure 3–21. *Distribution of Cd based on different zone in Quiberon bay surficial sediments for both samplings.*

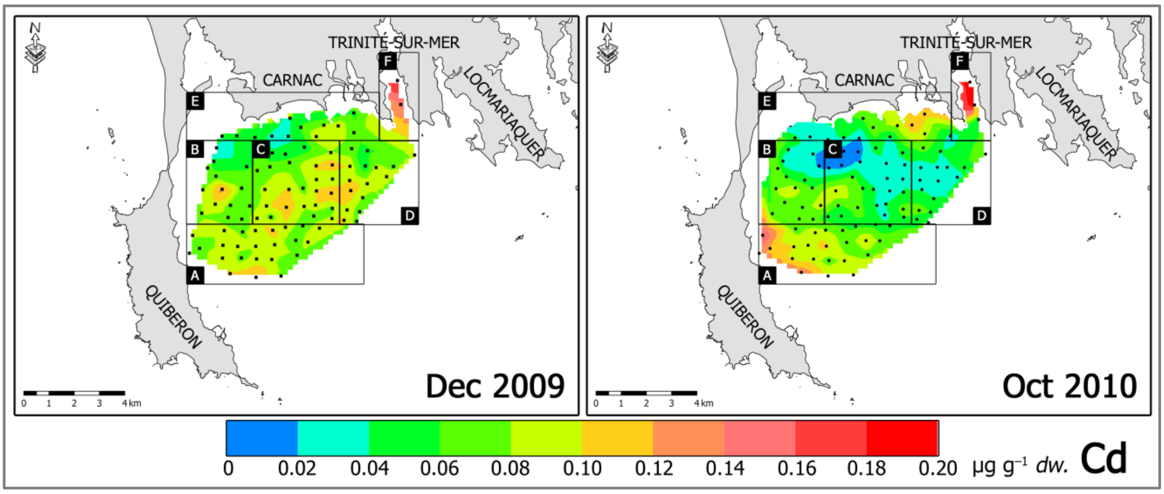

Figure 3–22. *Isopleth maps of Cd accumulation in Quiberon bay surficial sediments for both samplings.*

3.3.1.9 Levels of mercury in sediments

Figure 3–23 and *Figure 3–24* shows the spatial and temporal distributions and isopleth maps of mercury (Hg) concentrations in Quiberon bay surficial sediments. As shown in the geochemical map, the northern part exhibits a lower concentration while the higher concentration occurred in the southern part.

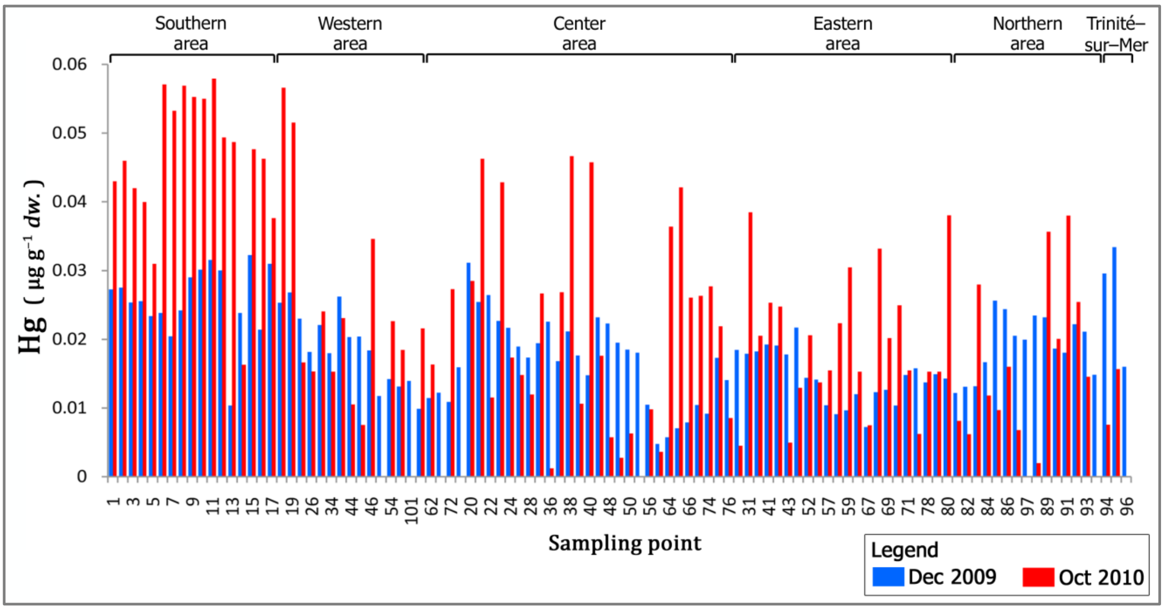

Figure 3–23. *Distribution of Hg based on different zone in Quiberon bay surficial sediments for both samplings.*

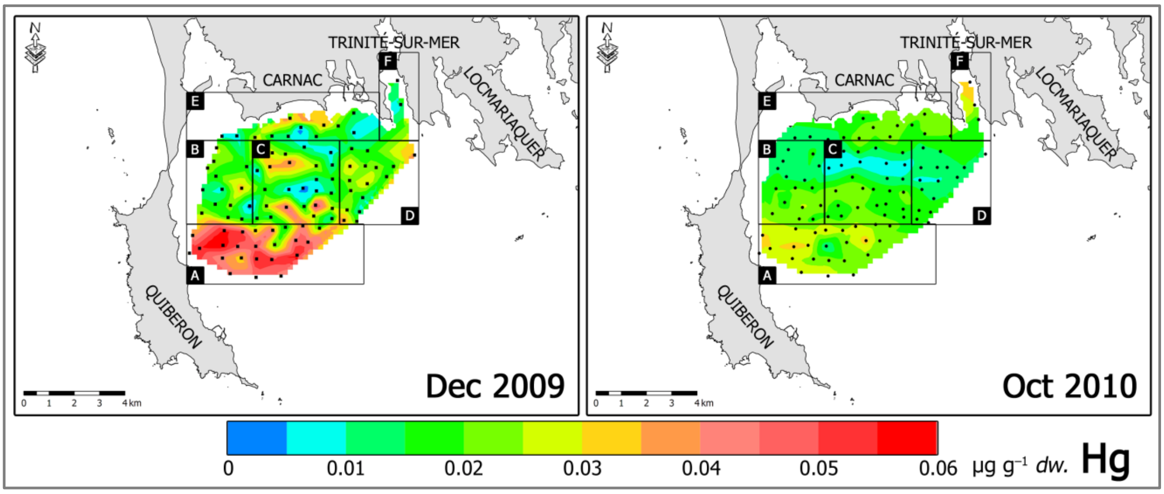

Figure 3–24. *Isopleth maps of Hg accumulation in Quiberon bay surficial sediments for both samplings.*

The mean values for Dec 2009 sampling was 0.025±0.016 µg g^{-1} *dw.*, and the mean value decrease to 0.019±0.007 µg g^{-1} *dw.* for Oct 2010 sampling. Considering Hg in more detail, the concentrations ranging from 0.001 to 0.060 µg g^{-1} *dw.* for Dec 2009 sampling and 0.005 to 0.033 µg g^{-1} *dw.* for Oct 2010 sampling. The *p* value less than 0.05 calculated from statistical analysis, *t*–Test shows that there are significant differences in the concentrations for Dec 2009 and Oct 2010 sampling periods.

3.3.1.10 Levels of lead in sediments

Figure 3–25 and *Figure 3–26* shows the spatial and temporal distribution of lead (Pb) concentrations in Quiberon bay surficial sediments. During Dec 2009 sampling, the concentrations were well distributed in the bay sediments where high concentrations were occurred in the southern zone near the coastal area. Higher concentrations of Pb also recorded at Trinité–sur–Mer area, and this pattern was also observed during Oct 2010 sampling. During Oct 2010 sampling, low concentrations were observed at the centre zone and innermost zone of the bay. The mean value 17.9±3.61 µg g^{-1} *dw.* (8.88–28.0 µg g^{-1} *dw.*) was higher during Dec 2009 sampling and decreased to 12.3±3.96 µg g^{-1} *dw.* (3.61–24.1 µg g^{-1} *dw.*) during the Oct 2010 sampling. There is no significant difference in the concentrations for the Dec 2009 sampling compared with Oct 2010 sampling with the *p* value smaller than 0.05 calculated from statistical test, *t*–Test.

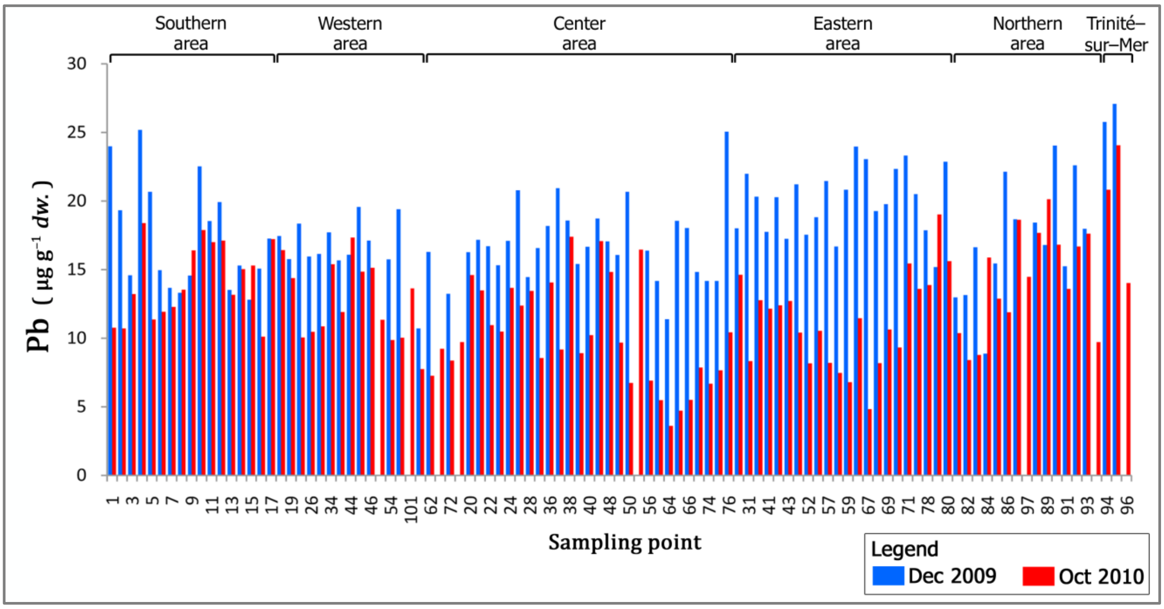

Figure 3–25. *Distribution of Pb based on different zone in Quiberon bay surficial sediments for both samplings.*

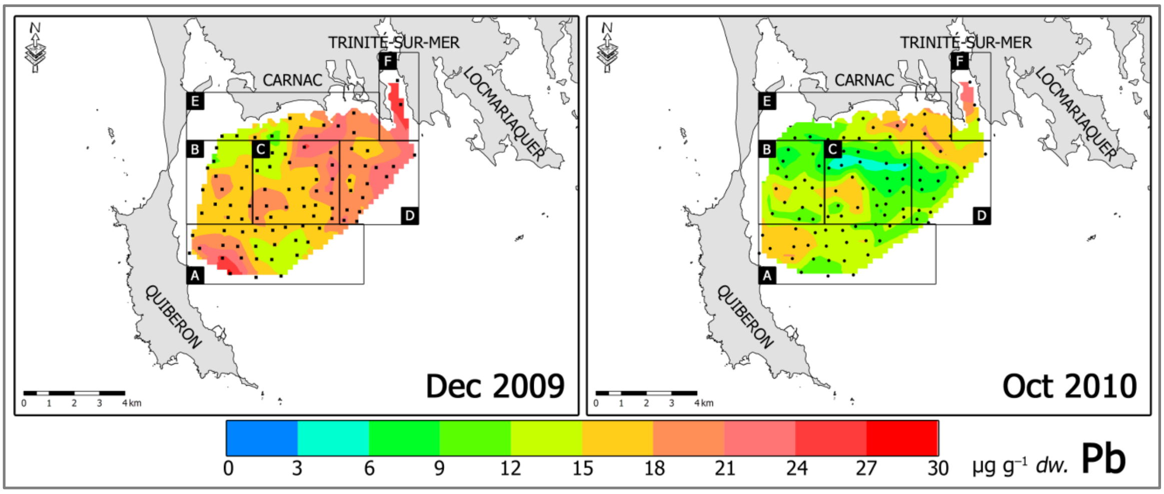

Figure 3–26. *Isopleth maps of Pb accumulation in Quiberon bay surficial sediments for both samplings.*

3.3.2 Gulf of Morbihan case study

3.3.2.1 Levels of chromium in sediments

Concentrations of chromium (Cr) in all sampling locations in the gulf of Morbihan surficial sediments are presented in *Figure 3–27* and geochemical maps by ArcGIS software are shown in *Figure 3–28*. The distribution exhibits a strong inclining trend in concentration from the gulf entrance zone towards the upper reached and eastern zone of the gulf. The isolated high values occurred in the rivers system zone (Auray, Marle and Noyalo rivers) throughout the catchment.

The concentrations of Cr ranged from 5.43 to 112 μg g^{-1} *dw.* for Dec 2009 sampling and 6.73 to 71.1 μg g^{-1} *dw.* for Oct 2010 sampling. The average concentrations for two sampling periods were about parallel, 36.2±23.9 μg g^{-1} *dw.* and 38.4±18.5 μg g^{-1} *dw.* in Dec 2009 and Oct 2010 sampling periods, respectively. Statistical analysis, *t*–Test shows that the concentrations between both sampling periods were varied significantly with the *p* value smaller than 0.05.

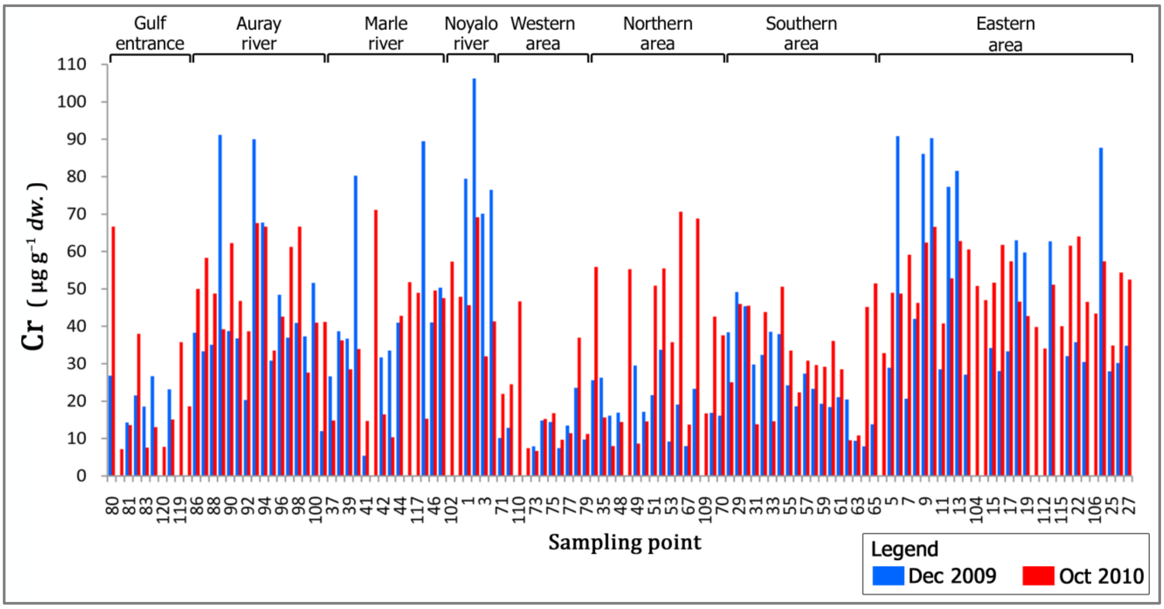

Figure 3–27. *Distribution of Cr based on different zone in gulf of Morbihan surficial sediments for both samplings.*

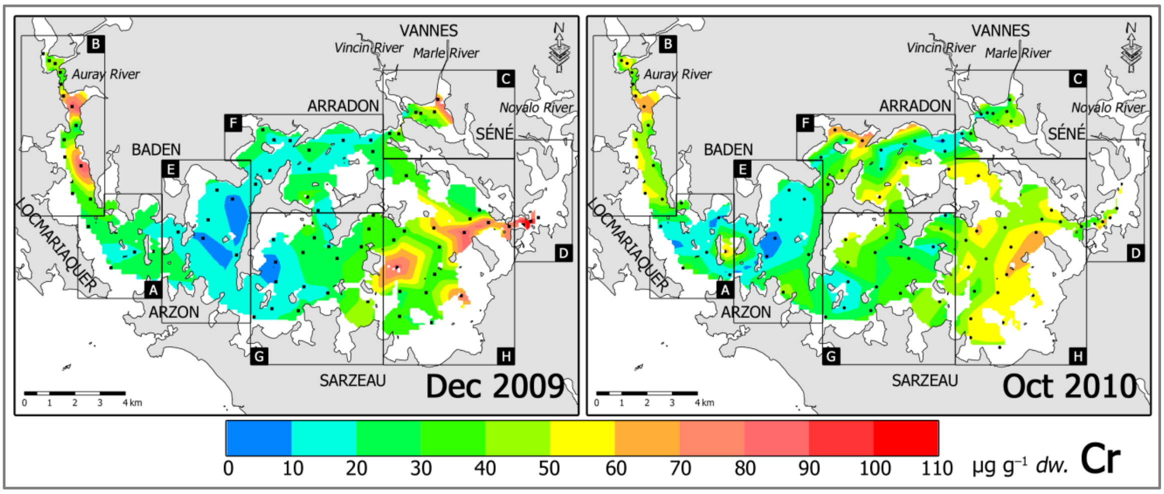

Figure 3–28. *Isopleth maps of Cr accumulation in gulf of Morbihan surficial sediments for both samplings.*

3.3.2.2 Levels of manganese in sediments

Distribution of manganese (Mn) concentrations in surficial sediments from the gulf of Morbihan is shown in bar graph (*Figure 3–27*) and in geochemical maps (*Figure 3–28*) for all sampling points. Higher concentrations occurred in sediment samples from the rivers and eastern zones throughout the gulf of Morbihan compared to the western zone.

The mean concentrations of Mn, 278±140 µg g^{-1} *dw.* in Dec 2009 sampling and increased to 380±107 µg g^{-1} *dw.* in Oct 2010 sampling. The concentrations ranged from 16.6 to 732 for Dec 2009 sampling and 128 to 652 µg g^{-1} *dw.* in Oct 2010 sampling. From the statistical analysis, *t*–Test, the concentrations were not differed significantly between the Dec 2009 and Oct 2010 sampling periods as the calculated *p* value greater than 0.05.

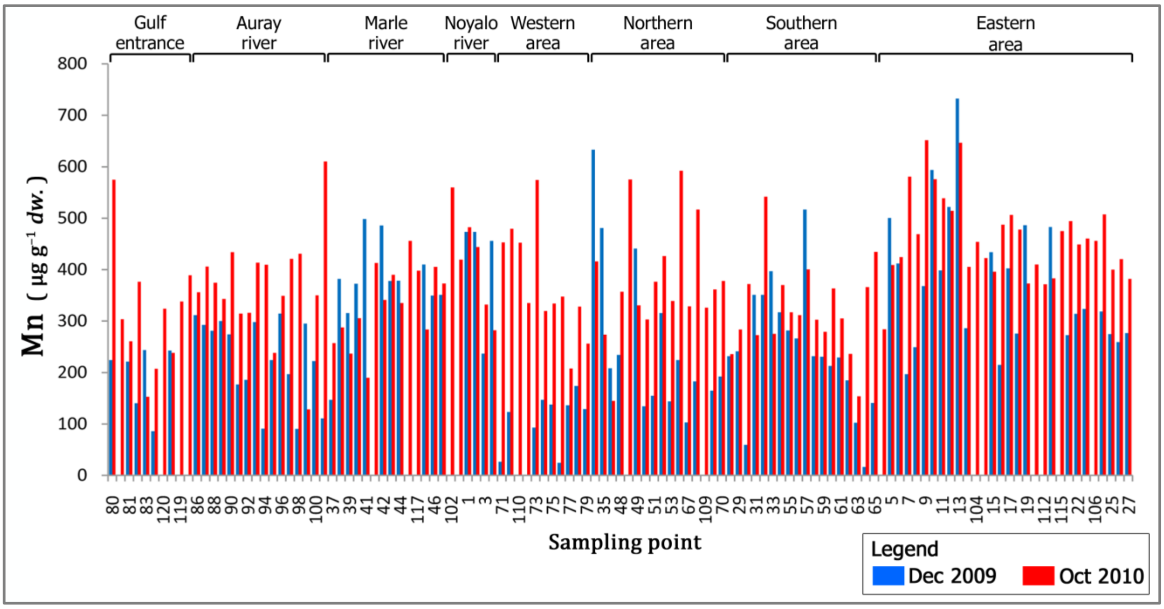

Figure 3–27. *Distribution of Mn based on different zone in gulf of Morbihan surficial sediments for both samplings.*

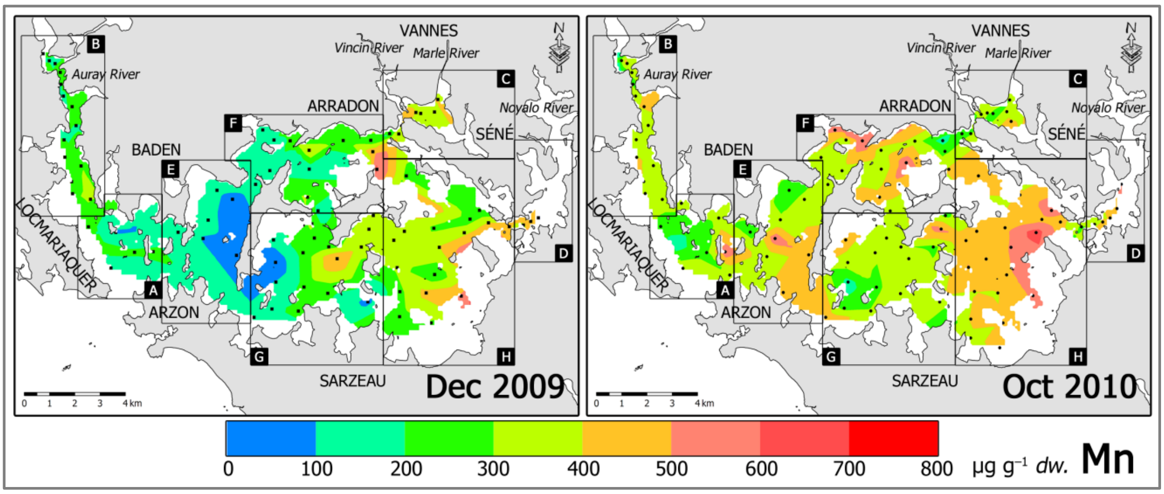

Figure 3–28. *Isopleth maps of Mn accumulation in gulf of Morbihan surficial sediments for both samplings.*

3.3.2.3 Levels of iron in sediments

The iron (Fe) concentrations of each sampling location in the gulf of Morbihan surficial sediments are shown in *Figure 3–29*. Meanwhile, the isopleths maps of the concentrations for both sampling periods are shown in *Figure 3–30*. Higher Fe concentrations occurred in the rivers zone in the gulf and the concentrations were found to increase towards the eastern zone of the gulf.

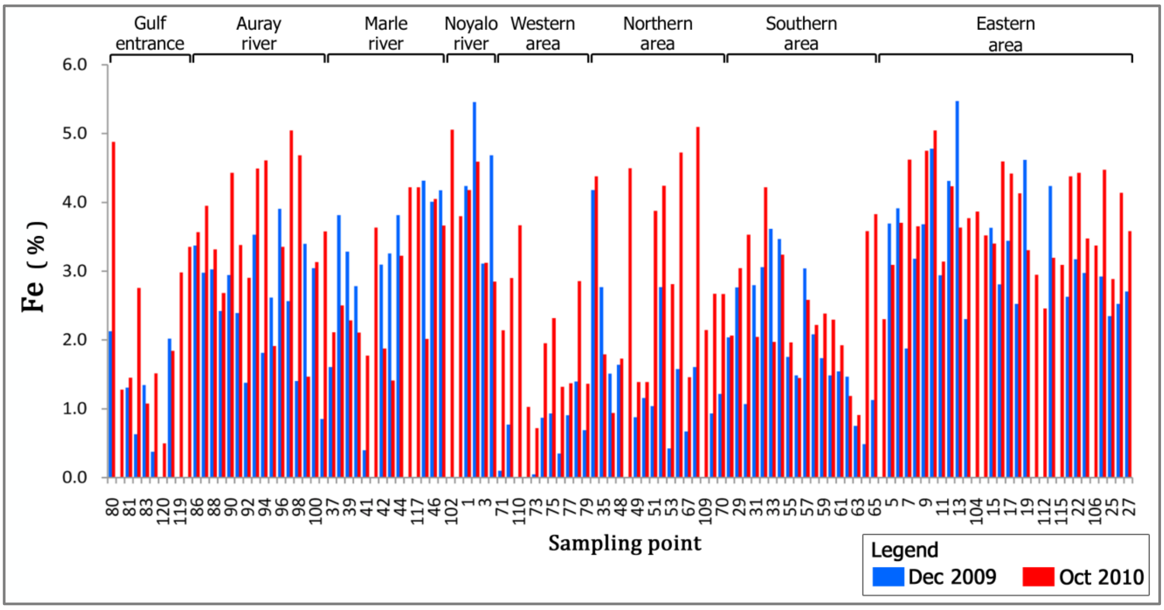

Figure 3–29. *Distribution of Fe based on different zone in gulf of Morbihan surficial sediments for both samplings.*

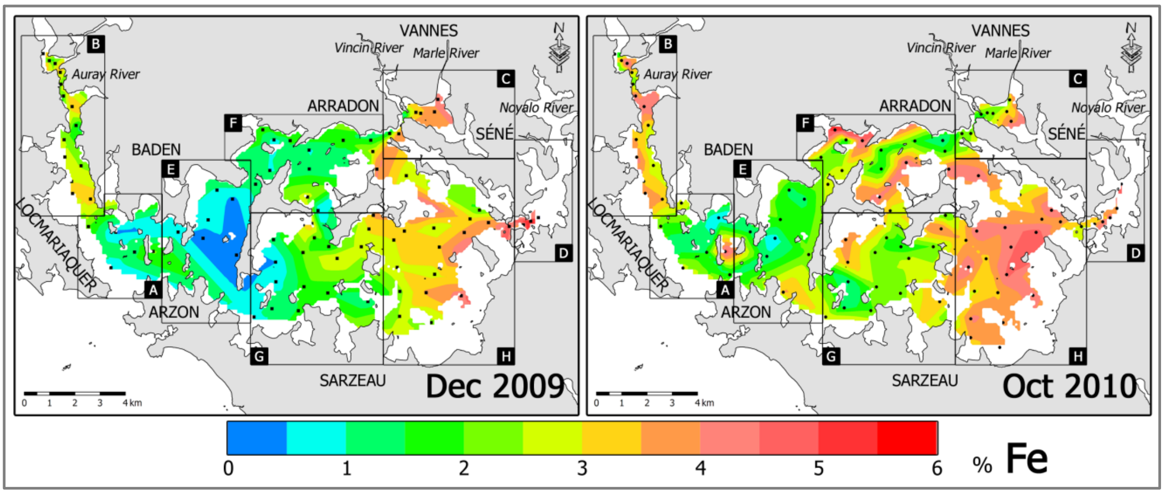

Figure 3–30. *Isopleth maps of Fe accumulation in gulf of Morbihan surficial sediments for both samplings.*

The concentrations of Fe varied from 0.05 to 5.47 % and 0.50 to 5.10 % for Dec 2009 and Oct 2010 sampling periods, respectively. Sediment samples from Oct 2010 sampling showed the higher mean total concentrations, 3.01±1.17 % than the Dec 2009 sampling, 2.40±1.29 %. The *p* value smaller than 0.05 calculated from the statistical test, *t*–Test shows that there is a significant difference in the concentrations during Dec 2009 and Oct 2010 sampling periods.

3.3.2.4 Levels of cobalt in sediments

The concentrations of cobalt (Co) for all sampling points are presented in *Figure 3–30*. The geochemical isopleth maps of the concentration in the surficial sediments are shown in *Figure 3–31*. Generally, uniform concentrations were occurred during Oct 2010 sampling compared to Dec 2009 sampling where high concentrations observed in the rivers and eastern zones of the gulf. Statistical analysis, *t*–Test shows that there is a significant difference between the two sampling periods as the *p* value smaller than 0.05. The mean concentrations for Dec 2009 sampling was 14.4±5.31 µg g^{-1} *dw.*, ranged between 0.19 and 6.16 µg g^{-1} *dw*. Meanwhile, the low mean value was recorded for Oct 2010 samplings, 10.9±3.06 µg g^{-1} *dw.* ranged from 1.27 to 6.30 µg g^{-1} *dw*.

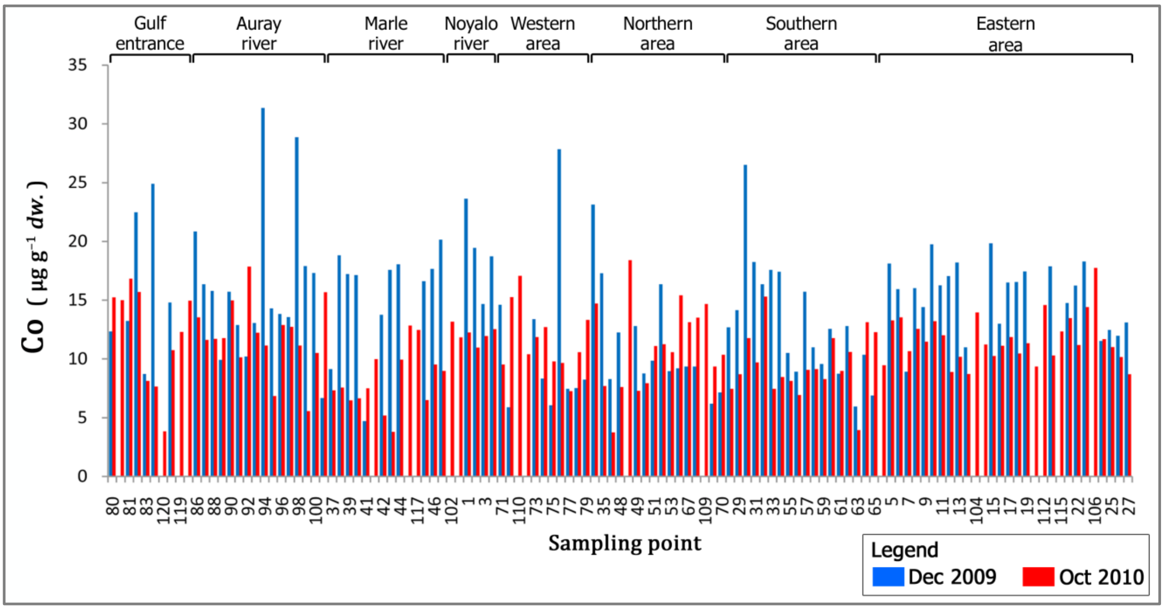

Figure 3–30. *Distribution of Co based on different zone in gulf of Morbihan surficial sediments for both samplings.*

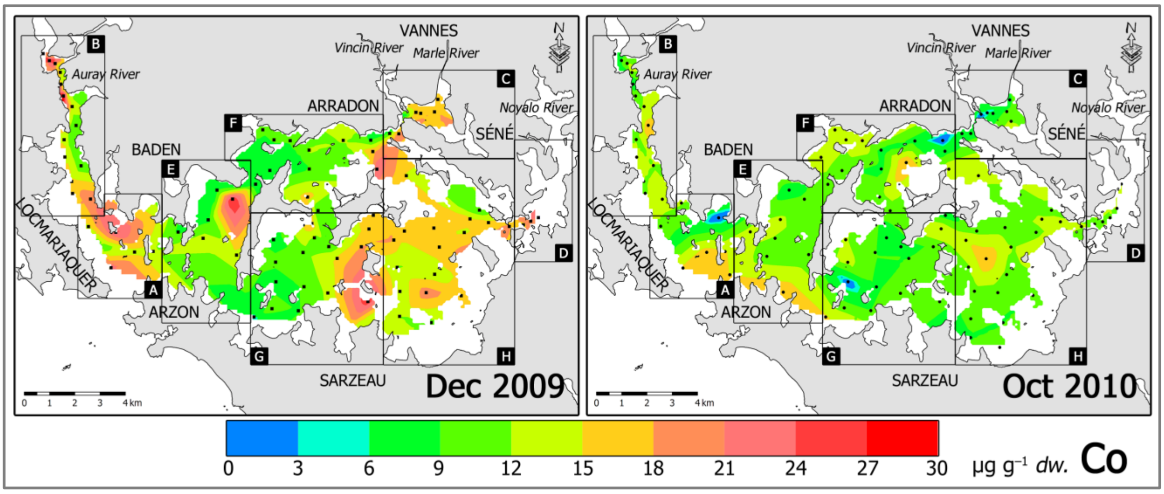

Figure 3–31. *Isopleth maps of Co accumulation in gulf of Morbihan surficial sediments for both samplings.*

3.3.2.5 *Levels of copper in sediments*

Figure 3–32 shows the concentrations of copper (Cu) in all sampling locations in bar graph and the geochemical isopleth maps are presented in *Figure 3–33*. As shown, the tendency from the gulf entrance zone to the gulf inner zone showed a better uniformity of the concentrations in Dec 2009 sampling, while during Oct 2010 sampling, the concentrations were observed to increase towards the eastern zone of the study area.

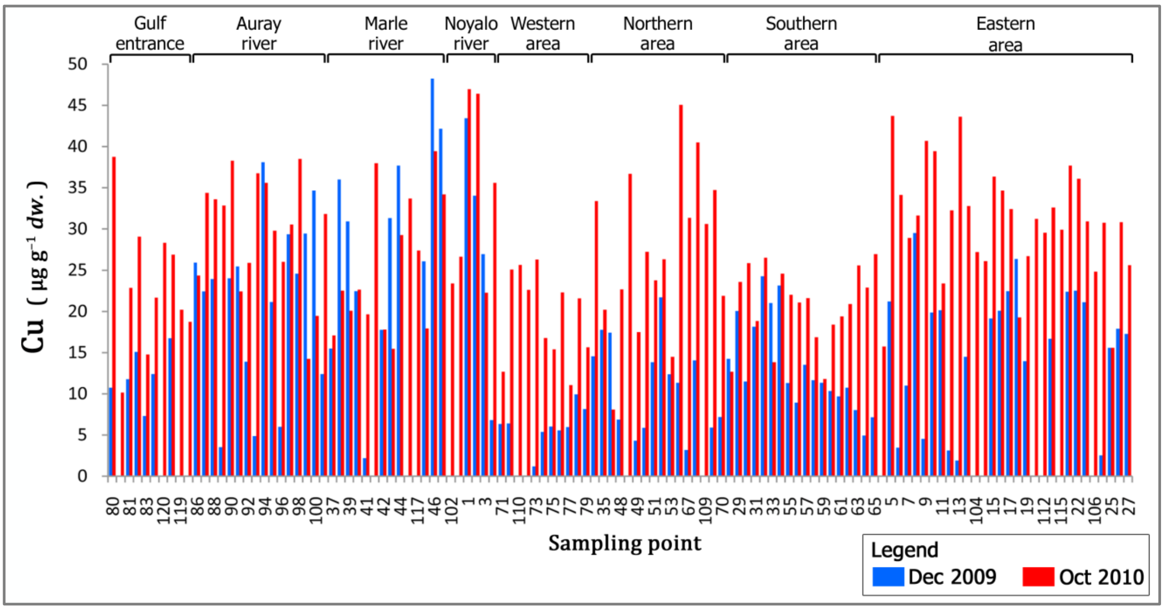

Figure 3–32. *Distribution of Cu based on different zone in gulf of Morbihan surficial sediments for both samplings.*

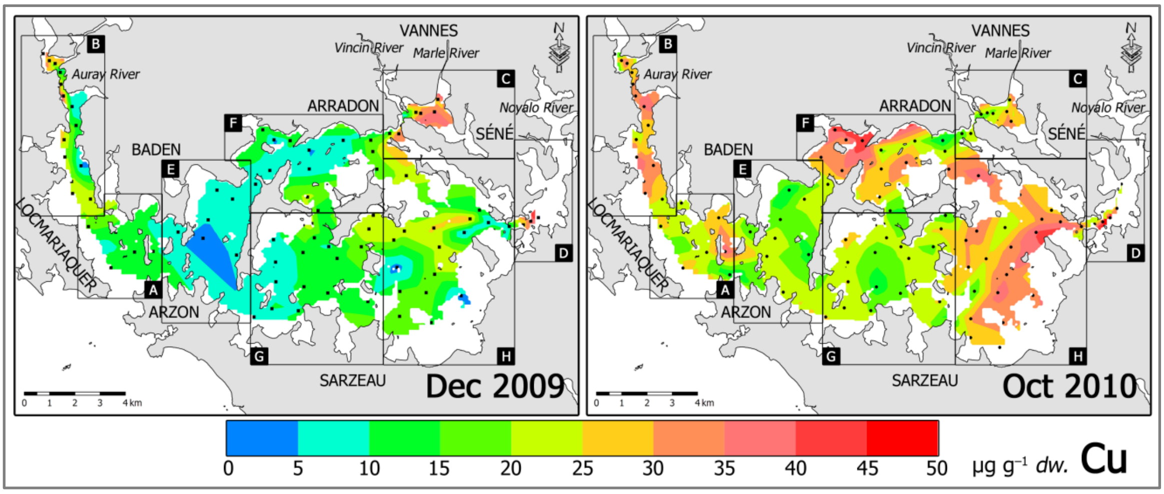

Figure 3–33. *Isopleth maps of Cu accumulation in gulf of Morbihan surficial sediments for both samplings.*

The mean concentrations differ significantly, 16.4 μg g^{-1} *dw.* (1.20–48.4 μg g^{-1} *dw.*) lower during Dec 2009 sampling and increase to 26.5 μg g^{-1} *dw.* (8.10–47.0 μg g^{-1} *dw.*) during the Oct 2010 sampling. This is also supported by statistical analysis, *t*–Test of the value of *p* smaller than 0.05.

3.3.2.6 Levels of zinc in sediments

Figure 3–34 shows the bar graph for the spatial distribution of zinc (Zn) concentrations in gulf of Morbihan surficial sediments for Dec 2009 and Oct 2010 sampling periods. To be more detail, the data are expressed as contour maps in *Figure 3–35*. The concentrations for both sampling periods showed a common trend; concentrations were found to increase toward the eastern zone of the gulf, while the low concentration occurred at the western zone near the entrance of the gulf.

Concentrations of Zn ranged from 4.78 to 85.4 μg g^{-1} *dw.* and 9.18 to 90.0 μg g^{-1} *dw.* in Dec 2009 and Oct 2010 sampling periods, respectively. The average concentrations do not differ significantly, 38.1±19.1 μg g^{-1} *dw.* for Dec 2009 sampling and 38.7±15.9 μg g^{-1} *dw.* for Oct 2010 sampling and proved by statistical analysis, *t*–Test where the *p* value greater than 0.05.

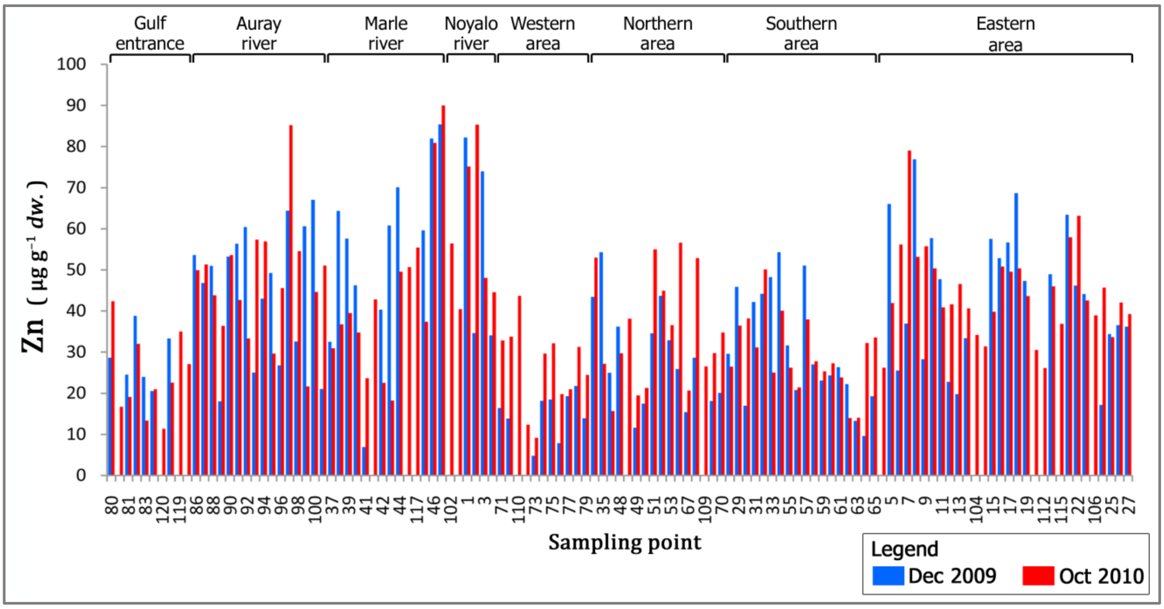

Figure 3–37. *Distribution of Zn based on different zone in gulf of Morbihan surficial sediments for both samplings.*

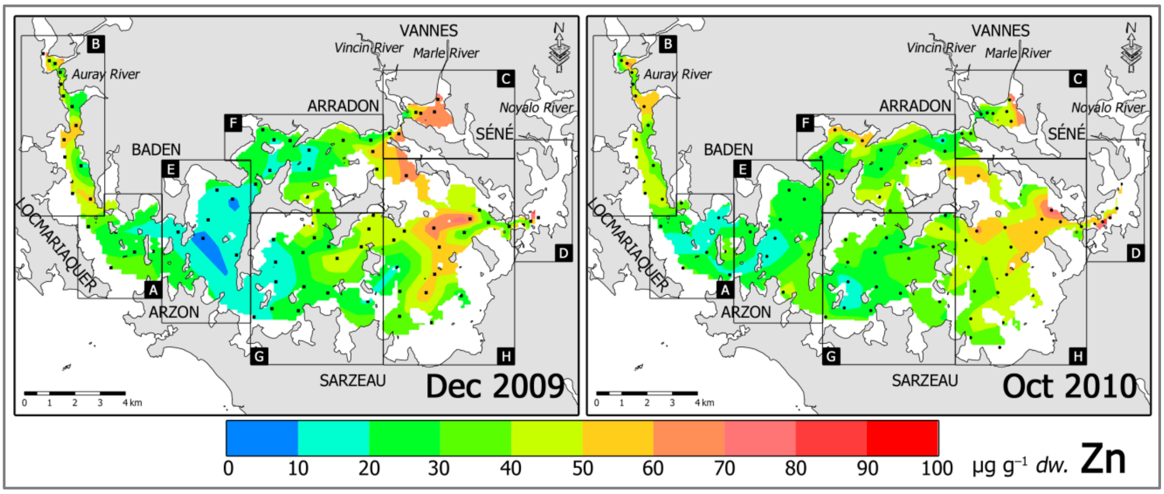

Figure 3–38. *Isopleth maps of Zn accumulation in gulf of Morbihan surficial sediments for both samplings.*

3.3.2.7 Levels of arsenic in sediments

For better precision, the concentrations of arsenic (As) for all sampling points are presented in *Figure 3–39*. The geochemical isopleth maps of the concentration of As in the surficial sediments are shown in *Figure 3–40*. Generally, lower and more uniform concentration occurred during Dec 2009 sampling compared to

Oct 2010 sampling where higher concentration observed in the rivers and eastern zones of the gulf. However, statistical analysis, *t*–Test shows that there is no significant difference between the two sampling periods. The mean concentrations for Dec 2009 sampling was 4.30±2.22 µg g^{-1} *dw.*, ranged between 0.19 and 6.16 µg g^{-1} *dw*. Meanwhile, the lower mean value was recorded for Oct 2010 samplings, 3.69±1.26 µg g^{-1} *dw.* ranged from 1.27 to 6.30 µg g^{-1} *dw*.

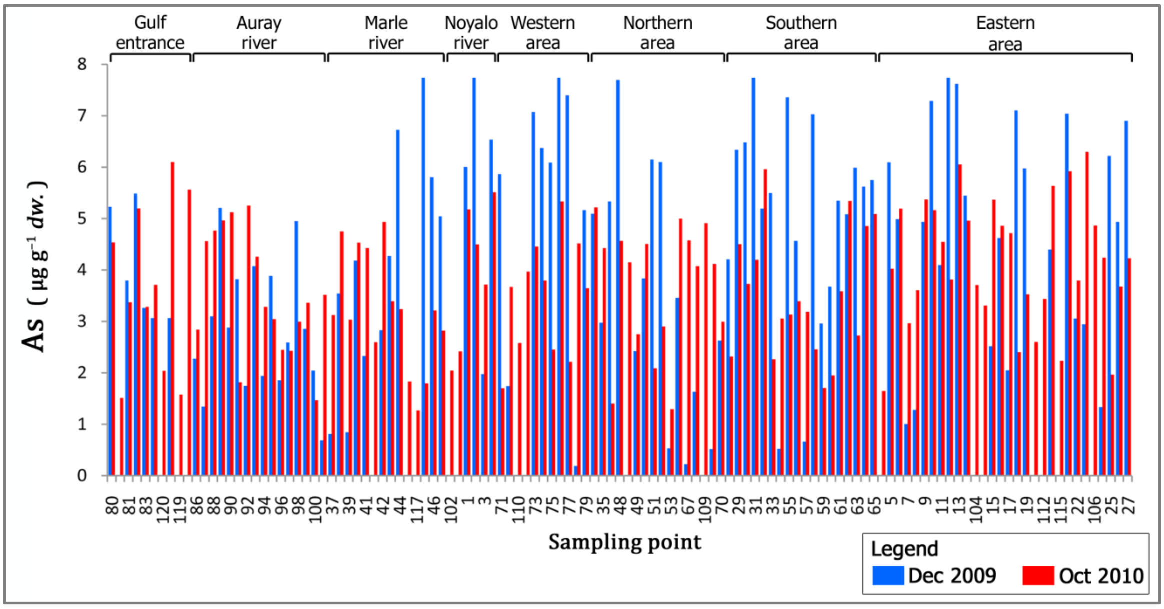

Figure 3–39. *Distribution of As based on different zone in gulf of Morbihan surficial sediments for both samplings.*

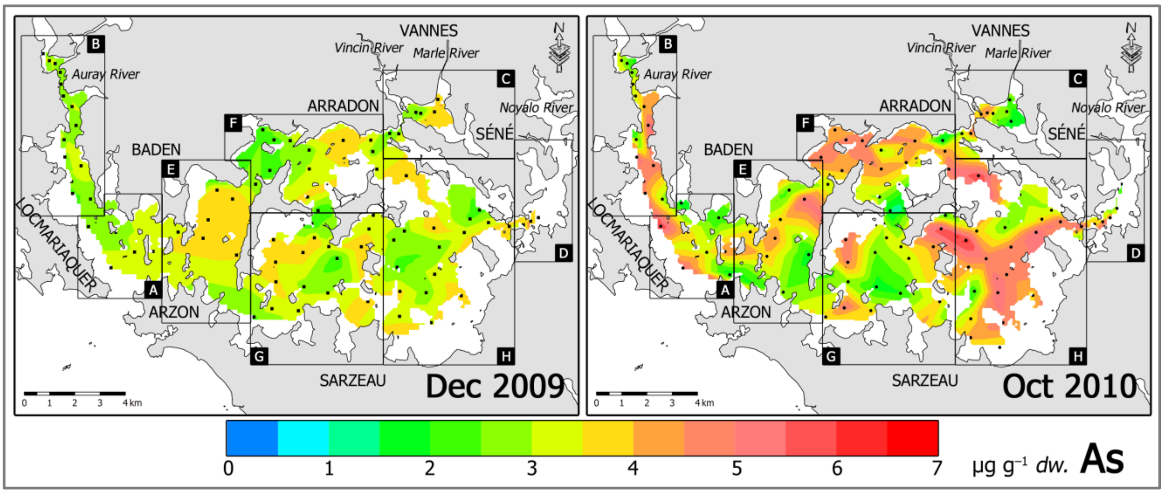

Figure 3–40. *Isopleth maps of As accumulation in gulf of Morbihan surficial sediments for both samplings.*

3.3.2.8 Levels of cadmium in sediments

Figure 3–41 shows the details distribution of cadmium (Cd) concentration for all sampling points, while the geochemical maps of Cd concentrations in gulf of Morbihan surficial sediments are shown in *Figure 3–42*. The eastern and rivers zones throughout the catchment were enriched with the concentrations compared to the western zone for both sampling periods, Dec 2009 and Oct 2010.

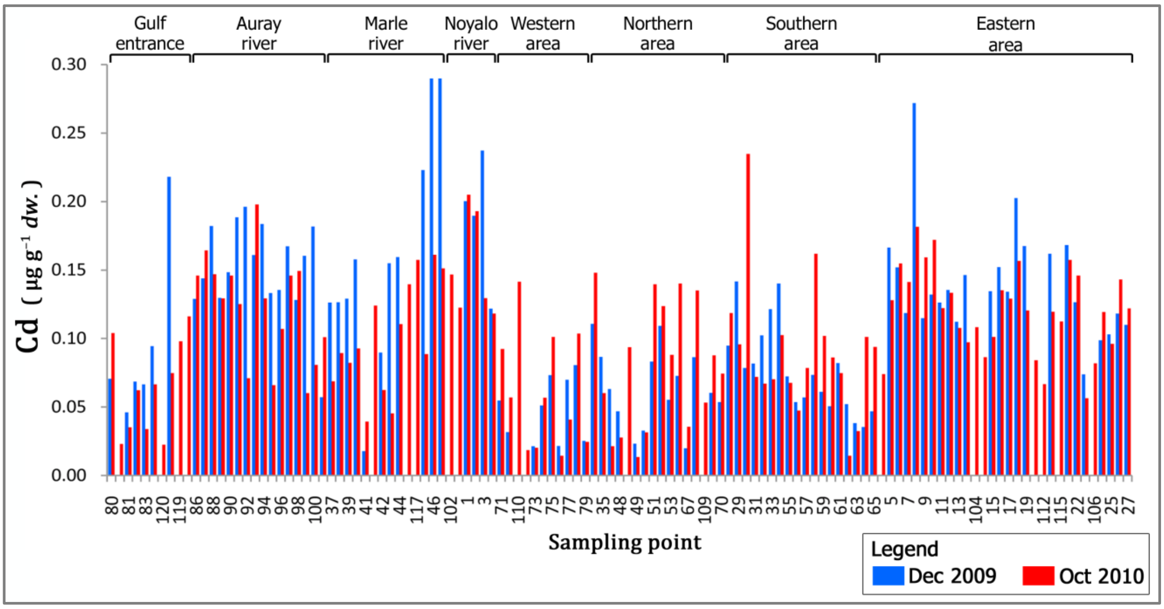

Figure 3–41. *Distribution of Cd based on different zone in gulf of Morbihan surficial sediments for both samplings.*

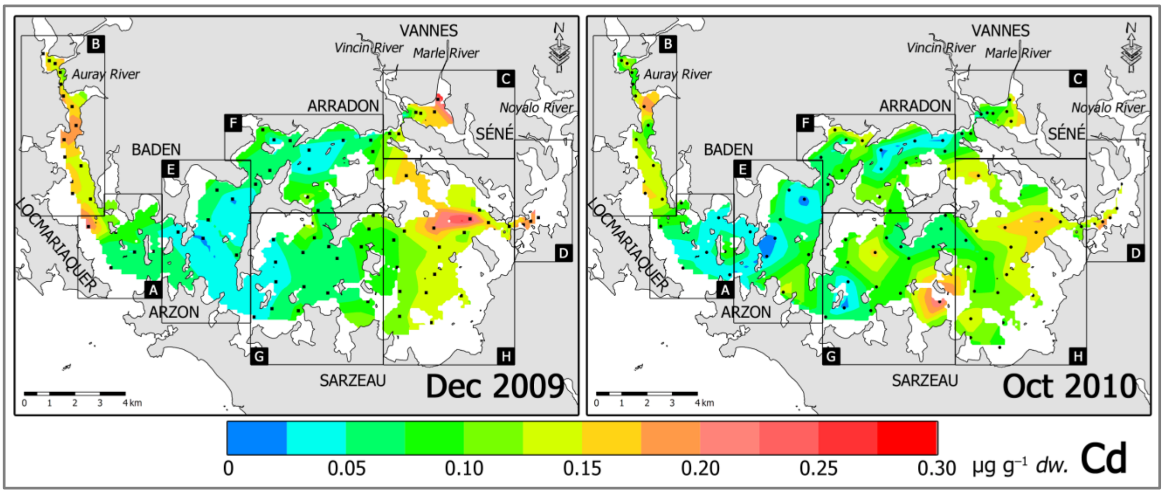

Figure 3–42. *Isopleth maps of Cd accumulation in gulf of Morbihan surficial sediments for both samplings.*

A similar mean concentrations for both sampling periods were recorded, 0.11±0.06 and 0.10±0.05 µg g^{-1} *dw.* for Dec 2009 and Oct 2010 sampling periods, respectively. The *p* value which greater than 0.05 calculated from statistical analysis, *t*–Test shows that there is no significant different in the concentrations between Dec 2009 and Oct 2010 sampling periods. The concentrations ranged globally 0.02 to 0.30 µg g^{-1} *dw.* for Dec 2009 sampling samples, while lower concentrations were observed in Oct 2010 sampling, ranged from 0.01 to 0.23 µg g^{-1} *dw*.

3.3.2.9 Levels of mercury in sediments

The spatial and temporal distribution of mercury (Hg) concentrations in gulf of Morbihan surficial sediments are shown in *Figure 3–43* and expressed in isopleth maps (*Figure 3–44*). During Dec 2009 sampling, the spatial distributions were increased towards the eastern zone of the gulf while, for Oct 2010 sampling, low concentrations were observed at the western and eastern zones, increasing towards the centre zone. On the other hand, high concentrations also recorded in Auray river upstream and the concentration decreases towards the downstream.

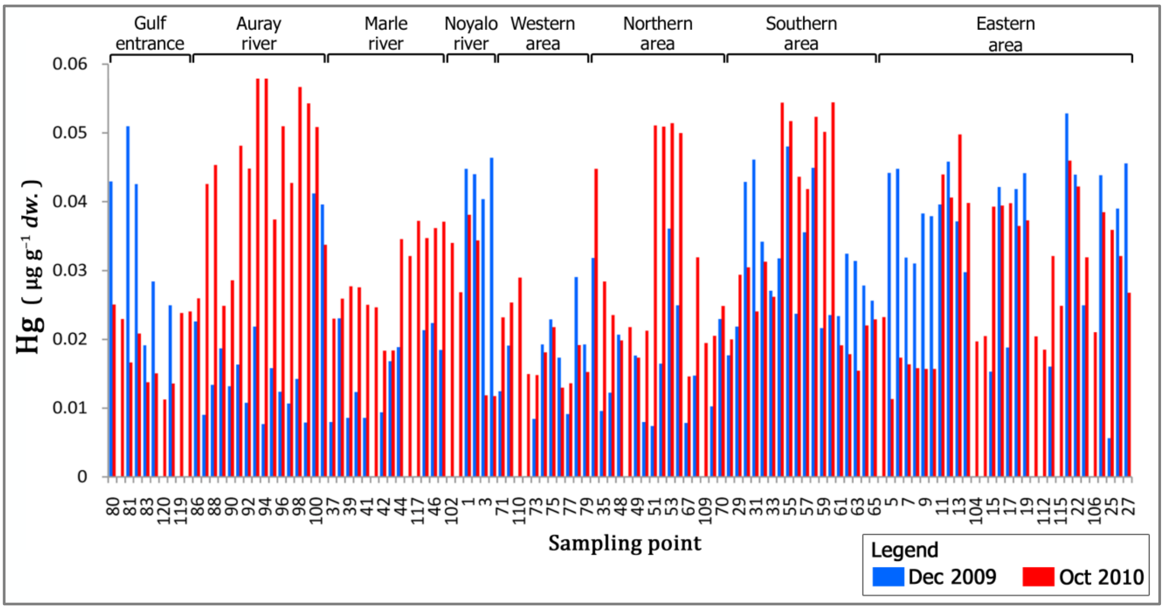

Figure 3–43. *Distribution of Hg based on different zone in gulf of Morbihan surficial sediments for both samplings.*

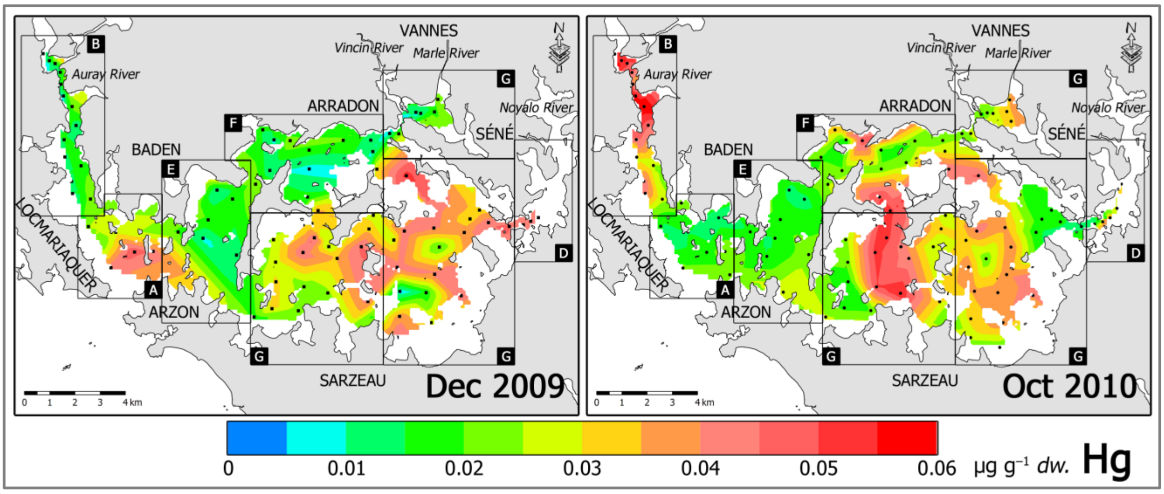

Figure 3–44. *Isopleth maps of Hg accumulation in gulf of Morbihan surficial sediments for both samplings.*

The mean concentrations for Dec 2009 sampling was 0.026±0.013 µg g^{-1} *dw.* (ranged from 0.006 to 0.053 µg g^{-1} *dw.*) and increase to 0.030±0.013 µg g^{-1} *dw.* (ranged from 0.011 to 0.060 µg g^{-1} *dw.*) in Oct 2010 sampling. From the statistical analysis, *t*–Test, the *p* value calculated was less than 0.05 and this analysis shows there is a significant difference in the concentrations for Dec 2009 and Oct 2010 sampling periods.

3.3.2.10 Levels of lead in sediments

Distribution of lead (Pb) concentrations in surficial sediments from the gulf of Morbihan is shown in bar graph (*Figure 3–45*) and in geochemical maps (*Figure 3–46*) for all sampling points. Higher concentrations occurred in sediment samples from the rivers zone and eastern zone throughout the gulf of Morbihan compared to the western zone.

The mean concentrations of Pb, 24.9±9.99 µg g^{-1} *dw.* in Dec 2009 sampling and increased to 31.6±6.30 µg g^{-1} *dw.* in Oct 2010 sampling, which can be explained an input of Pb to the study area. The concentrations ranged from 2.43 to 42.7 µg g^{-1} *dw.* for Dec 2009 sampling and 12.8 to 52.4 µg g^{-1} *dw.* in Oct 2010 sampling. From statistical analysis, *t*–Test, the concentrations were not differed significantly between the Dec 2009 and Oct 2010 sampling periods.

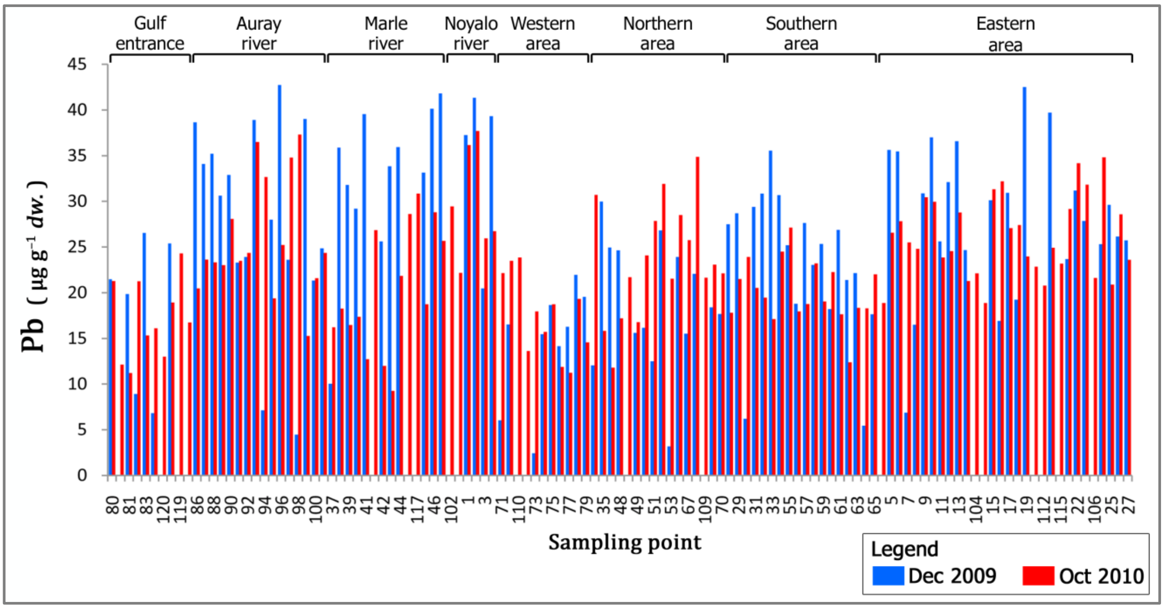

Figure 3–45. *Distribution of Pb based on different zone in gulf of Morbihan surficial sediments for both samplings.*

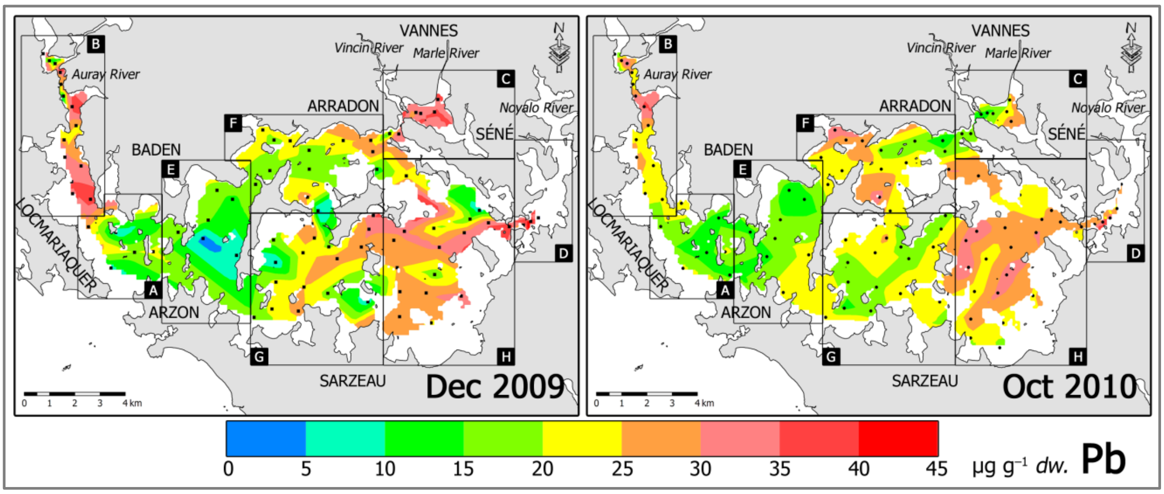

Figure 3–46. *Isopleth maps of Pb accumulation in gulf of Morbihan surficial sediments for both samplings.*

3.4 Sedimentation rate by ^{210}Pb dating technique in core sediments from gulf of Morbihan

The average activity concentrations of ^{210}Pb in 10 core sediments were ranged from 15.4 to 28.2 Bq kg^{-1} dry *wt*. Refer to the ranges, it was found that the activity concentrations of ^{210}Pb were significantly different depending on the sampling location. The ^{210}Pb activity concentrations in the core sediments from site G and E were found to be higher when compared to the activities from other cores. This could be due to the presence of the higher percentage of silt and clay sediments in that area. Furthermore, ^{210}Pb enrichment was found to increase with these contents and organic matter (Rajashekara *et al.*, 2008). The lower activity concentration of ^{210}Pb in particular site D, J and K can be explained by an increased deposition flux of low–activity sediments of ^{210}Pb supplied by the nearby river, and negligible scavenging of marine ^{210}Pb during rapid sediment deposition and burial (Sommerfield and Nittrouer, 1999). This lower value of ^{210}Pb activity concentration was also probably due to dissolution and leach out of organic matter from river run–off (Rajashekara *et al.*, 2008).

The sedimentation rate was determined from the slope of logarithms of ^{210}Pb activities versus the depth of the core sediment (*Figure 3–47*). Sedimentation rate can be calculated by dividing the decay constant of ^{210}Pb (0.0311/year) by the attenuation slope (Alexander *et al.*, 1991). The vertical profiles of ^{210}Pb were generally shown a non–linear decreased with increasing depth at all sampling locations in the gulf. If the sedimentation rate was constant with time during past 100–200 years for each core, the activity of excess ^{210}Pb in the sediments should decrease exponentially with depth except in the surface layer (Mohamed *et al.*, 1996). Additionally, their distributions were normal decay pattern, where fluctuated or uniform activities at the surface layer (<10 cm depth) as sediment mixing were caused by biological process or bioturbation and physical processes such as wave and tidal current, decreased activities with increasing depth as decaying zone (10–20 cm depth) and constant activity in the deepest layer, > 20 cm depth (Gokmen *et al.*, 1996; Wan Mahmood *et al.*, 2011).

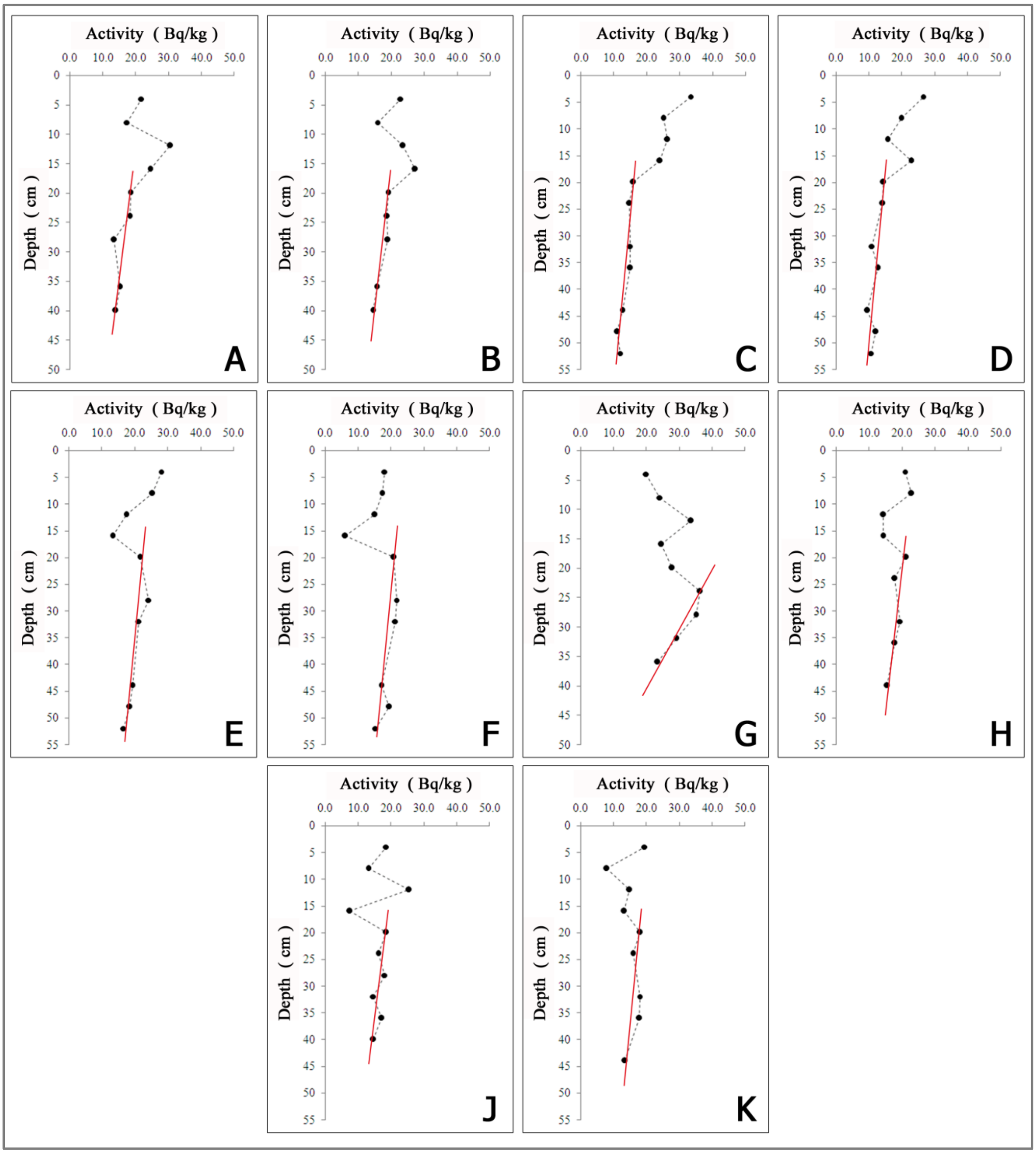

Figure 3–47. *Profiles pattern of $^{210}Pb_{ex}$ in the core sediments from gulf of Morbihan.*

From the figure, the profiles of ^{210}Pb indicated obviously fluctuate in all core sediments in the upper 20 cm, where the suspected thickness of mixing layer does not exceed 15 % of the total thickness of ^{210}Pb vertical profile (Lu and Matsumoto, 2005). In the upper layers of the cores, the activity profiles of ^{210}Pb is almost uniform due to a strong mixing process by biological and large physical impacts from waves and tidal current processes occurred in past time.

As shown in *Figure 3–48* applying the formula by Schink and Guinasso (1977), the sedimentation rate from 10 core sediments were estimated to be ranged from 0.10 to 0.14 cm/year, an average of 0.12 cm/year in the gulf of Morbihan core sediments. This calculation was estimated by selecting the best–curve from the establishment ^{210}Pb (Bq kg^{-1}) distribution with depth and no sediment compaction occur in the studied cores. This indicates that although the cores were obtained within a radius of one km, sedimentation processes differed from location to location due to environmental factors, geomorphology and types of sediment.

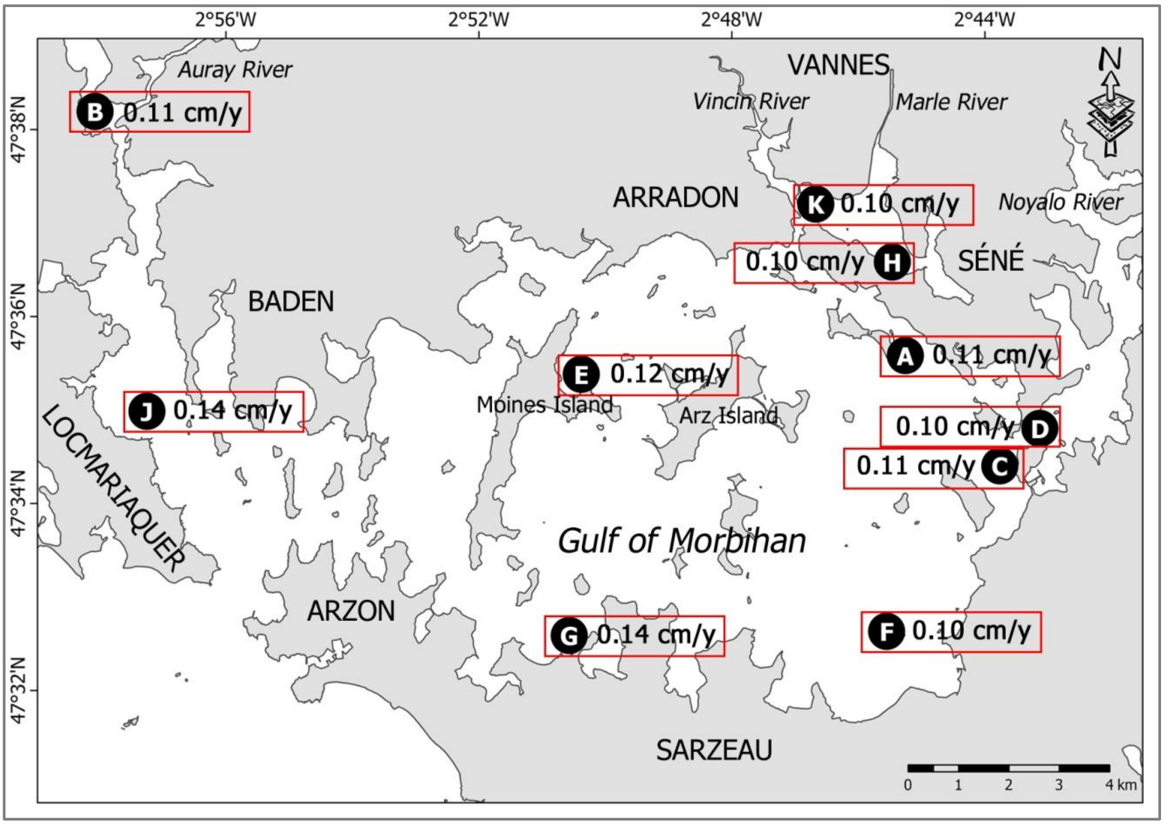

Figure 3–48. *Sedimentation rate calculated in the core sediments at gulf of Morbihan.*

3.5 Concentration of metallic trace elements in oyster in–toto

Oysters are one of the mollusc species used worldwide in biomonitoring for environmental pollution programs. In our study, we used *O. edulis* and *C. gigas*, where these species are well cultivated in the mariculture area in Quiberon bay and gulf of Morbihan. A total of 389 oyster samples comprises of *O. edulis* (41 samples) and *C. gigas* (348 samples) were used in this study. The shell lengths of the *O. edulis* and *C. gigas* were between 53.2 to 71.5 mm and 27.2 to 196.4 mm, respectively; tissue wet weight ranged from 3.42 to 8.71 g for *O. edulis* and 3.16 to 39.4 g for *C. gigas*.

Concentration of selected metallic trace elements (MTEs), copper (Cu), zinc (Zn), arsenic (As), cadmium (Cd), mercury (Hg) and lead (Pb) were measured in pure white muscle and in all soft tissue excluding the shell (in–toto). Data were analyzed as total MTEs concentrations on a dry weight basis and are expressed in mg kg^{-1} *dw*. It is significant to note that Cd, Pb, As and Hg, the most toxic of element analyzed, occurred in low concentration in both sampling areas. Analyses of variance showed that MTEs concentration were significantly higher ($p < 0.05$) in the oyster samples from the gulf of Morbihan compared to Quiberon bay.

3.5.1 Oyster samples from the Quiberon bay

The results of the analyzed MTEs; copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb), arsenic (As) and mercury (Hg) in oyster in–toto collected from the Quiberon bay are presented in *Table 3–3*. A total 171 *C. gigas* from four different locations and 41 *O. edulis* samples from the centre of the bay were collected to analyze those selected MTEs in their tissue. According to the data, there is a wide range of values for the MTEs concentration in all the oyster samples. Generally, the concentration of the MTEs analyzed exhibited the following order: Zn>Cu>Pb>As>Cd>Hg.

Table 3–3. *Metallic trace elements (mg kg^{-1} dw.) in oyster samples from Quiberon bay.*

	Q1 (n = 40)	**Q2 (n = 37)**	**Q3 (n = 45)**	**Q4 (n = 49)**	**Q5 (n = 41)**	**Average (n = 212)**
Zn	151±68.1 (23.7–324)	187±102 (57.9–459)	250±79.5 (70–411)	192±56.2 (72.2–353)	122±49.5 (43.1–204)	182±83.9 (23.7–459)
Cu	17.0±8.15 (1.36–29.3)	20.0±7.15 (4.62–29.4)	26.6±12.7 (3.72–47.9)	14.3±13.6 (5.38–59.7)	13.0±7.26 (3.5–28.8)	18.2±11.4 (1.36–59.7)
Pb	0.96±0.33 (0.35–1.92)	0.70±0.32 (0.08–1.59)	1.07±0.45 (0.32–2.06)	0.87±0.27 (0.27–1.67)	0.98±0.25 (0.43–1.61)	0.92±0.36 (0.08–2.06)
As	0.63±0.17 (0.29–1.26)	0.68±0.18 (0.12–1.03)	0.93±0.23 (0.31–1.36)	0.65±0.14 (0.20–0.92)	0.57±0.12 (0.29–0.83)	0.70±0.21 (0.12–1.36)
Cd	0.14±0.15 (0.01–0.46)	0.11±0.05 (0.02–0.31)	0.25±0.09 (0.06–0.40)	0.22±0.11 (0.07–0.40)	0.19±0.09 (0.03–0.39)	0.19±0.12 (0.01–0.46)
Hg	0.020±0.014 (0.006–0.053)	0.017±0.008 (0.007–0.037)	0.029±0.009 (0.010–0.054)	0.032±0.006 (0.007–0.045)	0.021±0.011 (0.009–0.055)	0.024±0.012 (0.006–0.055)

The concentrations of zinc (Zn) were the most abundant elements among all the interest MTEs (with an average of 182±83.9 mg kg^{-1} *dw*., ranged from 23.7 to 459 mg kg^{-1} *dw*.). The *C. gigas* cultivated from southern zone, Q1 had the lowest concentrations, while *C. gigas* from the northern zone farm, Q2 recorded the highest concentrations of Zn. No maximum levels of Zn have been set by the Commission of the European Communities (EC, 2006). A comparison with the Food and Agricultural Organization (FAO) limits for Zn, 204 mg kg^{-1} *dw*. (FAO, 1983), several of the oyster samples concentrations were at the upper limits for Zn. Statistical analysis of the *t*–Test showed that concentrations for Zn were significantly different in the studied oyster samples.

The second abundant MTE studied was the copper (Cu), an average of 18.2±11.4 mg kg^{-1} *dw*., ranged between 1.36 and 59.7 mg kg^{-1} *dw*. Lowest concentrations of Cu were observed in *C. gigas* from the southern zone farm, Q1 and the highest concentrations were recorded in *C. gigas* collected from the innermost zone of the bay, Q4. Similar with Zn, no maximum levels of Cu have been set by the Commission of the European Communities (EC, 2006). A comparison with the Food and Agricultural Organization (FAO) limits for Cu, 204 mg kg^{-1} *dw*. (FAO, 1983), no oyster samples were exceeded the maximum limit. Statistical analysis of the *t*–Test showed that concentrations of Cu were significantly different in the studied oyster samples.

The average concentrations of lead (Pb) analyzed in oyster samples from the five mariculture farms were 0.92±0.36 mg kg^{-1} *dw*. Cultivated *C. gigas* collected from northern zone, Q2 showed the lowest concentrations of Pb, 0.08 mg kg^{-1} *dw*., while *C. gigas* sampled from Trinité–sur–Mer site, Q3 showed the highest concentrations of Pb, 2.06 mg kg^{-1} *dw*. Pb values were lower than the maximum residual level of 10.2 mg kg^{-1} *dw*. recommended by the Commission of the European Communities (EC, 2006). From the *t*–Test analysis, it can be concluded that there was no significant variation in the concentrations between all the sampling sites.

The average concentrations of arsenic (As) found in oyster samples were 0.70±0.21 mg kg^{-1} *dw*. Lowest concentrations of As, 0.12 mg kg^{-1} *dw*. were observed in *C. gigas* collected from the northern zone farm, Q2 whereas *C. gigas* collected from Trinité–sur–Mer site, Q3 showed the highest concentrations, 1.36 mg kg^{-1} *dw*. For As, no maximum levels have been settled, so far, in European legislation, due to a lack of information for the determination in different food commodities. From the *t*–Test statistical analysis, it can be concluded that there was no significant variation in the concentrations between all the oyster samples studied.

The lowest and highest concentrations of cadmium (Cd) were observed in cultivated *C. gigas* collected from the southern zone farm, Q1 with the range of 0.01 to 0.46 mg kg^{-1} *dw*., respectively. From all oyster samples, the calculated average value of Cd was 0.19±0.12 mg kg^{-1} *dw*. The concentration level did not exceed the maximum residual level of 6.8 mg kg^{-1} *dw*. set by Commission of the European Communities (EC, 2006). The *t*–Test statistical analysis showed that there is no significant different between all sites for concentrations of Cd.

Concentrations of mercury (Hg) recorded the lowest concentrations range, 0.006 to 0.055 mg kg^{-1} *dw*. with an average of 0.024±0.012 µg g^{-1} *dw*. in oyster samples among all studied MTEs. The lowest concentrations of Hg were noted in *C. gigas* from the southern zone farm, Q1 while *O. edulis* collected from centre zone of the bay, Q5 exhibit the highest concentrations of Hg. A comparison with the Commission of the European Communities (EC, 2006) limits for Cu, 3.4 mg kg^{-1} *dw*., none of the concentrations of Hg in oyster samples were exceeded the maximum limit. Statistical analysis of the *t*–Test showed that there is no significant different between all sites for this studied elements.

A great deal of data has been obtained on the MTEs studied levels in the oyster samples, particularly for site where MTEs pollution is already recognized as a problem. In this case, oyster samples taken at site Q3 (Trinité–sur–Mer) show the high contents of all MTEs content in their tissue than other sampling sites. This may be due to Q3 is located at shipping activities and Crac'h river runoff, while other sites are located within the bay area. The concentration of MTEs was found to change according to concentrations in the environment.

3.5.2 Oyster samples from the gulf of Morbihan

The concentrations of the same six MTEs were measured in 177 oyster in–toto only from *C. gigas* species from five locations from the gulf of Morbihan are presented in *Table 3–4*. The concentration of the MTEs analyzed exhibit similar decreasing order to that of the samples collected from the Quiberon bay, Zn>Cu>Pb>As>Cd>Hg.

Table 3–4. *Metallic trace elements (mg kg^{-1} dw.) in oyster samples from gulf of Morbihan.*

	M1 (n = 53)	**M2 (n = 47)**	**M3 (n = 51)**	**M4 (n = 16)**	**M5 (n = 10)**	**Average (n = 177)**
Zn	173±89.3 (24.7–331)	171±94.2 (76.2–529)	179±55.7 (86.4–250)	223±151 (66.6–511)	225±175 (85.8–549)	182±96.5 (24.7–549)
Cu	16.7±9.11 (3.07–39.9)	22.6±11.9 (10.1–68.0)	25.7±16.8 (9.61–69.4)	27.9±15.3 (7.82–54.4)	34.5±16.2 (17.4–57.9)	22.9±14.1 (3.07–69.4)
Pb	1.95±0.86 (0.75–4.10)	1.74±0.75 (0.58–4.50)	2.09±1.29 (0.29–4.32)	2.75±1.30 (0.59–4.88)	3.37±1.89 (1.49–6.46)	2.08±1.16 (0.29–6.46)
As	0.91±0.32 (0.45–1.80)	0.99±0.36 (0.41–2.00)	0.77±0.31 (0.24–1.30)	0.98±0.46 (0.26–1.66)	1.12±0.30 (0.63–1.56)	0.91±0.35 (0.24–2.00)
Cd	0.28±0.09 (0.09–0.48)	0.27±0.11 (0.11–0.52)	0.25±0.11 (0.07–0.41)	0.34±0.22 (0.07–0.81)	0.59±0.36 (0.22–1.15)	0.29±0.16 (0.07–1.15)
Hg	0.027±0.010 (0.010–0.054)	0.024±0.009 (0.012–0.058)	0.021±0.010 (0.005–0.038)	0.031±0.017 (0.009–0.061)	0.036±0.024 (0.012–0.070)	0.025±0.012 (0.005–0.070)

Zinc (Zn) was the most dominant MTEs in all the oyster in–toto. Concentrations of Zn in *C. gigas* samples were detected in the range between 24.7 to 549 mg kg^{-1} *dw*., with an average value of 182±96.5 mg kg^{-1} *dw*. This average value was lower than the maximum level of 204 mg kg^{-1} *dw*. recommended by FAO (1983) even some of the oyster samples were exceeded the safety limit. The lowest concentrations were found in *C. gigas* samples from Moines island farm, M1 while the highest concentrations was observed in *C. gigas* samples collected from Auray river upstream, M5. Statistical analysis, *t*–Test showed that there is a significant difference between Zn levels and all the sampling sites.

Like Zn, the lowest concentrations of copper (Cu) were examined in *C. gigas* samples from Moines island farm, M1 with the value of 3.07 mg kg^{-1} *dw*. The highest concentrations of Cu, 69.4 mg kg^{-1} *dw*. were analyzed in *C. gigas* sample from the Auray river farm, M3. The average concentrations of Cu were 22.9±14.1 mg kg^{-1} *dw*. and this value was lower to FAO (1983) recommendation, 204 mg kg^{-1} *dw*. Statistical analysis, *t*–Test showed that there is a significant difference between concentrations of Cu in all *C. gigas* samples collected.

The average concentrations of lead (Pb) found in all *C. gigas* samples were 2.08±1.16 mg kg^{-1} *dw*. *C. gigas* samples from the Auray river farm (M3) exhibited the lowest concentrations of Pb, 0.29 mg kg^{-1} *dw*. The highest concentrations of Pb, 6.46 mg kg^{-1} *dw*. were observed at Auray river upstream, M5. The values do not exceed the maximum residual level of 10.2 mg kg^{-1} *dw*. recommended by Commission of the European Communities (EC, 2006). According to the statistical test, *t*–Test, concentrations of Pb did not show a significant difference between all *C. gigas* sites.

For As element, the average concentrations were 0.91±0.35 mg kg^{-1} *dw*. *C. gigas* cultured in the Auray river site, M3 exhibited the lowest concentration, 0.24 mg kg^{-1} *dw*., while *C. gigas* samples from Baden farm, M2 recorded the highest level, 2.00 mg kg^{-1} *dw*. According to the statistical test, *t*–Test, concentrations of As did not show a significant difference between all *C. gigas* sampling sites.

The highest concentrations of cadmium (Cd) in *C. gigas*, 1.15 mg kg^{-1} *dw*. were found at Auray river upstream, M5 and this concentration was approximately 16 times higher that detected in *C. gigas* from the Auray river farm, M3 which showed the lowest concentrations, 0.07 mg kg^{-1} *dw*. The average concentrations were 0.29±0.16 mg kg^{-1} *dw*. and this value was lower compared to the Commission of the European Communities, 6.8 mg kg^{-1} *dw*. (EC, 2006). No significant differences between Cd and oyster sites were observed and proved by statistical analysis, *t*–Test.

As observed in the Table 3–4, *C. gigas* samples collected from Auray river upstream, M5 showed the highest concentrations of mercury (Hg), 0.036 mg kg *dw*., while cultivated *C. gigas* samples from the Auray river farm, M3 showed the lowest concentrations, 0.005 mg kg^{-1} *dw*. The average concentrations found in all collected *C. gigas* samples was 0.025±0.012 mg kg^{-1} *dw*., lower than the value set by the Commission of the European Communities, 3.4 mg kg^{-1} *dw*. (EC, 2006). From *t*–Test, the concentrations did not differ significantly between the sampled *C. gigas* sites.

Generally, *C. gigas* samples from Auray river upstream, M5 recorded the highest average of all studied MTEs. This may be due to the sampling location where freshwater is always influencing the environment compared to other locations. In addition, these are wild and natural *C. gigas* taken from the bottom river.

CHAPTER 4

DATA INTERPRETATION AND DISCUSSION

4.1 Data comparison – European and Asian regions

To gather preliminary information about the levels and the status of geochemistry contamination and pollution levels in the Quiberon bay and gulf of Morbihan surficial sediments, the analyzed results were compared with other values concerning surface sediments from various marine environments presenting various levels of contamination obtained by other geochemists. Data were only compared between European region and Asian region as much geochemistry research had been conducted in these continents, particularly in the bay and the gulf ecosystems to avoid any interference. In addition, the studies of metallic trace elements (MTEs) and total organic carbon (TOC) contents in the surficial sediments are used for the evaluation as only the surficial sediments from the Quiberon bay and the gulf of Morbihan were analysis in this study.

Figure 4–1 shows the data from various sampling locations conducted by other investigators to compare the contamination levels for the Quiberon bay area. Because of the Quiberon bay characteristic which can be considered as an open marine system, the data were compared with others bay and coastal water environments. Whereas, the gulf of Morbihan can be categorized as a closed marine environment, therefore the comparisons are with the gulf and estuary environments. The sampling locations for the gulf and estuary by else investigators are shown in *Figure 4–2*.

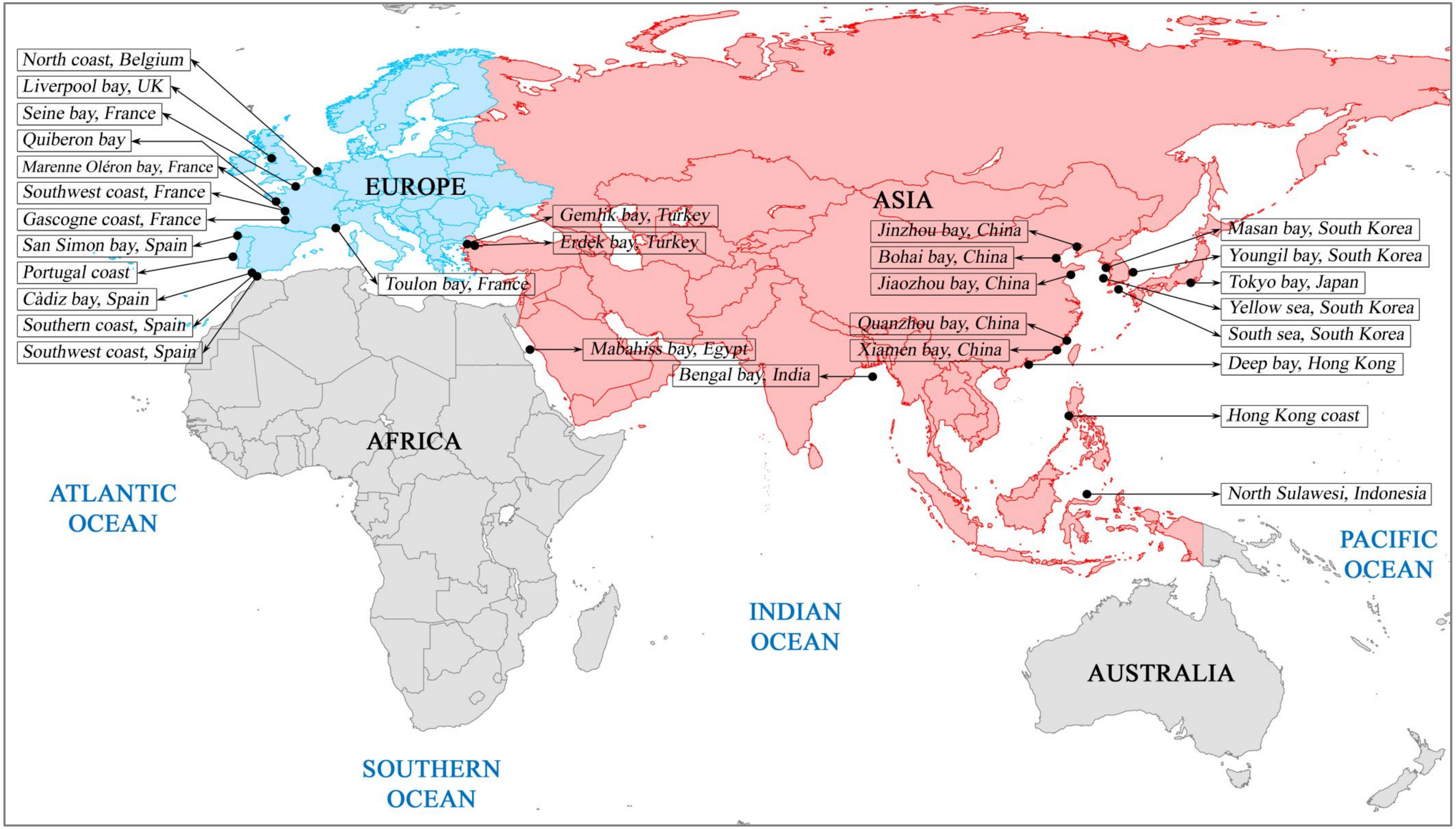

Figure 4–1. *Comparison of geochemistry results in Quiberon bay surficial sediments with other studies reported from European and Asian regions.*

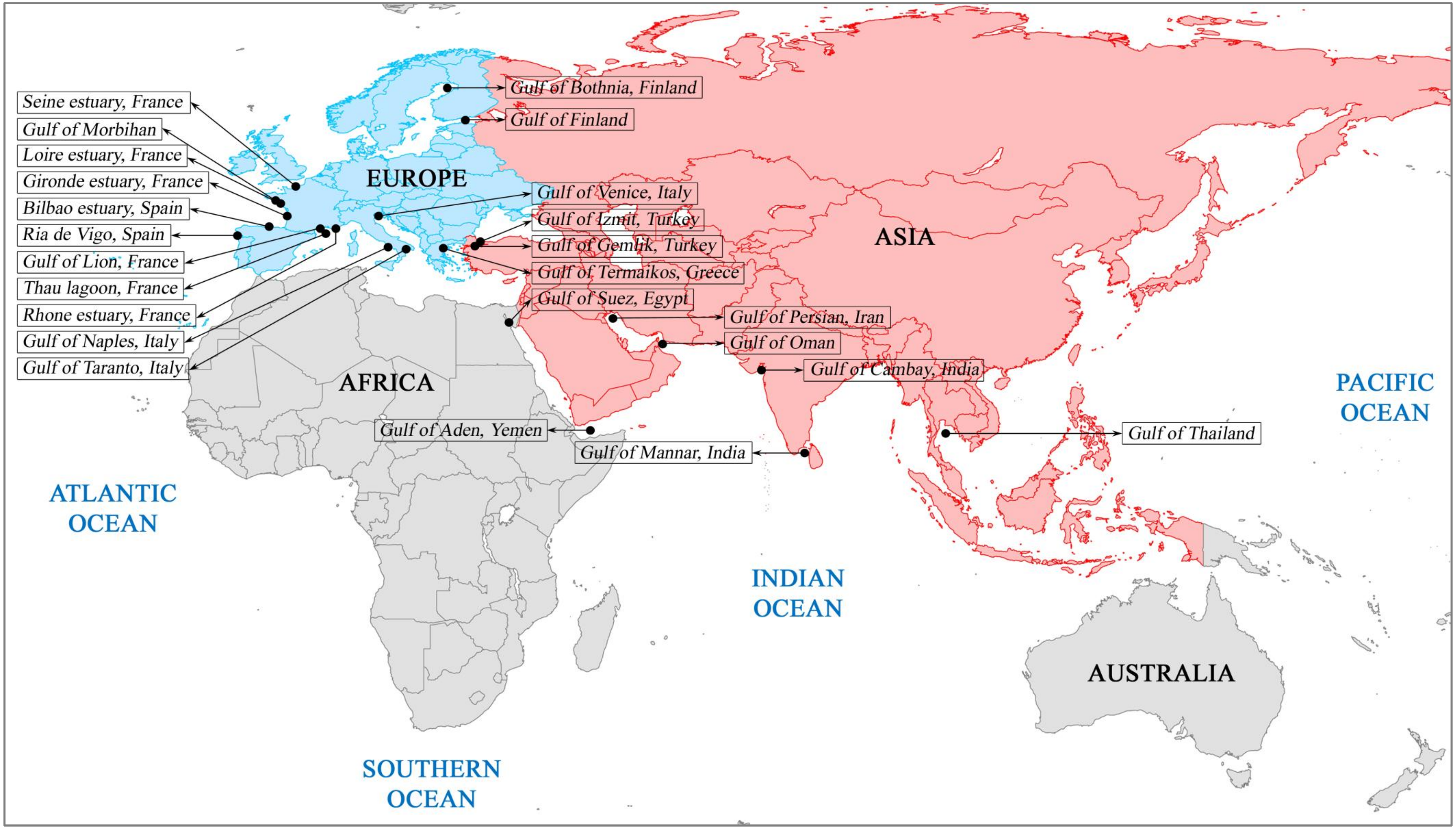

Figure 4–2. *Comparison of geochemistry results in gulf of Morbihan surficial sediments with other studies reported from European and Asian regions.*

4.2 Spatial and temporal distribution of surficial sediment characteristics

Sediment grain size has widely been used by sedimentologist from different regions to infer the sediment transport and deposition processes in the marine aquatic environment (Mason and Folk, 1958; Visher, 1969). Sediment grain size distributions are generally related to two main factors (Folk and Robbles, 1964), namely:

(1) the availability and source of sediments to the depositional environments,
(2) the hydrodynamic conditions during transport and deposition of the sediments.

In this study, surficial sediments collected from the Quiberon bay and gulf of Morbihan were analyzed for their mean grain size distribution using both dry sieving for sandy sediments and laser particle counter for muddy sediments. The continuous spectrum of differential volume fraction for each size range combined into four size classification, namely clay (<4 μm), fine silt (4–32 μm), coarse silt (32–64 μm) and sand (>64 μm).

For a better interpretation, sedimentary facies isopleth maps of Quiberon bay and gulf of Morbihan surficial sediments for two sampling periods, Dec 2009 and Oct 2010 were visualized by ArcGIS 9.3 software.

4.2.1 Quiberon bay surficial sediment characteristics

Likewise, surficial sediments in the Quiberon bay can be grouped into sandy–silt sediments for both seasons. From the sediments texture graph (*Figure 4–3*), sand was the most dominant fraction in the Oct 2010 samples collection compared to Dec 2009 samples. The average of sand fraction during Dec 2009 was 57 %, the silt fraction was 41 % and the clay fraction makes up the remaining

2 % of the sediments; while during Oct 2010, the sand fraction was increased to 77 %, and silt and clay fractions make up the remaining 23 %. The silt fraction especially in the inner bay zone was replaced by sand fraction (*Figure 4–3*). This replacement can be derived from the varying energy levels between the uprushing and backwashing wave (*Figure 4–4*). With the uprush wave, larger amounts of sand fraction are deposited on nearshore, whiles during backrush with lower energy, only a small portion of sand fraction is transported offshore (Ergin *et al.*, 2007).

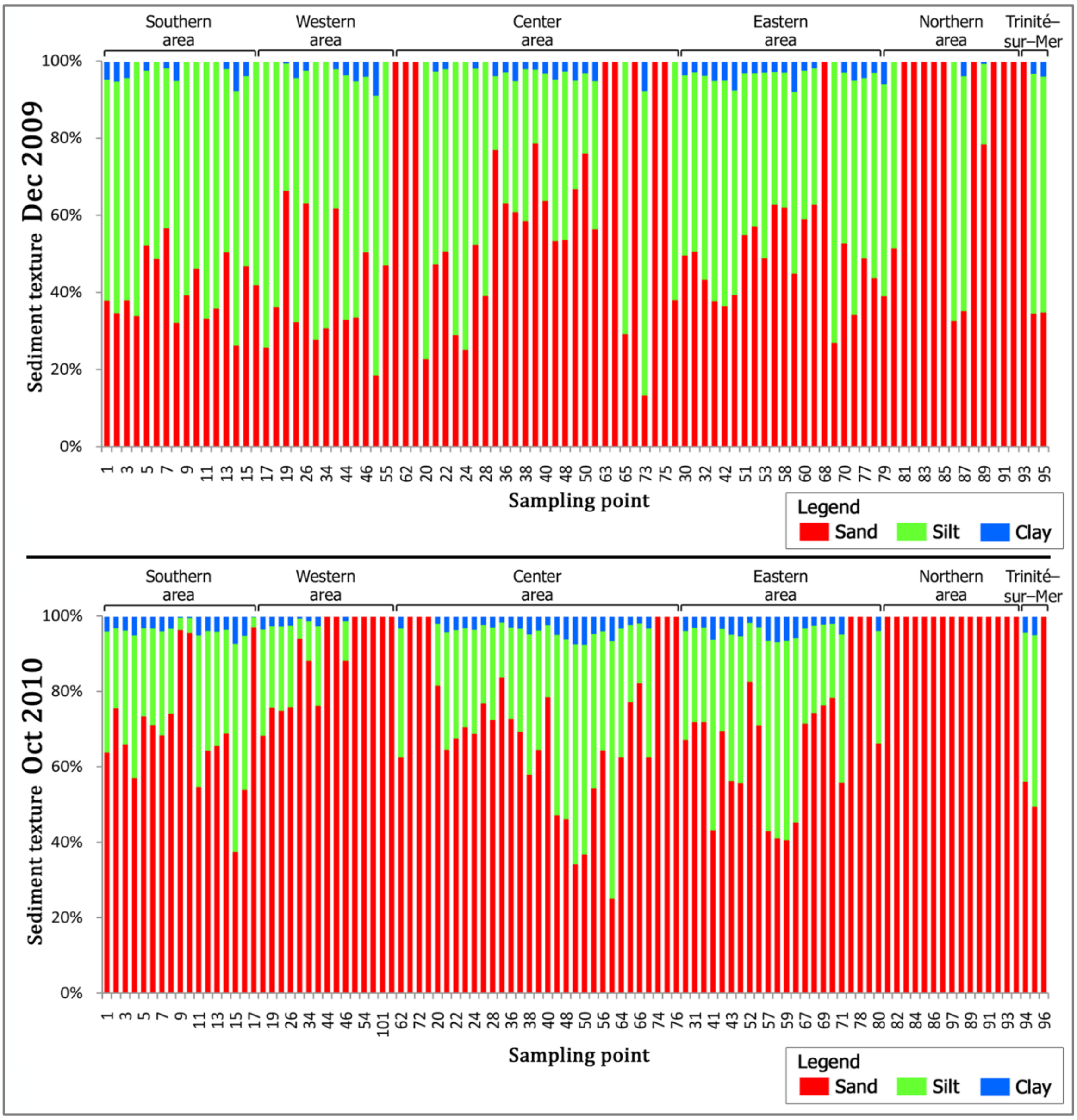

Figure 4–3. *Percentage of sediment texture based on different zone in Quiberon bay surficial sediments for both samplings.*

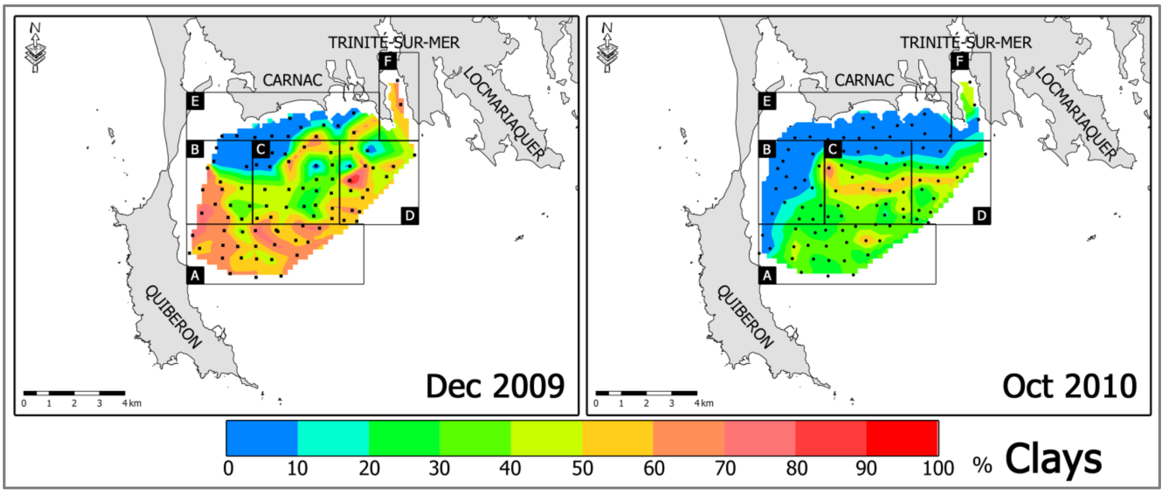

Figure 4–4. *Isopleth maps of percentage clay fraction in Quiberon bay surficial sediments for both samplings.*

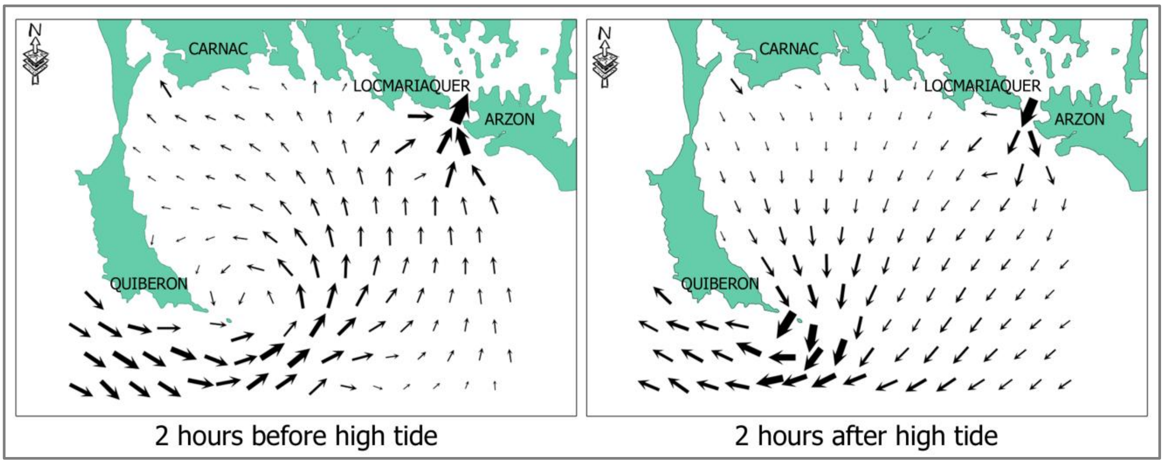

Figure 4–5. *Water current speed and direction distribution in Quiberon bay.*

4.2.2 Gulf of Morbihan surficial sediment characteristics

Sand fraction also dominated the gulf of Morbihan area for both seasons. From *Figure 4–6*, a similar texture of sediment can be observed for both seasons. These areas are evidently controlled by the changes in coastal morphology, wave, tidal and wind climate in this region, as also known from other coastal regions (Komar, 1998; Davis and Fitzgerald, 2004; Menier *et al*., 2011). The move of sand fraction into and out of the entrance of the gulf is a complex phenomenon because of the interaction of tidal, wave and freshwater transport processes especially from Auray river. Most of the sand fraction transported out of the entrance by these processes is deposited on or near the entrance bar from where it is carried to the updrift coastline by a process known as littoral bypassing (Mangor *et al*., 2010).

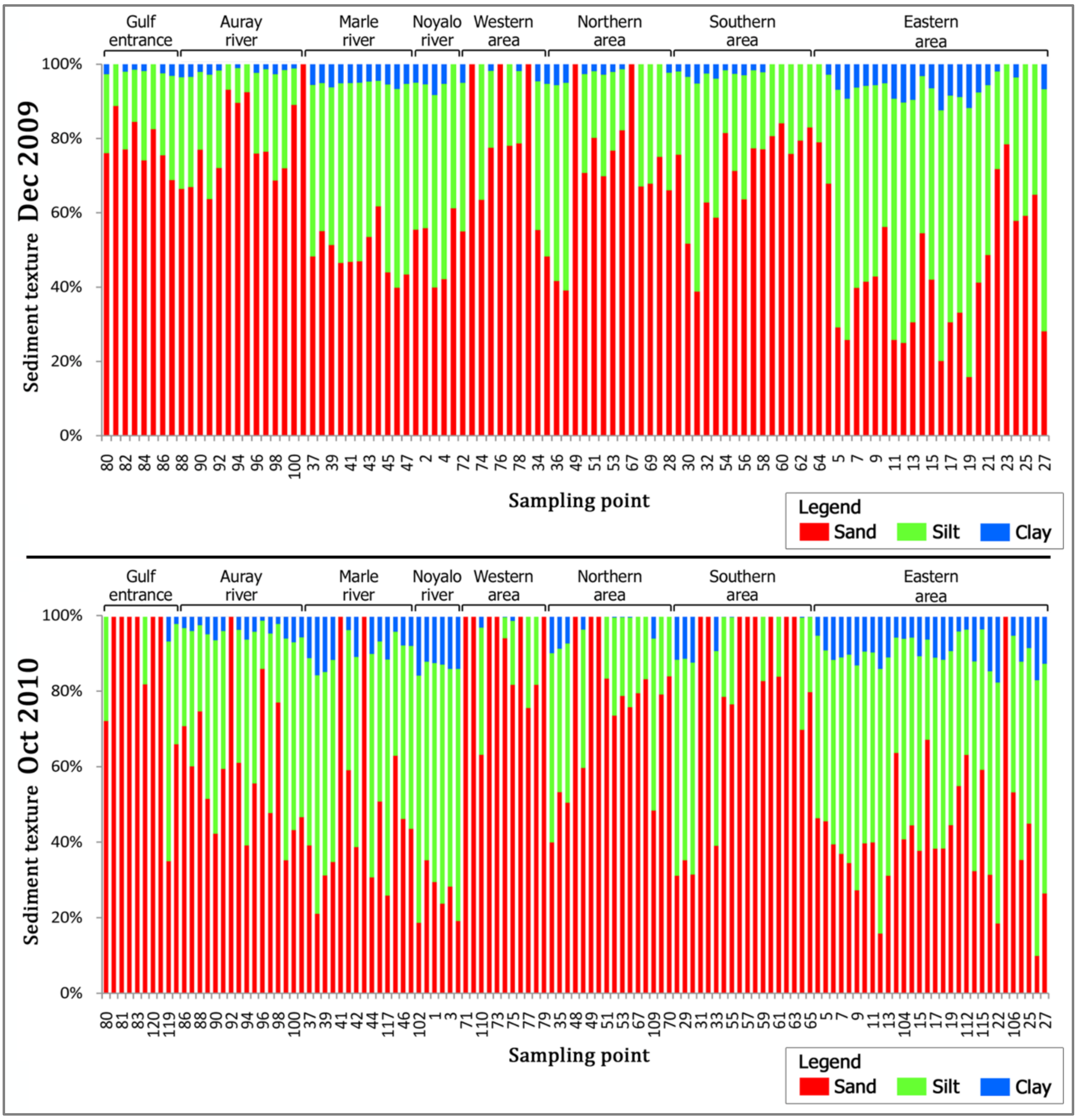

Figure 4–6. *Percentage of sediment texture based on different zone in gulf of Morbihan surficial sediments for both samplings.*

Sand fraction dominates in the gulf at about 63 %, while the silt fraction is about 33 %, and the clay fraction makes up the remaining 4 % of the sediments for both Dec 2009 and Oct 2010 sampling periods. There is practically low sand fraction at the eastern part of the gulf, where the silt and clay fraction dominated that area (*Figure 4–7*). Silt and clay fractions decrease in the center part, and being replaced by sand fraction during Oct 2010. This may be due to strong current occurred during high tide in this area and flushed the fine sediment fraction to the eastern part and those sediments settle down at the bottom during calm periods (*Figure 4–8*). This process also occurred in Auray river, where the freshwater and tidal current cause movement of the sediments. The faster these current, the greater the shear stress and turbulence generated at sediment bed, and the greater the movement of sediment by bedload and suspended load transport (Menier *et al*., 2011).

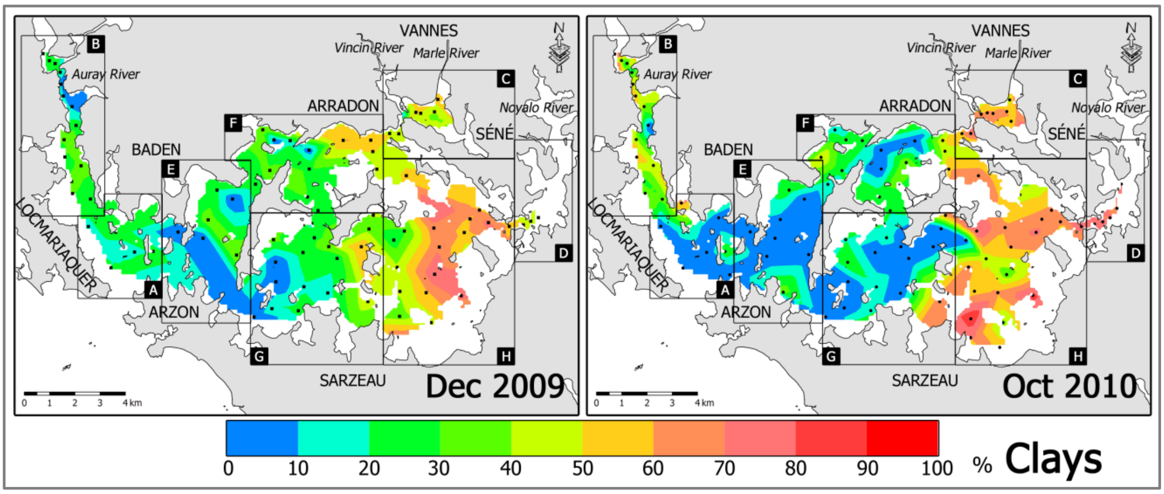

Figure 4–7. *Isopleth maps of percentage clay fraction in gulf of Morbihan surficial sediments for both samplings.*

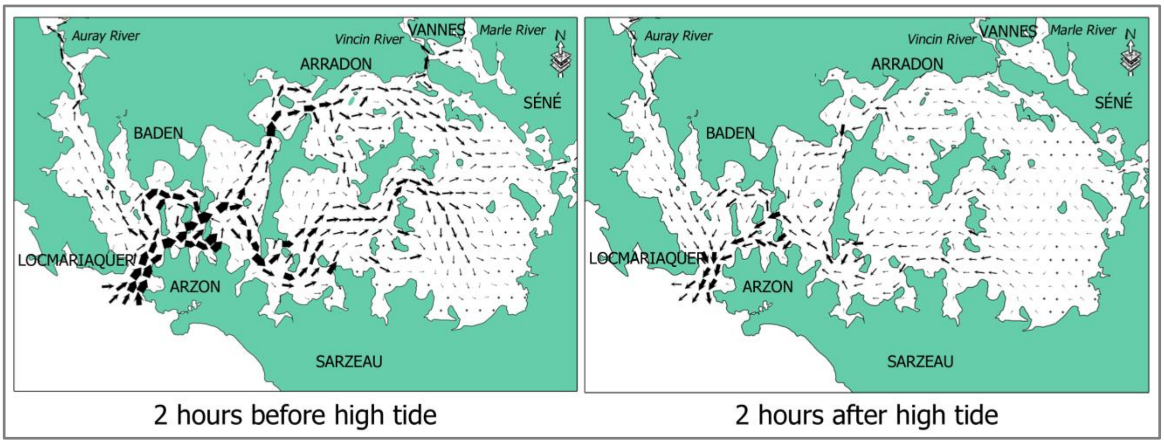

Figure 4–8. *Water current speed and direction distribution in gulf of Morbihan.*

4.2.3 *Comparison between Quiberon bay and gulf of Morbihan system*

Two main sediment types are recognized in the study area, sand and silt fractions, where sand fraction dominates the Quiberon bay sediments while gulf of Morbihan sedimentary facies is more dominant by the mixed sand and silt fractions (*Figure 4–9*). The similarity findings were also observed by S.H.O.M. and Menier *et al*. (2011) in their study from the Quiberon bay and gulf of Morbihan, respectively (*Figure 4–10*).

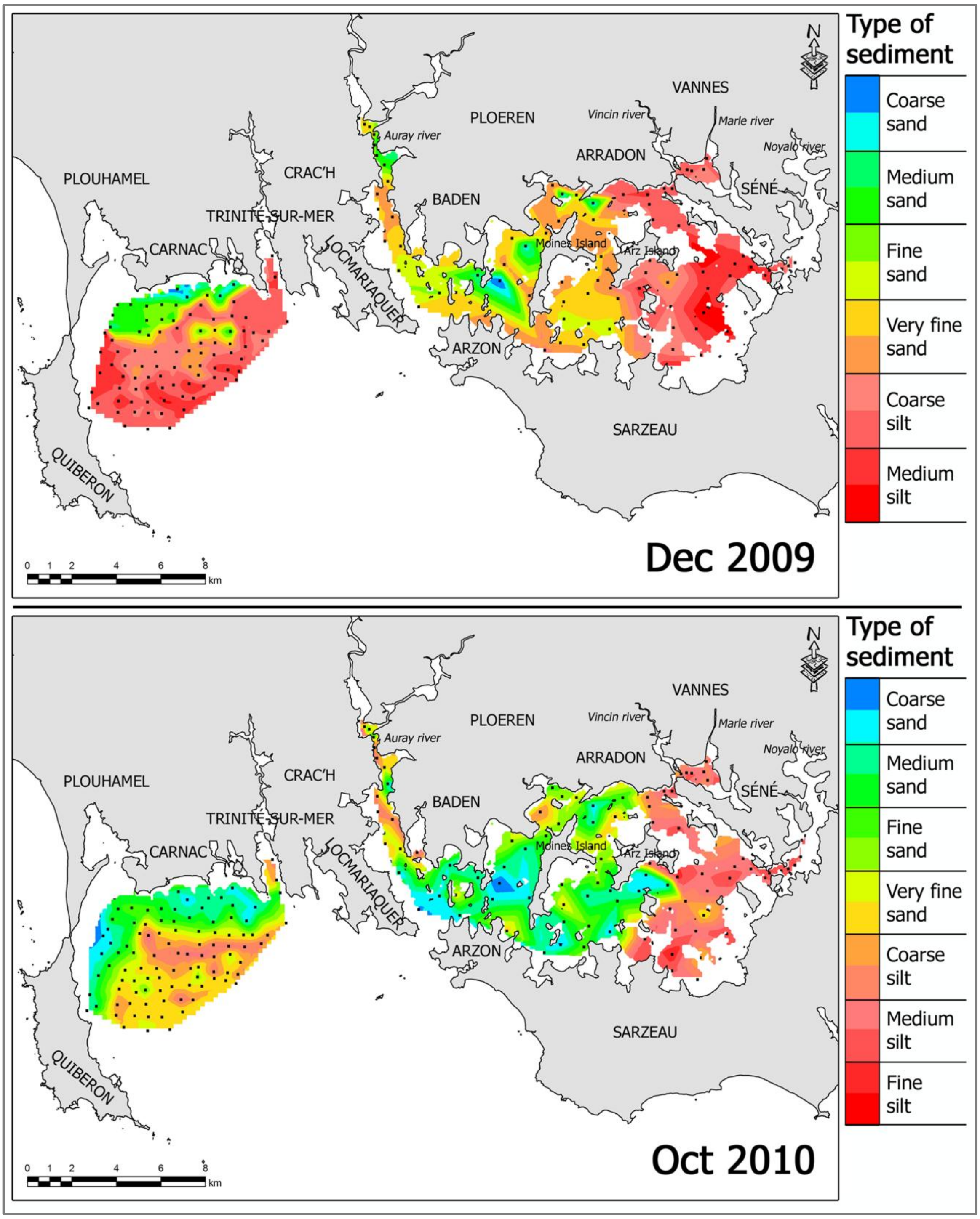

Figure 4–9. *Comparison of sedimentary facies between Quiberon bay and gulf of Morbihan surficial sediments.*

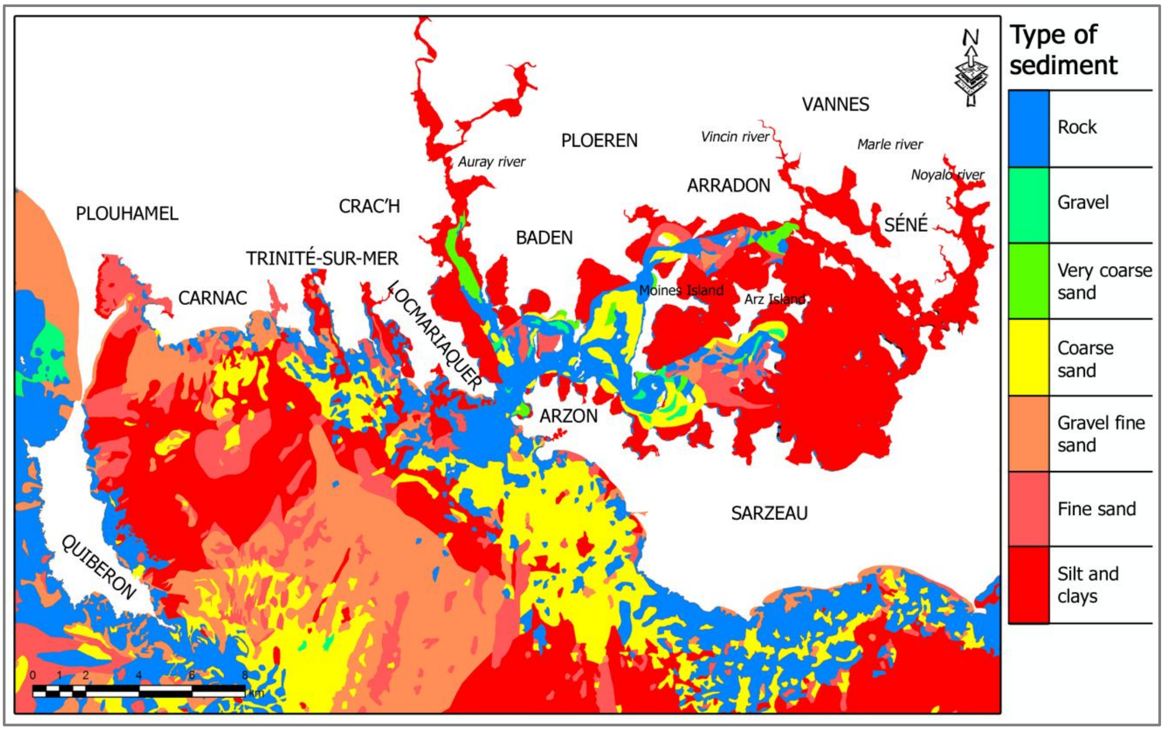

Figure 4–10. *Sedimentary map proposed by S.H.O.M and Menier et al. (2011) in Quiberon bay and gulf of Morbihan sediments.*

These suspended sediment plumes are then transported by surface current over the mud patch, where the material may fall out of suspension by gravity or flocculation processes. In the calm period, e.g. eastern zone of the gulf of Morbihan, suspended particle will settled to the bottom. Other continental shelves and in particular the bay of Biscay (Barthe and Castaing, 1989) one notices that there is a bathymetric limit, where fine grain sediments deposit cannot form perennial because of resuspension due to storm wave activity (Jouanneau *et al.*, 2008).

This situation could explain the types of sediment distribution in the Quiberon bay area particularly where deeper area (>15 m) which are not much influenced by wave and current have the fine sediment fraction compared to the near shore area at the inner bay zone. On the other hand, the opposite situation occurs in the gulf of Morbihan system. Rock type sediments were observed at the entrance of the gulf where in this area, the water depth was recorded more than 15 m. This may be due to the strong current occurred in this area and flush away the fine sediments at the bottom. In the eastern part, fine sediment fraction dominated the area due to water current action is very low and calm, thus the suspended particles are easily settling down to the bottom.

As revealed by factor analysis, the grain sizes partitioning in the surficial sediments show two trends. The first trend can be considered to be controlled by a combination of hydrodynamic energy and bay/gulf morphology: finer sediments are removed from the nearshore areas to be deposited in the deeper parts. By contrast, the second trend appears to be related to the hydrodynamic energy alone. Sediment grain size changes from coarser types in the western zone of the gulf, a relative higher energy area, to finer types in the western zone, a lower energy area as indicated by the clay content (Ergin and Bodur, 1999; Flemming, 2000).

4.3 Spatial and temporal total organic carbon contents in surficial sediments

The organic matter in sediments, expressed as total organic carbon (TOC) and total nitrogen (TN), represents an important reservoir for the global carbon cycle (Hedges and Keil, 1995; Weston and Joye, 2005). It is linked to early diagenesis (Bordovskiy, 1965) and plays an important role in the ocean chemistry (Lee, 1994). The largest fraction of carbon entrained in sediments is generated by means of inorganic carbon fixation of atmospheric CO_2 by photosynthesis in the water column (Lee, 1994), and only a small fraction (1.5 % in open ocean primary productivity, and >17 % on the slope) reaches the sediment, since most of it is oxidized (Seiter *et al.*, 2004). Near 80 % of the carbon is sequestered in the continental margins, thus representing the largest carbon storage in the current world ocean (Wollast, 1998). At the global scale, the storage of organic matter (in terms of TOC) mirrors the distribution pattern of phytoplankton biomass (Seiter *et al.*, 2004).

Sources of organic carbon include organic matter from surface runoff and shoreline erosion (mostly marshes), and primary productivity within the bays, all of which eventually settle to the bay bottom and are incorporated into the sediments. A conservative, qualitative, interpretation of the overall trend is that sediments with high organic contents are dominated by terrestrial organic carbon sources, while sediments with low organic contents are dominated by marine carbon sources (Smith *et al.*, 2004). This spatial separation between terrigenous input and accumulation suggests that dispersal and grain size are more important than local biogeochemical processes in controlling TOC distribution in sediments.

TOC contents have a major influence on both the chemical and biological processes that take place in sediments. The amount of organic carbon has a direct role in determining the redox potential in sediments, thus regulating the behavior of other chemical species such as MTEs. TOC contents in sediments have been used as an indicator of pollution and the eutrophication rate (Folger 1972; EPA 2002) and as a proxy for the past biological productivity (Mitlner *et al*., 2005; Song *et al*., 2002). TOC contents in coastal water such as estuary is found in much higher concentrations than in oceanic waters and has a highly variable composition since it derives from autochthonous as well as terrestrial sources and is further transformed into the marine environment by microbiological, chemical and photochemical processes (Chester, 1990).

Organic matter compound in sediment is an important food source for macrobenthos in marine soft–bottom ecosystems. It also causes oxygen depletion and generates by–products such as ammonia and sulphides when sediment organic content is high, potentially causing stress for macrobenthos. Since organic matter is a primary source of food for marine benthic organisms, they play an important role in maintaining a viable marine aquatic ecosystem. However, too much organic matter content can lead to the depletion of oxygen in the sediments and overlying water, which can have a deleterious effect on the benthic and fish communities (Wells, 2002).

The average TOC content distribution by zone in the Quiberon bay is shown in *Figure 4–11*. Overall, the TOC contents are low in the zones A to E which is located within the bay. Meanwhile, zone H, located at Trinité–sur–Mer area has a relatively higher TOC contents for both sampling periods, Dec 2009 and Oct 2010. This may be due to this zone is not much influenced by the physical process condition such as wave and current of the bay, but influenced by river run–off and urban waste through surface run–off. On the other hand, this zone is characterized by low hydrodynamic process and dominant by a muddy sediments fraction. The zones A to E within the bay environment are more exposed areas and characterized by higher energy and the action of wind–induced waves which can cause the bottom sediments re–suspension and resulting the transport the finer particles and associated organic matter towards the deeper area.

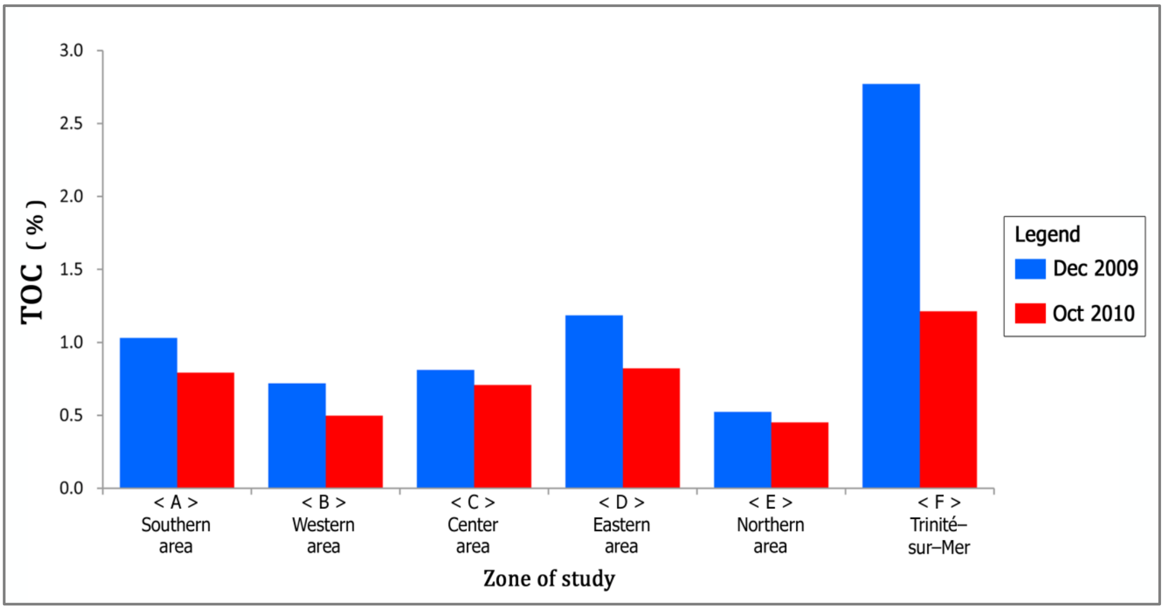

Figure 4–11. *Average concentrations of TOC based on different zone in Quiberon bay surficial sediments for both samplings.*

To obtain the status of TOC contents in Quiberon bay, our data was compared with other researchers finding from European and Asian region as shown in *Table 4–1*. Our finding shows that the TOC contents in the Quiberon bay were comparable with Ogrinc *et al*. (2007) study on the Mediterranean sea and slightly lower than others comparable areas such as Seine bay, France northern coast (Caplat *et al*., 2005).

Table 4–1. *Comparison of TOC contents in Quiberon bay surficial sediments with other studies reported.*

Region	**TOC (%)**	**Reference**
Quiberon bay	0.35	This study
European region		
Seine bay, France	6.3	Caplat *et al.*, 2005
Cadiz bay, Spain	3.56	Ligero *et al.*, 2002
Mediterranean sea	0.54	Ogrinc *et al.*, 2007
Asian region		
Bengal bay, India	2.1	Muthu Raj and Jayaprakash, 2008
Erdek bay, Turkey	0.9	Balkis and Cagatay, 2001
Gemlik bay, Turkey	1.3	Balkis *et al.*, 1999
Masan bay, South Korea	2.28	Hyun *et al.*, 2007
Quanzhou bay, China	1.35	Yu *et al.*, 2008
Youngil bay, South Korea	1.0	Lee *et al.*, 2008
Yellow sea, South Korea	0.3	Cho *et al.*, 1999

The high inputs of terrigenous material from the adjacent land mass and urbanization effluents nearby have increased the TOC contents in the gulf. It should be noted that the sampling was conducted during the wet season, whereas the annual flux delivered to the sediments will be dominated by the input of sediments transported by river discharge during the rainy season through river and surface run–off (Wattayakorn *et al.*, 1990). Lower levels of TOC contents are found in the coarser sediments and the energetic environments at the entrance of the gulf. This area is characterized by high hydrodynamic process and the bottom sediment is more dominated by sand fraction (Sakamaki and Nishimura, 2006; Menier *et al*., 2011).

In our observation during the sampling in the gulf of Morbihan, we found that the eastern zone of the gulf is the habitat for the seagrass, *Zostera marine.* Bottom sediments with seagrass has a high percentage of TOC content as they play a vital role in mud formation and trap suspended particulate matter and fine sediments with high chemical elements and high organic carbon contents causing their accumulation in the seagrass beds (Caccia *et al.*, 2003).

Beside seagrass, benthic biological metabolisms related to organic matter dynamics in tidal flats are very active and well documented (Ehrenhauss *et al.*, 2004). Sakamaki and Nishimura (2006) reviewed that organic matter in the sediments and those depositing to the sediments were dominated by decomposing algal material. If a tidal flat is more topographically enclosed and calm hydrodynamic process such as the gulf of Morbihan, the fluxes of physical processes could be small and biological processes may become relatively important (Defew *et al.*, 2002; Friend *et al.*, 2003).

Tidal process is characterized by long residence times of water and particles, which result in extensive modification of organic matter in the inner gulf (Frankignoulle *et al.*, 1998). Concentrations of suspended particulate matter can be high in particular in the maximum turbidity zone (Uncles *et al.*, 2002) and may even result in the transient presence of mud in the bottom layers

(Abril *et al.*, 1999). The sediments of the gulf has returned to be dominated by tidal influence and an increase of the organic material accumulation from the high eutrophication process in the gulf itself (Carreira *et al.*, 1995; Niell *et al.*, 1996; Clavero *et al.*, 2000).

From *Figure 4–12*, high TOC contents were observed in all three zones of rivers (Auray, Vincin, Marle and Noyalo rivers) and the eastern zone of the gulf. Zone A, which is located at the entrance of the gulf, recorded a low TOC contents. From the entrance, toward the eastern and northern zones, TOC contents were found to increase significantly.

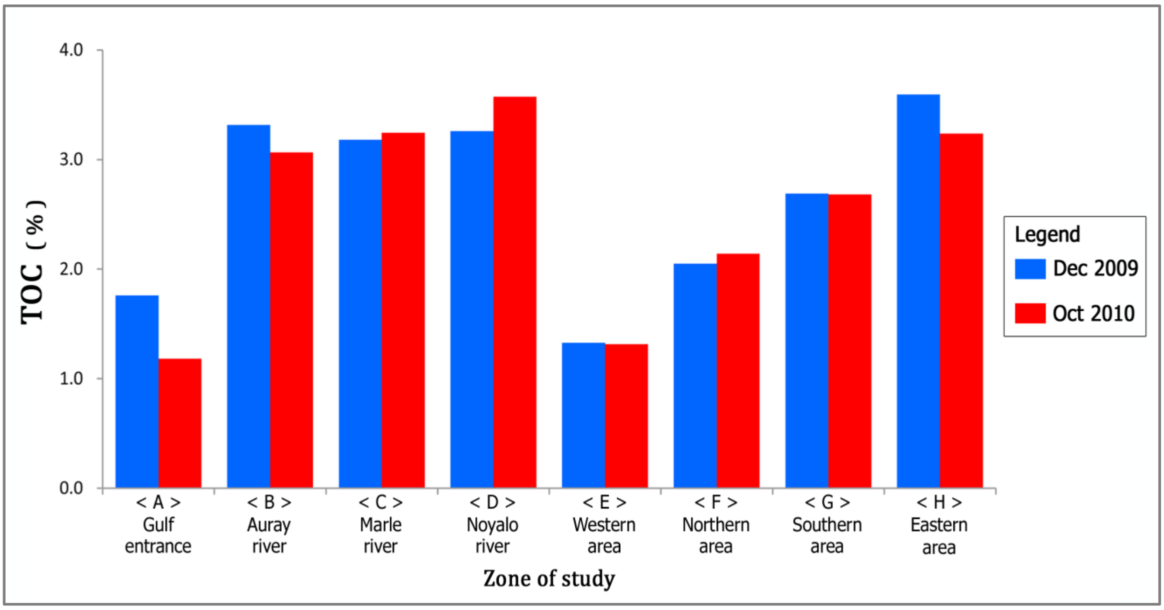

Figure 4–12. *Average concentrations of TOC based on different zone in gulf of Morbihan surficial sediments for both samplings.*

Table 4–2 shows the comparison of TOC contents from the gulf of Morbihan with other studies conveyed from European and Asian regions. TOC contents in gulf of Morbihan were higher compared to Thau lagoon in the Mediterranean Sea area studied by Rigollet *et al.* (2004), but lower compared to the Bilbao estuary (Ruiz and Saiz–Salinas, 2000) and Ria de Vigo (Alvarez–Iglesias *et al.*, 2007) at Spain located at the Atlantic coast.

Table 4–2. *Comparison of TOC contents in gulf of Morbihan surficial sediments with other studies reported.*

Region	**TOC (%)**	**Reference**
Gulf of Morbihan	2.76	This study
European region		
Thau Lagoon, France	0.97	Rigollet *et al.*, 2004
Bilbao estuary, Spain	3.69	Ruiz and Saiz–Salinas, 2000
Ria de Vigo, Spain	5.35	Alvarez–Iglesias *et al.*, 2007
Gulf of Venice, Italy	0.3–2.0	Sfriso *et al.*, 1992
Gulf of Thermaikos, Greece	1.1	Christophoridis *et al.*, 2009
Asian region		
Gulf of Izmit, Turkey	0.6–2.0	Ergin *et al.*, 1991
Bardawil, Egypt	1.2	Taher, 2001

4.3.1 Comparison between Quiberon bay and gulf of Morbihan systems

In the closed marine environment, TOC contents are generally higher than those found in coastal marine environments (Tyson, 1995), although coastal sites heavily affected by human activities (Delgado *et al.*, 1999; Cancemi *et al.*, 2003). This agreed with our study where the TOC contents in gulf of Morbihan surficial sediments were higher compared to the Quiberon bay surficial sediments (*Figure 4–13*). The gulf ecosystem itself receives inputs from multiple sources of organic matter, including allochthonous terrigenous materials (soil–derived organic matter; plant debris and riverine phytoplankton) exported from land by rivers, allochthonous marine materials brought in through tidal action from the open ocean and autochthonous (estuarine or marine phytoplankton, zooplankton and fecal pellets) production of algae and intertidal vegetation (Goñi *et al.*, 2003; Tesi *et al.*, 2007).

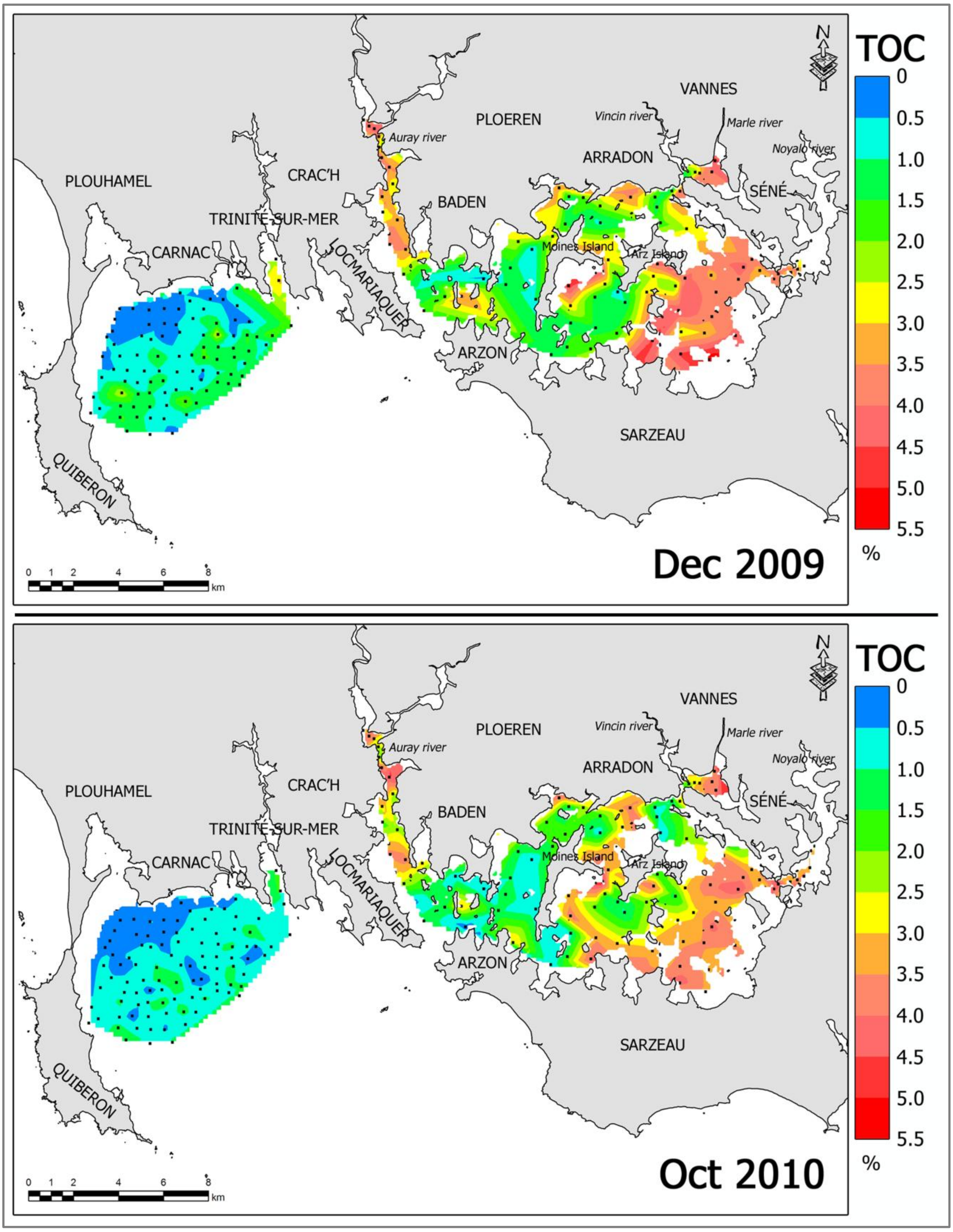

Figure 4–13. *Comparison of TOC contents between Quiberon bay and gulf of Morbihan.*

4.3.2 *Correlation between total organic carbon contents and types of sediment*

In general, the TOC contents increase as the grain size decrease and this relationship is shown in *Figure 4–14*, where TOC contents and mean grain sizes are well correlated. The linear relationship between TOC contents and the surficial sediments of the Quiberon bay and gulf of Morbihan suggest that the sediment texture plays an important key role in controlling TOC contents in both environments. This phenomenon was also found by Lee *et al*. (1991) and attributed to geographical variation. The clayey silt and sandy silt sediments in these areas also support the deposition of organic debris (Rajamanickam and Setty, 1973). In contrast, the lower TOC contents were measured in samples that contained a high sand fraction. Thus, sediment organic content, which is generally positively related to content of fine grain–size fraction in sediments, has been known to be an important descriptor for macrobenthos habitat quality (Thrush *et al.*, 2003; Hyland *et al.*, 2005).

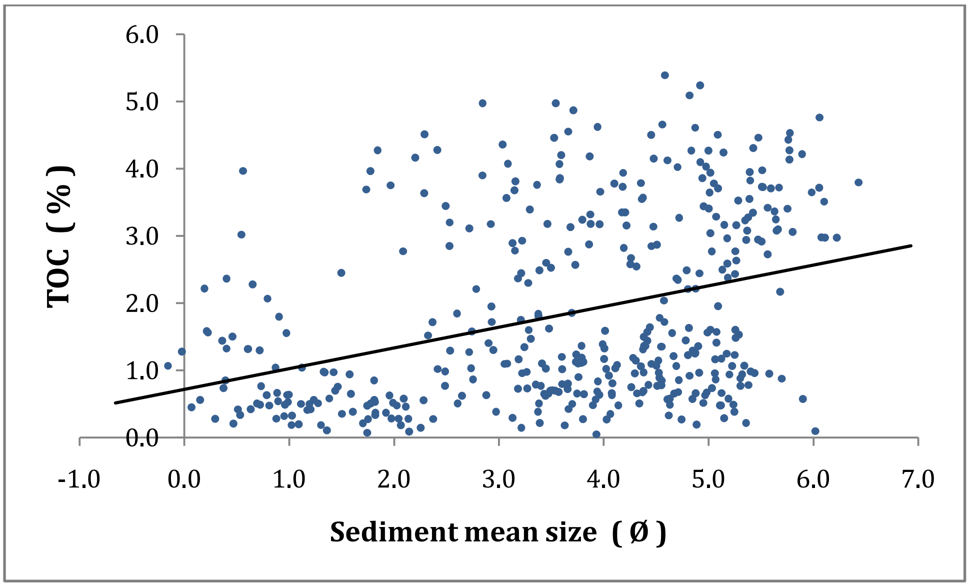

Figure 4–14. *Relationship between TOC contents and sediments grain sizes from Quiberon bay and gulf of Morbihan.*

4.4 Spatial and temporal metallic trace elements distribution in surficial sediments

Today, in many coastal environments including the Quiberon bay and gulf of Morbihan, anthropogenic inputs of some metallic trace element (MTEs) significantly exceed natural inputs or background values. It is difficult to quantify the anthropogenic input of MTEs into the Quiberon bay and gulf of Morbihan environments as frequently no direct evidence of MTEs content in sediments from pre–industrial period is available in this region (de Groot *et al*., 1976). The regional geochemical background values for these MTEs are not available. Therefore, the world's average upper continental crust (UCC) often used to provide the background values of MTEs concentration. The background concentrations of Cr, Mn, Fe, Co, Cu, Zn, As, Cd, Hg and Pb in the UCC obtained from Wedepohl (1995), Bowen (1979) and Mason and Moore (1982) are used in this study (*Table 4–3*). These values are commonly used as background values in sediment studies to quantify the extent and degree of MTEs pollution by various investigators (Datta and Subramanian 1998; Loska and Wiechula 2003; Cevik *et al*., 2008; Nobi *et al*., 2010).

Table 4–3. *Metallic trace elements concentration in the earth's crust as reported.*

MTE	Upper continental crust	Mean crustal material	
	Wedepohl (1995)	**Bowen (1979)**	**Mason & Moore (1982)**
Cr	35	71	100
Mn	527	500	950
Fe	3.09	4.1	5
Co	11.6	8	25
Cu	14.3	32	55
Zn	52	127	70
As	2.0	1.5	1.8
Cd	0.102	0.2	0.2
Hg	0.056	0.12	0.08
Pb	17	16	13

*All elements are expressed in µg g^{-1} *dw*. except Fe in %

Marine sediments can be sensitive indicators for monitoring the natural and anthropogenic contaminants in aquatic environments (Pekey *et al*., 2004). MTEs that exist naturally at the background levels in the environment include Cr, Cu, Fe and Zn, which are essential elements in living organisms and classified as a second class of dangerous contaminants. However, some trace element or heavy metals such as Hg, Cd, As and Pb which classified as first class of dangerous metals are not required for metabolic activity and are toxic to the ecosystem and ability to be incorporated into the food chain (Tam and Wong, 2000; Kishe and Mahchiwa, 2003). The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous even occurred at low concentrations.

As sediments in the marine shelves are good indicators of the nature of the marine environment, a detailed study of the geochemistry of surficial sediments from the Quiberon bay and the gulf of Morbihan has been taken up. The role of MTEs pollution in terrigenous sediments, and the processes involved can be inferred from the variation of geochemical characters of sediments. Pollution associated by MTEs is a serious problem due to their toxicity and their ability to accumulate in the biota through the food chain. One of the most crucial properties of MTEs is that they are not biodegradable in the aquatic environment (Nuremberg, 1984; Forstner, 1990; Harte *et al*., 1991; Schuurmann and Market, 1998). The levels of MTEs in aquatic ecosystems have increased drastically in recent decades as a result of inputs from anthropogenic activities through river and surface run–off (Forstner and Wittmann, 1979; Nriagu, 1989; Gómez–Parra *et al*., 2000).

MTEs found in coastal surficial sediments may be derived from a variety of natural and anthropogenic sources (Burridge *et al*., 1999). In most circumstances, the major part of the MTE contents in the water and the seabed sediments is anthropogenic and associated with terrestrial sources related to untreated municipal sewage (Shear *et al*., 1996; Isaac *et al*., 1997; Majori *et al*., 1978), intensive aquaculture activities (Tovar *et al*. 2000), harbor and shipping activities (Tanner *et al*., 2000) as well as riverine fluxes loaded with urban and agricultural run–off (Pope *et al*., 1978; Granier *et al*., 1990). The somewhat high MTE contents in sediments from the gulf of

Morbihan can be explained by the sources suggested by those researchers. On the other hand, a lot of mariculture farms surrounding the gulf and the bay ecosystem may be sources of MTEs in the environment.

A wide range of values for MTEs concentration was observed for the surficial sediment. Two distinct zones can be identified in Quiberon bay and gulf of Morbihan, which appear to reflect the heavy metals distribution: (1) an internal area (zones F in the Quiberon bay; zones B, C, D, H in the gulf of Morbihan) of lower hydrodynamic energy conditions with high in MTEs content in sediment, ranged from clayey to sandy sediments; and (2) an external zone (zones A, B, C, D, E in the Quiberon bay; zones A, E in the gulf of Morbihan) of generally higher hydrodynamic energy and overall lower MTEs content in sediments. Sediments in these zones are dominated by sand fraction.

The internal zones register a higher concentration of the most of the MTEs, especially Cu, Pb, Cd, As and Zn. These locations are associated with shallow hydrodynamics and limited depth, so high organic loads can also be associated with non–point pollution run–off and deposition due to human activities (Quevauviller *et al.*, 1989; Cortesão and Vale, 1995) such as mariculture and shipping activities in the study area. In addition, the distribution of MTEs in sediments is regulated not only by their concentrations, but also by sediment physic–chemical characteristic, mineralogy composition, organic matter content, as well as several environmental conditions such as water current, wind and tidal process (Solomons and Förstner, 1984).

In Quiberon bay, it is not surprising that station 94 to 96, Trinité–sur–Mer area, situated in the vicinity of the mouth of Crac'h river, had the highest mean concentrations for all studied MTEs. Apart from receiving the industrial and domestic wastewater from the upstream, Trinité–sur–Mer area also houses a busy marina with around 1500 ships and boats, fishing port and shipyard to build and repair boats. The same situation also occurred in the gulf of Morbihan region where the river run–off environment recorded the high contents of MTEs. Along the rivers, there are many ports and harbors for shipping activities. In addition, because of this area is well sheltered, shellfish mariculture activities especially oysters and mussels become very important to this surrounding area. Past studies from other regions have shown that these activities particularly shipping activities are accountable for the significant input of MTEs into the sediments (Berrow, 1991; Legorburu and Canton, 1991; Schintu *et al.*, 1991; Sanin *et al.*, 1992).

In our study, MTEs concentration was found to be high particularly in gulf of Morbihan surficial sediments during monsoon season in Oct 2010 where high rainfall was recorded at that period (*Figure 4–15*). The monsoon season is the period of heavy rainfall, leading to high fluvial inputs and river run–off process. The four rivers, namely Auray, Vincin, Marle and Noyalo rivers, flow through several river basins (*Figure 4–16*) into the gulf carrying MTEs, aquaculture, industrial and urban wastes from the upstream might have been responsible for the increased concentration of MTEs during the monsoon period. In addition, the increased level of organic compounds, nutrients, phosphate, organic matter and decreased salinity during the monsoon period enhances the formation of metal complex and its deposition in sediment by reducing the mobility (Melamed and Villas Boas, 1998; Kamala–Kannan and Krishnamoorthy, 2006).

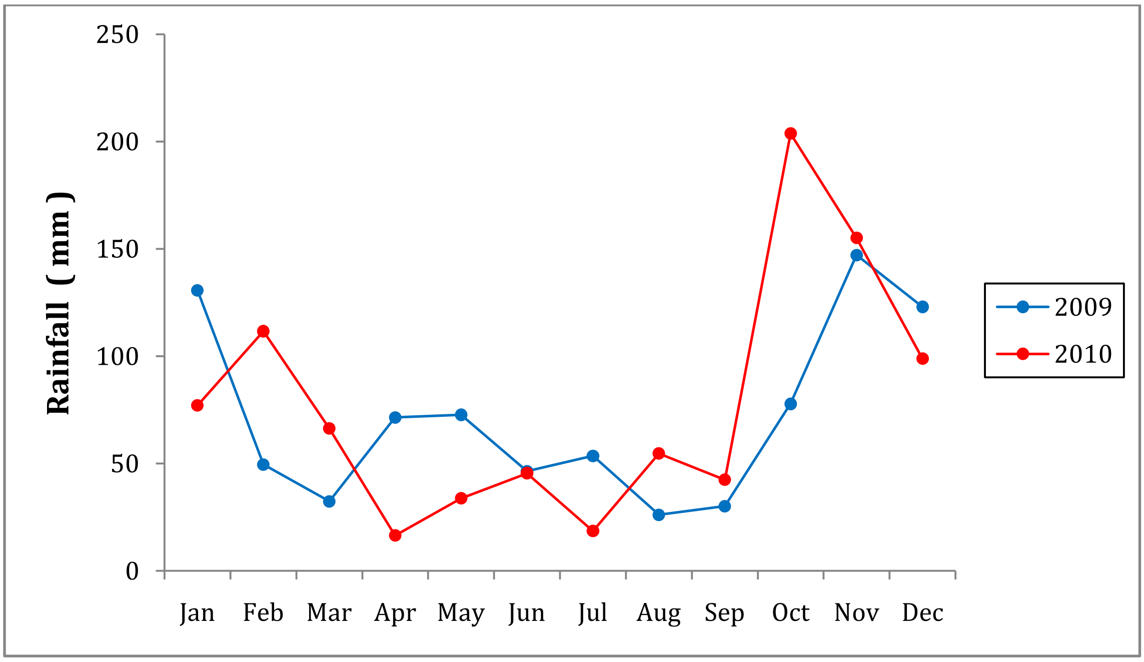

Figure 4–15. *Average annual precipitation input for year 2009 and 2010 at Quiberon bay and gulf of Morbihan area.*

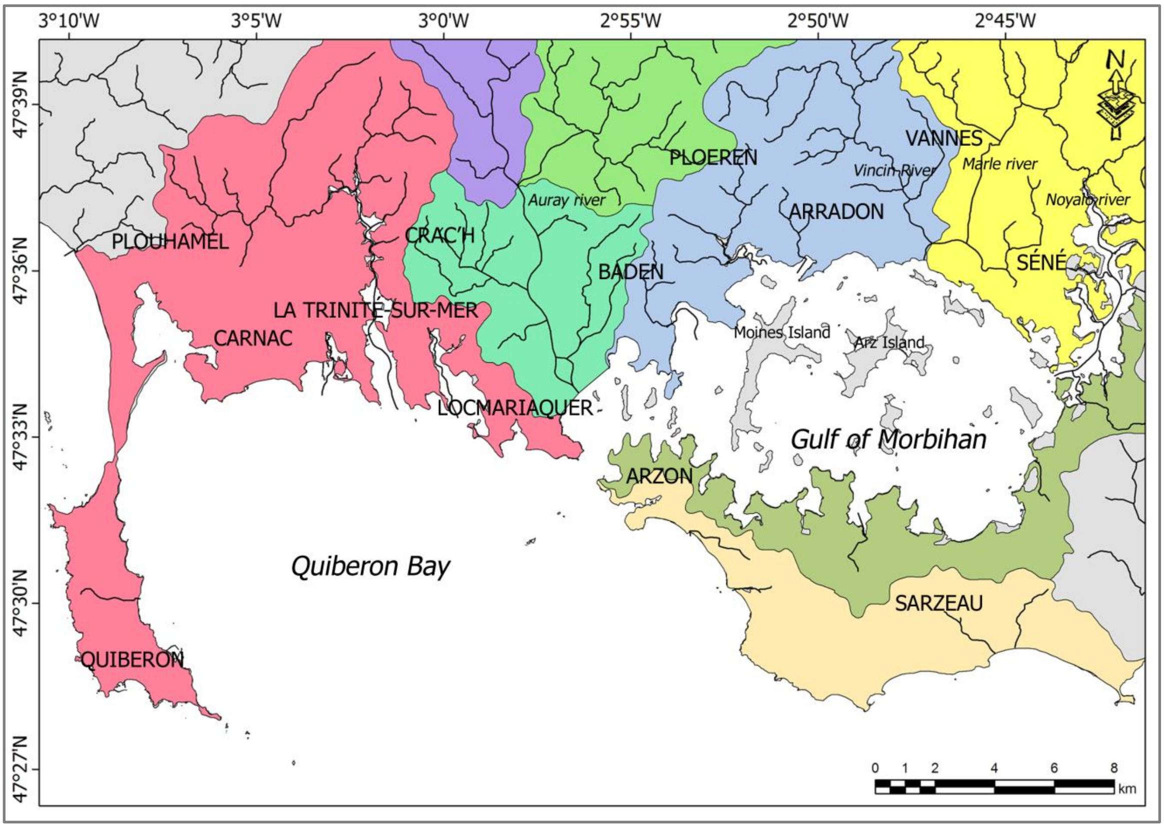

Figure 4–16. *Division of river basin zone surrounding Quiberon bay and gulf of Morbihan.*

Overall, MTEs content in gulf of Morbihan sediments were higher compared to sediments from the Quiberon bay. Among the possible explanations from the data obtained, gulf of Morbihan ecosystem always receives the source of organic pollution from upstream regions as described above, especially during monsoon season. Incidentally, sampling was also carried out during the end of the season that may reflect the present pollution status.

Meanwhile, this region is a closed marine environment and has a high density of human population, high density of traffic and surrounding by agriculture activities (*Figure 4–17*). In contrast, Quiberon bay is located in an area of strong tidal flushing and low density of population, and the MTEs tend to be diluted by shell rich sediments (Deely, 1991; Lin and Chen, 1996).

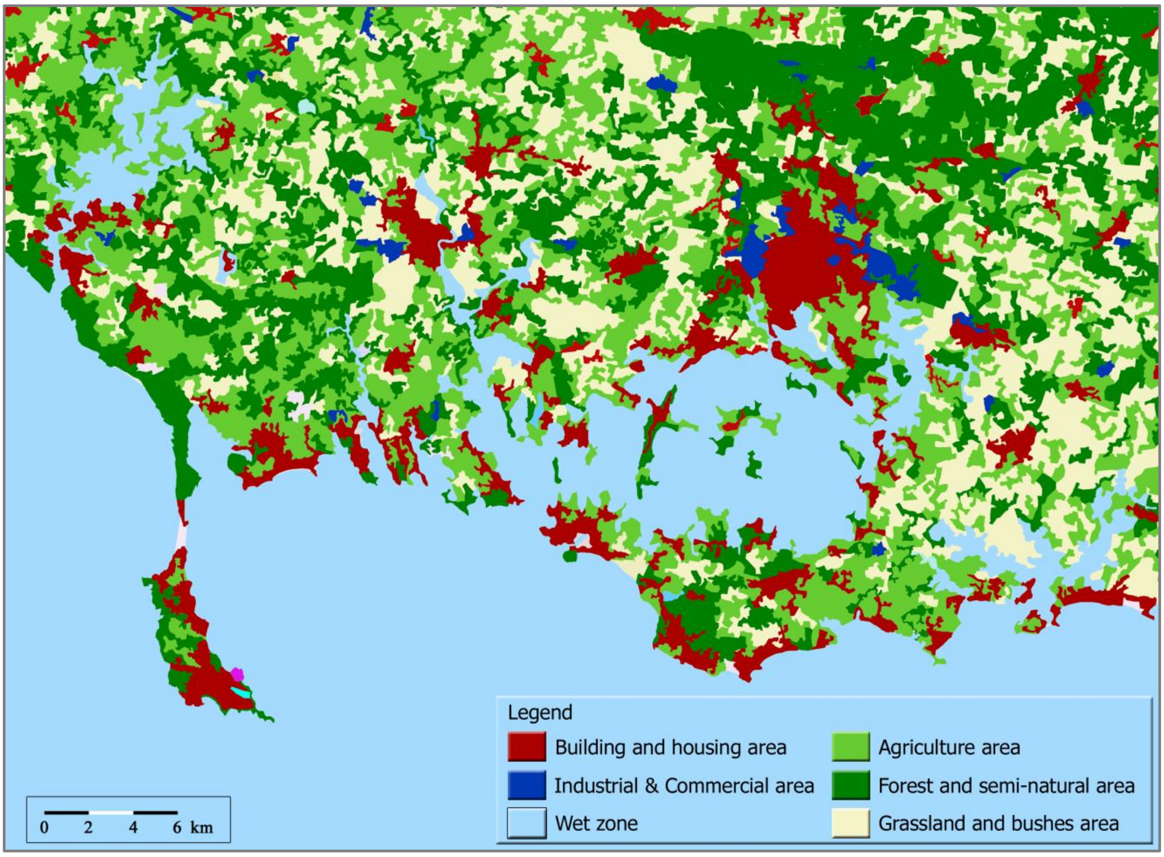

Figure 4–17. *Land–use activities surrounding Quiberon bay and gulf of Morbihan.*

In order to obtain a clear explanation for each MTEs studied, all elements were discussed separately. Overall resources and possible sources of the MTEs to Quiberon bay and the gulf of Morbihan surficial sediments were also described. Furthermore, the current situation of the pollution status of those MTEs was also compared with UCC value (Wedepohl, 1995) and two threshold values N1 and N2 proposed by GEODE (2000) and established by France under the OSPAR convention, particularly on dredging and dumping activities. Under the N1 values, the impact was considered as neutral or negligible, whereas above N2 values indicate that the dumping process should be prohibited and further action plan should be taken to control the levels. If the values lie between N1 and N2 values, further investigation may be necessary depending on the particular project in the area. Besides compared to those values, our results were also compared with those conveyed from European and Asian regions.

4.4.1 Concentrations of chromium in sediments

Chromium (Cr) is an element found in many minerals, which are widely distributed in the earth's crust and considered to be essential to a part of the living organism (Catsiki and Florou, 2006; Bošnir *et al*., 2010). According to Moore (1991), Cr is considered only moderately toxic to marine aquatic organisms. Two ionic forms of Cr, Cr(III) and Cr(VI) are present in various forms in sediment, water and in the biota (Besser *et al*., 2004). Environmental concentration of Cr is known to increase these days due to industrial development. The atmosphere has become a major pathway for long–range transfer of Cr to the different ecosystems. Cr–containing particles in the atmosphere are carried over different distances by the wind, before they fall or washed put from the air onto the terrestrial and water surfaces (Bielicka *et al*., 2005) before they settled down to the sediment in the aquatic environment.

Cr present in the sediment originates from anthropogenic sources which account for 60–70 %, as well as from natural sources which account for the remaining 30–40 %. The main human activities contributing to the Cr increase in the sediment are: manufacture of chemicals mainly pigments for color, chrome plating (McConnell *et al*., 1996), treated domestic sewage (Hench 2003), metallurgical industrial and combustion of fuels (Bielicka *et al*., 2005). The main natural sources are volcanic eruptions (Adamo *et al*., 2006; Zampella *et al*., 2010) and erosion of soils and rocks (Shtiza *et al*., 2005; Bini *et al*., 2008), airborne sea salt particles and smoke from forest wildfires (Kotas and Stasicka, 2000).

The comparison isopleth maps between the Quiberon bay and the gulf of Morbihan is shown in *Figure 4–18*. From the concentration maps, it is noted that the concentrations in the gulf of Morbihan were higher compared to Quiberon bay surficial sediments for both sampling periods, Dec 2009 and Oct 2010. The statistical analysis, *t*–Test shows that the concentrations were significantly different between the Quiberon bay and gulf of Morbihan for both sampling periods with the *p* value smaller than 0.05.

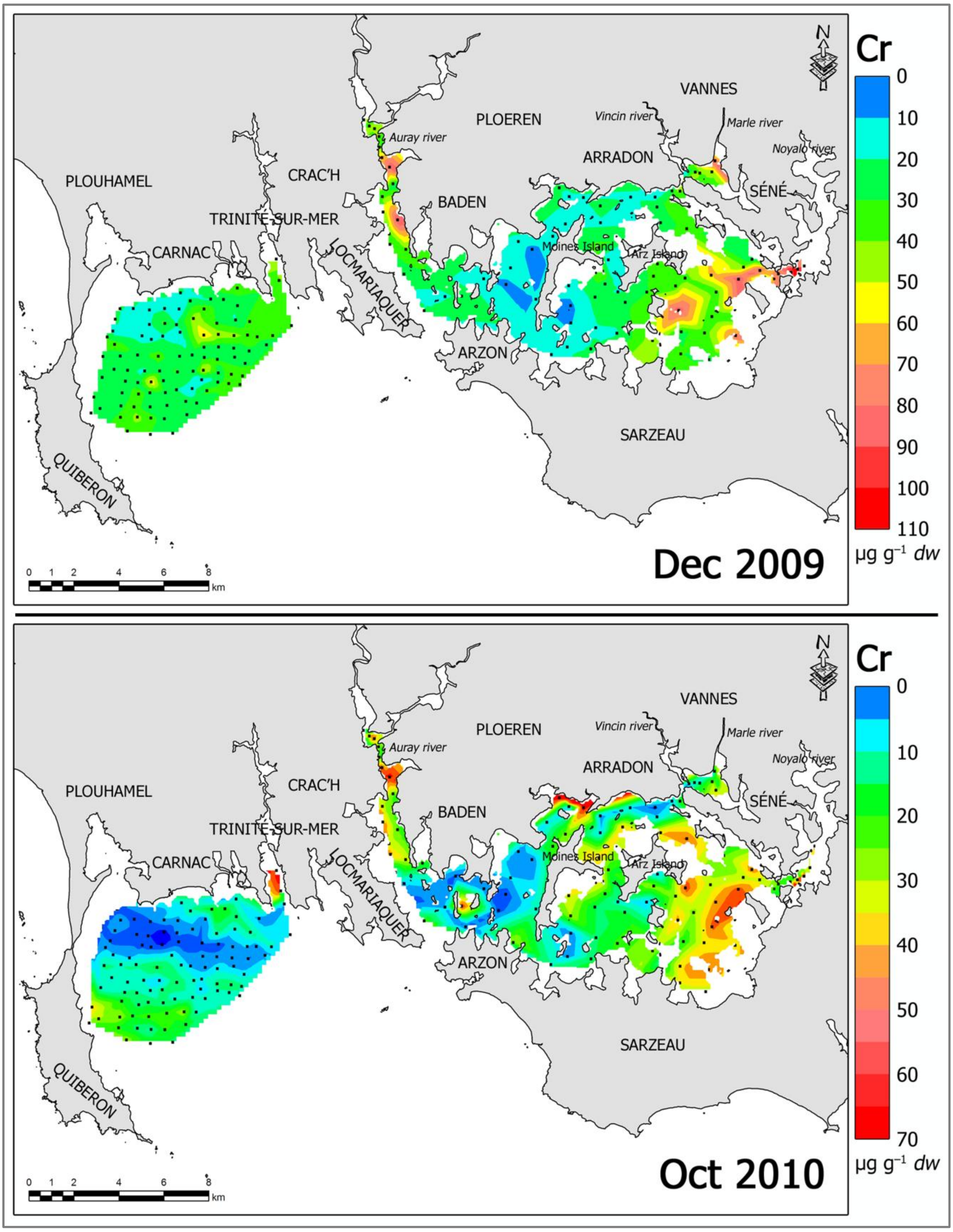

Figure 4–18. *Isopleth maps of Cr accumulation in South Brittany waters.*

Figure 4–19 shows the average graph for concentrations of Cr distribution by zone in Quiberon bay surficial sediments. Generally, the mean concentrations followed the order: E>B>C>D>A>F. The mean concentrations were lower in the zones A to E, which is located within the bay area and the concentrations were lower than the UCC value, 35 µg g^{-1} *dw*. (Wedepohl, 1995) for both sampling periods except in zone A, (southern zone) which slightly higher than the UCC value. Meanwhile, zone H which located at Trinité–sur–Mer area has relatively higher mean concentrations for both sampling periods and these concentrations were above the UCC values. However, the concentrations were far lower than the N1 values set by the GEODE.

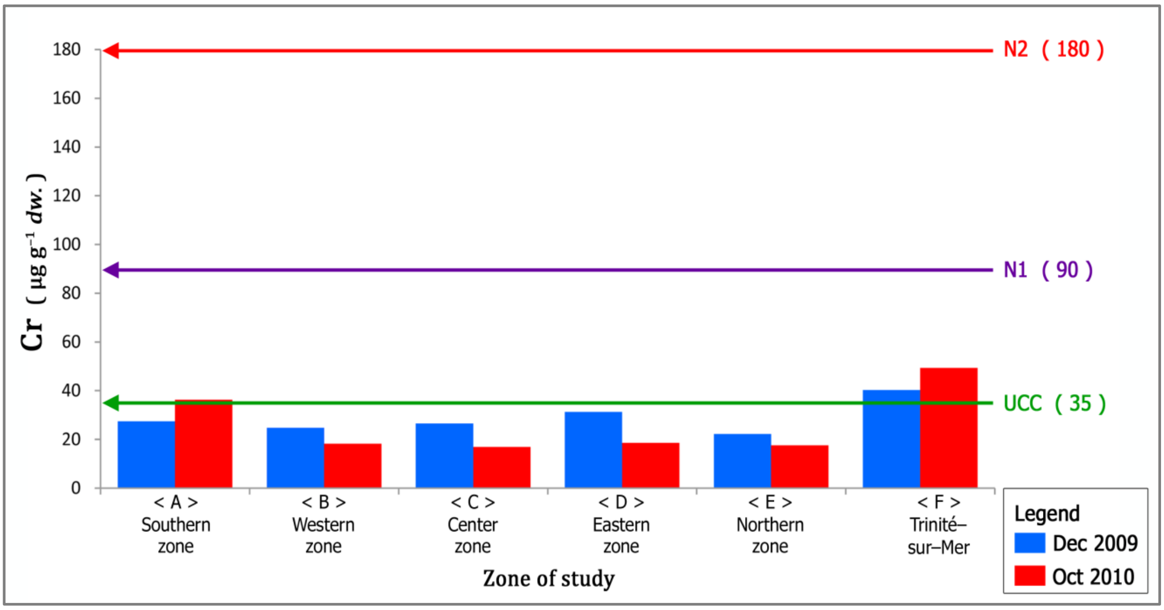

Figure 4–19. *Average concentrations of Cr based on different zone in Quiberon bay surficial sediments for both sampling periods.*

Table 4–4 shows the levels of Cr reported from European and Asian regions. The comparison revealed that the levels were comparable and lower than N'guessan *et al*. (2009) study at Gascogne coast and Toulon bay by Tessier *et al*. (2011) in the France region. Yet, our levels were slightly higher than the samples from Southern Spain analyzed by Usero *et al*. (2005).

Table 4–4. *Comparison of Cr levels in Quiberon bay surficial sediments with other studies reported from European and Asian regions.*

Region	**Cr (µg g^{-1} *dw*.)**	**Reference**
Quiberon bay	24.4	This study
European region		
Gascogne coast, France	53	N'guessan *et al*., 2009
Toulon bay, France	33.7	Tessier *et al*., 2011
Càdiz bay, Spain	23–180	Araujo *et al*., 2009
Southern Spain, Spain	21.7	Usero *et al*., 2005
Southwest coast, Spain	32–92	Morillo *et al*., 2004
San Simon bay, Spain	42.5	Alvarez–Iglesias *et al*., 2007
Asian region		
Gemlik bay, Turkey	109	Balkis *et al*., 1999
Bengal bay, India	57	Selvaraj *et al*., 2004
Bohai bay, China	110	Meng *et al*., 2008
Masan bay, South Korea	67.1	Hyun *et al*., 2007
Penny bay, Hong Kong	28	Chan *et al*., 2001

The mean concentrations of Cr in gulf of Morbihan surficial sediments are shown in *Figure 4–20*. From the figure, the sequence of the concentrations follows the decreasing order: D>H>B>C>G>F>A>E, where higher mean concentrations were observed in the rivers and eastern zones of the gulf, and were above the UCC value (Wedepohl, 1995), 35 µg g^{-1} *dw*. In contrast, western and gulf entrance zones had lower mean concentrations and slightly below the UCC value. When compared with the GEODE N1–N2 values, only sediment samples from Noyalo river during Dec 2009 sampling were close to the N1 value, 90 µg g^{-1} *dw*. and far below than N2 value, 180 µg g^{-1} *dw*. The somewhat higher concentrations in some sampling location may be derived from human activities surrounding from the gulf area.

A further comparison with published data from European and Asian regions (*Table 4–5*) showed that the levels of Cr in Quiberon bay were lower than the study by Robbe *et al*. (1985) at Loire estuary, Gironde estuary by Larrose *et al*. (2010) and Rhône estuary by Ferrand *et al*. (2012) studies in France region. However, our levels were higher compared to Thau lagoon in France examined by Rigollet *et al*. (2004) and Ria de Vigo in Spain (Rubio *et al*., 2000)

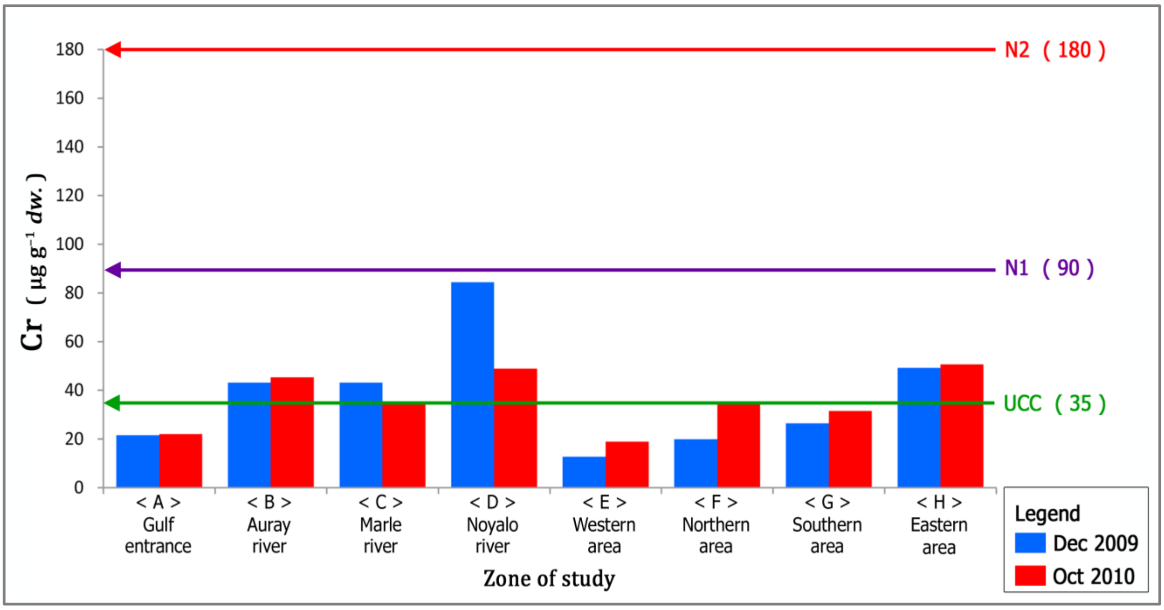

Figure 4–20. *Average concentrations of Cr based on different zone in gulf of Morbihan surficial sediments for both sampling periods.*

Table 4–5. *Comparison of Cr levels in gulf of Morbihan surficial sediments with other studies reported from European and Asian regions.*

Region	Cr (µg g^{-1} *dw.*)	Reference
Gulf of Morbihan	37.4	This study
European region		
Loire estuary, France	93.8	Robbe *et al.*, 1985
Gironde estuary, France	66.8	Larrose *et al.*, 2010
Gulf of Lion, France	92.3	Radakovitch *et al.*, 2008
Thau lagoon, France	21.8	Rigollet *et al.*, 2004
Rhône estuary, France	44.6	Ferrand *et al.*, 2012
Bilbao estuary, Spain	106	Ruiz and Saiz–Salinas, 2000
Ria de Vigo, Spain	34.0	Rubio *et al.*, 2000
Gulf of Finland, Finland	85	Leivouri, 1998
Gulf of Naples, Italy	72.5	Adamo *et al.*, 2005
Gulf of Taranto, Italy	85.9	Buccolieri *et al.*, 2006
Gulf of Thermaikos, Greece	47	Christophoridis *et al.*, 2009
Asian region		
Gulf of Izmit, Turkey	32	Ergin *et al.*, 1991
Gulf of Gemlik, Turkey	117	Unlü *et al.*, 2008
Gulf of Oman, Oman	3.36–303	de Mora *et al.*, 2004
Gulf of Suez, Egypt	7.6	Hamed and Emara, 2006
Gulf of Mannar, India	177	Jonathan *et al.*, 2004
Gulf of Thailand, Thailand	27.2–1105	Censi *et al.*, 2006

4.4.1 Concentrations of manganese in sediments

Manganese (Mn) is the eleventh element in term of abundance in the earth's crust (Anschutz, 2005) and an essential micronutrient for all aquatic organisms (Rehm and Reed, 1986). However, at high concentrations, it can be toxic to those organisms (Gadd and Griffiths, 1977). According to Allen (1989), sediments in unpolluted environment contain 5–500 µg g^{-1} Mn. In the marine oxygenated environment, Mn is present in the form of Mn(IV) oxide and Mn(III) oxyhydroxides (Burdige, 1993; Post, 1999). Mn mainly occurs as Mn(II) carbonates in anoxic sediments and is generally in solid solution with $CaCO_3$. Oxidized forms of Mn are very reactive and have a strong capacity to accumulate other trace metals (Stumm and Morgan, 1996).

The main sources and input of Mn compound to coastal waters are from river run–off (Bender *et al.*, 1977; Jones and Murray, 1985) and dissolved Mn flux from margin sediments (Johnson *et al.*, 1992). Most of the Mn produced is used for the manufacturing of steel, production of non–ferrous alloys (Lison *et al.*, 1997), dry cell batteries (Nan *et al.*, 2006), wood preservatives (Demirezen and Aksoy, 2006) agriculture fertilizer and fungicide (Pearson and Greenway, 2005).

The comparison concentration of Mn isopleth maps between the Quiberon bay and the gulf of Morbihan are shown in *Figure 4–21*. From the concentration maps, a comparable concentration was observed between the Quiberon bay and gulf of Morbihan surficial sediments for both sampling periods, Dec 2009 and Oct 2010. The *p* value calculated from statistical analysis, *t*–Test shows that there were no significant differences in the concentrations during Dec 2009 and Oct 2010 sampling period with a *p* value greater than 0.05.

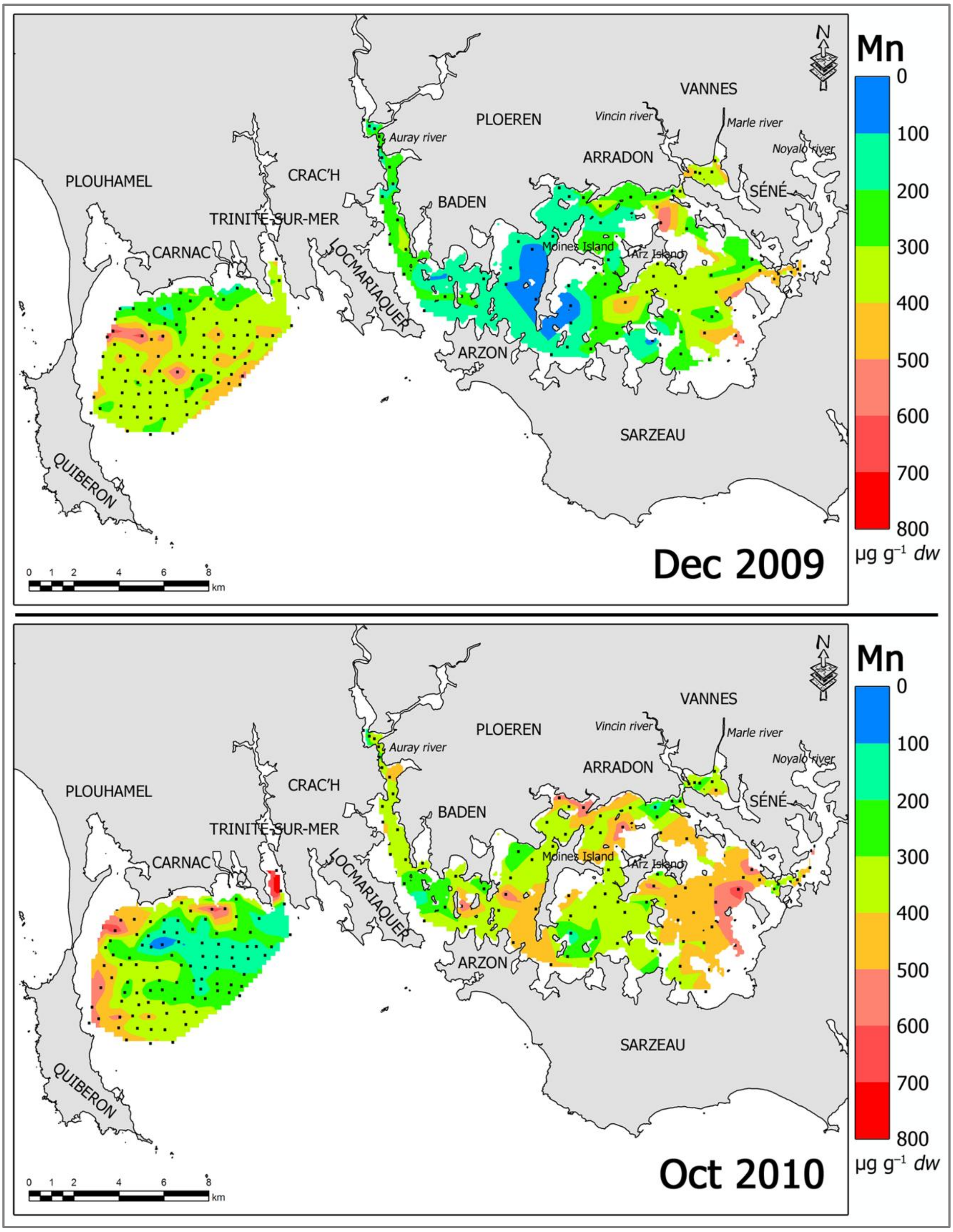

Figure 4–21. *Isopleth maps of Mn accumulation in South Brittany waters.*

Figure 4–22 shows the mean concentrations of Mn in Quiberon bay surficial sediments in different zones. The sediments that enrich with Mn followed the decreasing order: F>B>D>A>C>E. Higher mean concentrations were observed in zone F located at the Trinité–sur–Mer area while the lower mean concentrations were found in zone E, northern of the bay. In comparison with the UCC value, 527 µg g^{-1} *dw*. proposed by Wedepohl (1995), the analyzed mean concentrations were relatively lower except the concentrations in Oct 2010 sampling where the concentrations were equal to the UCC value. However, no comparison between the concentrations and N1–N2 classification values due to lack of Mn data from the report.

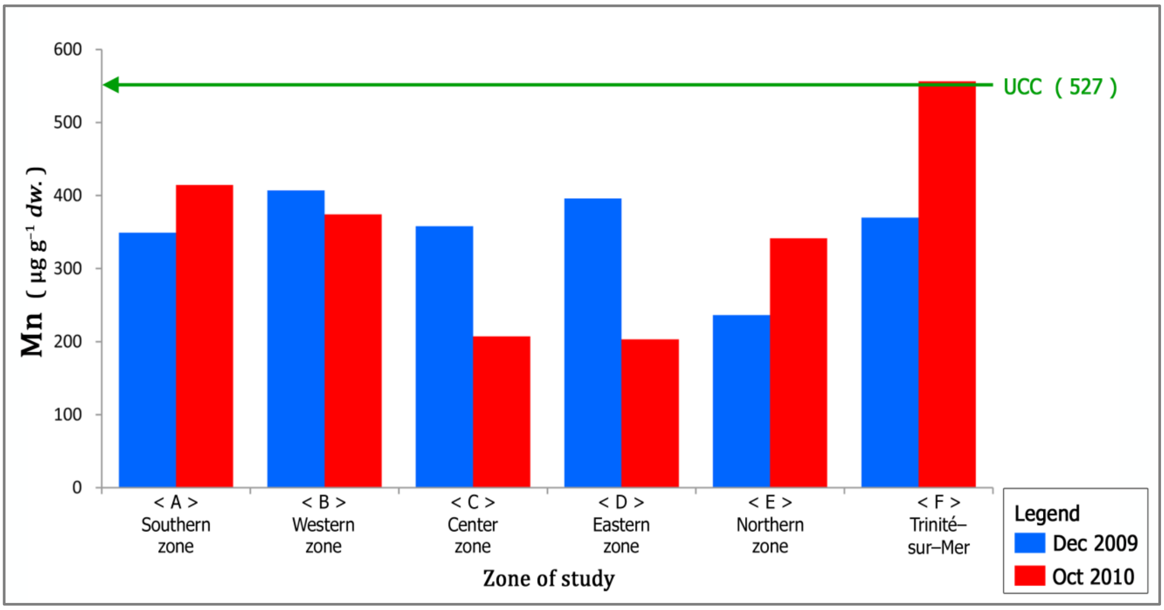

Figure 4–22. *Average concentrations of Mn based on different zone in Quiberon bay surficial sediments for both sampling periods.*

Table 4–6 shows the comparison of Mn levels from Quiberon bay and other studies conducted from in European and Asian regions. We found that the levels in the Quiberon bay were slightly lower compared to study by Caplat *et al*. (2005) in Seine bay and three times lower than the Gascogne region analyzed by N'guessan *et al*. (2009) in the France region. Conversely, the levels in San Simon bay (Alvarez–Iglesias *et al*., 2007) were three times lower than the levels in our study.

Table 4–6. *Comparison of Mn levels in Quiberon bay surficial sediments with other studies reported from European and Asian regions.*

Region	Mn (µg g^{-1} *dw.*)	Reference
Quiberon bay	328	This study
European region		
Seine bay, France	415	Caplat *et al.*, 2005
Gascogne region, France	1050	N'guessan *et al.*, 2009
Càdiz bay, Spain	110–450	Araujo *et al.*, 2009
San Simon bay, Spain	110	Alvarez–Iglesias *et al.*, 2007
Southwest coast, Spain	180–576	Morillo *et al.*, 2004
Belgian north sea, Belgium	80–430	Alsenoy *et al.*, 1993
Liverpool bay, UK	292	Camacho–Ibar *et al.*, 1992
Milos bay, Greece	1685	Karageorgis *et al.*, 1998
Asian region		
Gimlik bay, Turkey	613	Balkis *et al.*, 1999
Bengal bay, India	373	Muthu Raj and Jayaprakash, 2008
Jinzhou bay, China	210–730	Wang *et al.*, 2010
Yellow sea, South Korea	360	Cho *et al.*, 1999
Youngil bay, South Korea	286	Lee *et al.*, 2008

Figure 4–23 shows the mean concentrations of Mn in gulf of Morbihan surficial sediments based on different zones. The enrichment of Mn according to following orders: A<E<G<F<B<C<D<H. Sediments from near the entrance of the gulf, zones A and E, show the lower mean concentrations compared to the rivers and eastern zone (zones H, B, C, D), which exhibit a higher mean concentration. From the figure, all the mean concentrations were below the UCC value, 527 µg g^{-1} *dw.* suggested by Wedepohl (1995). Based on the comparison, Mn compounds may enter the sediments by natural weathering process and from crustal material.

When compared to Seine estuary investigated by Chiffoleau *et al.* (1994) and Rhône estuary by Ferrand *et al.* (2012) in France coastal waters, the levels of Mn in gulf of Morbihan were lower than their findings. On the other hand, our levels were slightly higher when we make a comparison to Rigollet *et al.* (2004) study of Thau lagoon in France Mediterranean sea.

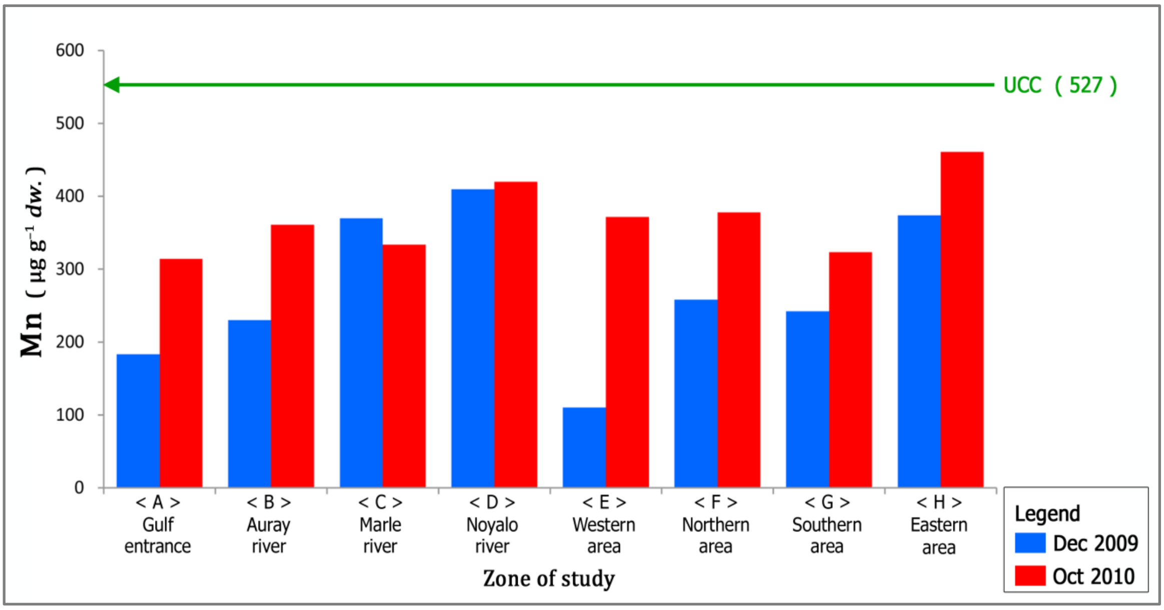

Figure 4–23. *Average concentrations of Mn based on different zone in gulf of Morbihan surficial sediments for both sampling periods.*

Table 4–7. *Comparison of Mn levels in gulf of Morbihan surficial sediments with other studies reported from European and Asian regions.*

Region	**Mn (µg g^{-1} *dw.*)**	**Reference**
Gulf of Morbihan	329	This study
European region		
Seine estuary, France	494	Chiffoleau *et al.*, 1994
Thau lagoon, France	190	Rigollet *et al.*, 2004
Rhône estuary, France	483	Ferrand *et al.*, 2012
Ria de Vigo, Spain	244	Rubio *et al.*, 2000
Bilbao estuary, Spain	299	Ruiz and Saiz–Salinas, 2000
Gulf of Naples, Italy	389	Adamo *et al.*, 2005
Gulf of Taranto, Italy	893	Buccolieri *et al.*, 2006
Gulf of Finland, Finland	507	Leivouri, 1998
Asian region		
Gulf of Gemlik, Turkey	634	Unlu *et al.*, 2008
Gulf of Izmit, Turkey	186	Ergin *et al.*, 1991
Gulf of Oman, Oman	13.2–360	De Mora *et al.*, 2004
Gulf of Aden, Yemen	721	Mostafa *et al.*, 2009
Gulf of Cambay, India	1488	Tewari *et al.*, 2001
Gulf of Mannar, India	305	Jonathan *et al.*, 2004
Gulf of Thailand, Thailand	330–12270	Censi *et al.*, 2006

4.4.3 Concentrations of iron in sediments

Redox cycle of iron (Fe) is known to interact with many biogeochemically important elements (Burdige, 1993; Canfield *et al*., 2005). In marine sediments, solid–phase Fe occurs in several phases: as amorphous or crystalline Fe(III) (oxyhydr)oxides, ions bound to mineral surfaces, structurally coordinated Fe in crystalline silicates such as clay minerals (Whiteley and Pearce, 2003), phosphates, reduced Fe(II) sulfides (Lyons and Severmann, 2006), and even carbonates in anoxic sediments (Haese *et al*., 1997; Hyacinthe and van Cappellen, 2004).

In oxic marine sediments, secondary solid–phase Fe occurs dominantly as Fe(III) (oxyhydr)oxides (hereafter collectively referred to as Fe(III) oxides) with a wide spectrum of mineralogy, crystallinity, morphology and chemical composition, and, therefore, displays quite variable chemical reactivity towards dissolving sulfide and/or microbial reduction (Canfield, 1989; Poulton *et al*., 2004; Haese, 2006; Hyacinthe *et al*., 2006). Reactive Fe(III) oxides in oxic marine sediments are an important sink for phosphate and a number of transition elements including metal pollutants (Rozan *et al*., 2002; Hyacinthe and van Cappellen, 2004). On the other hand, reductive dissolution of the Fe pool in anoxic environments is a crucial switch for the release and benthic efflux of adsorbed and incorporated elements (Otero *et al*., 2003; Sundby, 2006). Continental sources of Fe to the marine environment are numerous and include airborne dust, riverine input, continental shelf sediment resuspension, submarine ground–water discharge, and remobilization during sediment digenesis (Rozan *et al*., 2002; Hyacinthe and van Cappellen, 2004;).

Figure 4–24 shows the isopleth maps of Fe concentrations comparison in surficial sediments between the Quiberon bay and gulf of Morbihan systems. Lower concentrations were recorded in the Quiberon bay sediments compared to sediment from the gulf of Morbihan for both sampling periods, Dec 2009 and Oct 2010. This comparison was then proved with the statistical analysis, *t*–Test where the calculated p value was smaller than 0.05 which explained that the concentrations between both areas were varied significantly.

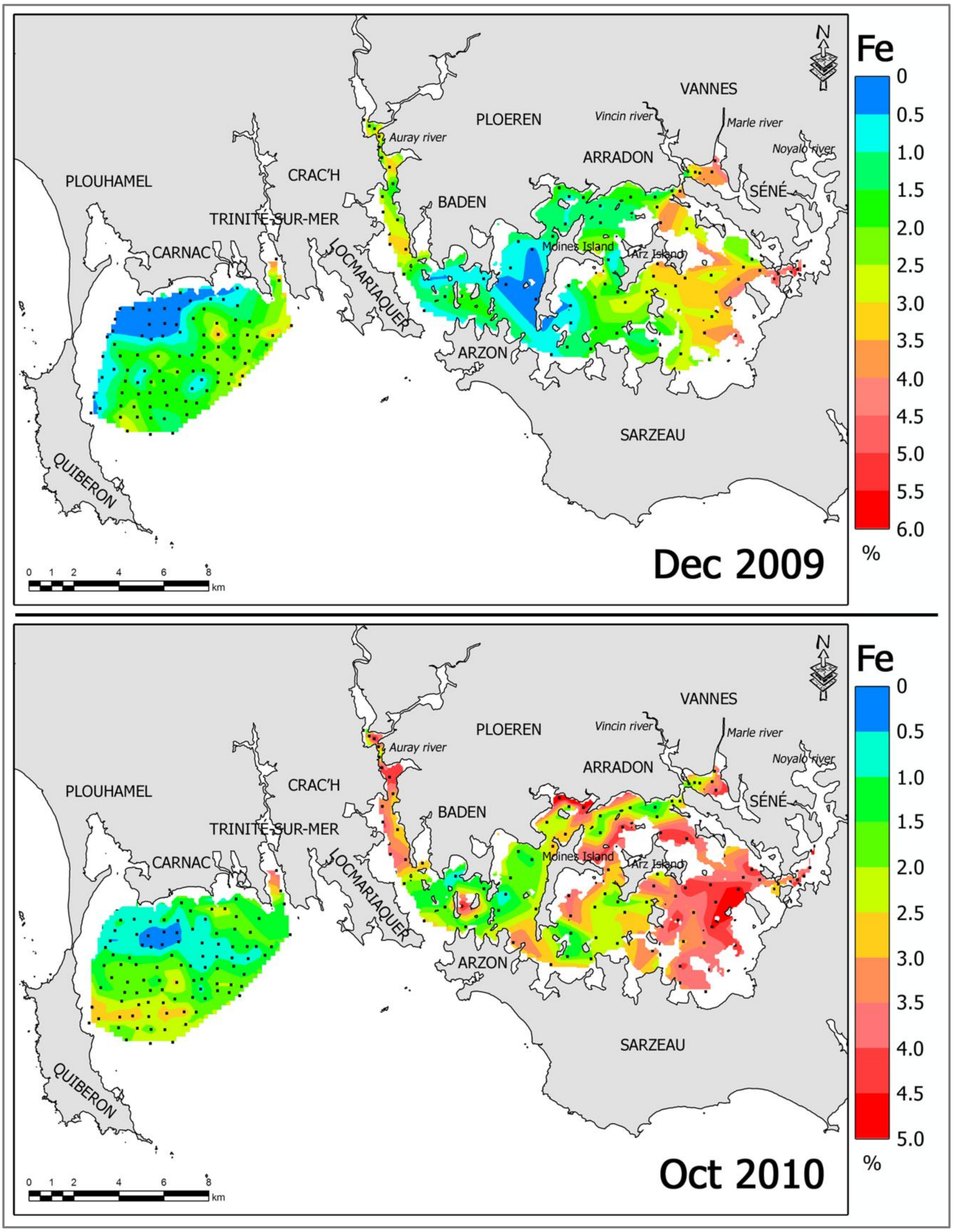

Figure 4–24. *Isopleth maps of Fe accumulation in South Brittany waters.*

Figure 4–25 shows the mean concentrations of Fe based on the zone division in Quiberon bay surficial sediments. The sequence of the mean concentrations follows the increasing pattern: E<B<C<D<A<F. Lower mean concentration occurred at innermost of the bay, while zone Trinité–sur–Mer had the higher mean concentration. Generally, the mean concentrations did not exceed the UCC value, 3.09 % by Wedepohl (1995) except the sediments from Trinité–sur–Mer during Dec 2009. However, the concentrations did not compare with N1–N2 data from GEODE due to lack of the data from the report. From the comparison, Fe in Quiberon bay sediments can be concluded to be entirely from crustal materials or natural weathering processes.

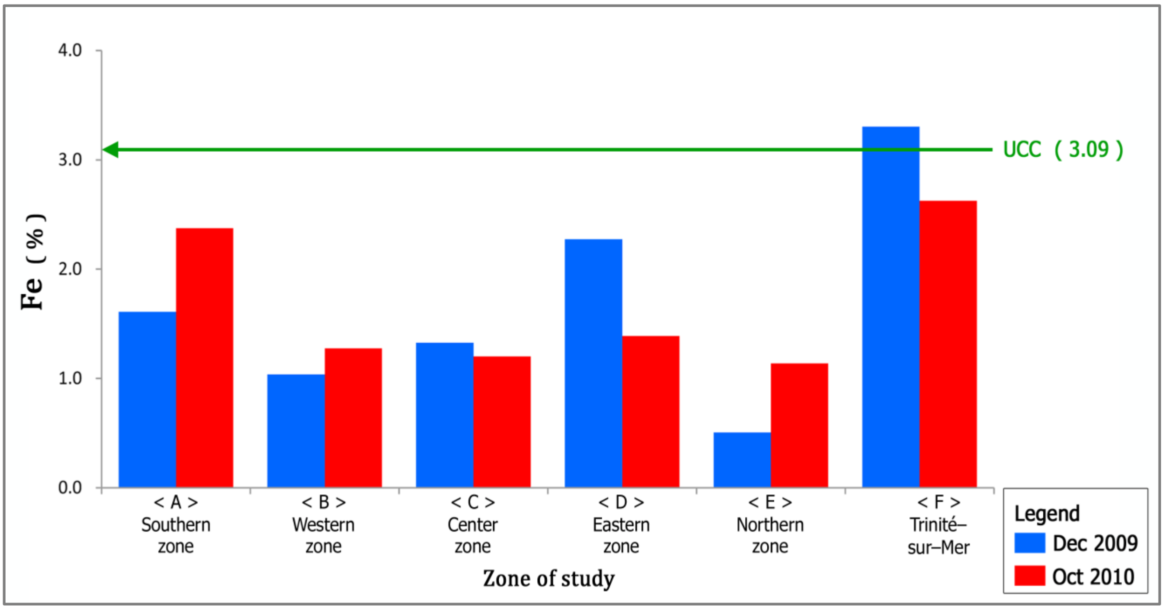

Figure 4–25. *Average concentrations of Fe based on different zone in Quiberon bay surficial sediments for both sampling periods.*

The low levels of Fe reported in this Quiberon bay surficial sediments agree favorably with some measurements that have been reported in other regions from European and Asian such as from the Càdiz bay in Spain and Bengal bay in India (*Table 4–8*). The levels were found to be quite low through most of the regions compared; two times lower compared to the Gascogne coast by N'guessan *et al*. (2009) and far below to Caplat *et al*. (2005) study at Seine bay in France northern coast.

Table 4–8. *Comparison of Fe levels in Quiberon bay surficial sediments with other studies reported from European and Asian regions.*

Region	**Fe (%)**	**Reference**
Quiberon bay	1.48	This study
European region		
Seine bay, France	4.29	Caplat *et al.*, 2005
Gascogne coast, France	2.8	N'guessan *et al.*, 2009
North coast, Belgium	0.25–2.85	Alsenoy *et al.*, 1993
Càdiz bay, Spain	0.64–3.4	Araujo *et al.*, 2009
Southwest coast, Spain	1.59–3.53	Morillo *et al.*, 2004
Liverpool bay, UK	0.46	Camacho–Ibar *et al.*, 1992
Asian region		
Gemlik bay, Turkey	4.1	Balkis *et al.*, 1999
Bengal bay, India	1.5	Selvaraj *et al.*, 2004
Jinzhou bay, China	0.94–4.3	Wang *et al.*, 2010
Youngil bay, South Korea	2.4	Lee *et al.*, 2008
Manila bay, Philippines	15.1	Prudente *et al.*, 1994

The mean concentrations of Fe in gulf of Morbihan surficial sediments are shown in *Figure 4–26*. The sequence of the contaminations follows the decreasing order: D>H>B>C>F>G>A>E, where the lower mean concentration was observed in gulf entrance and western zone, while higher mean concentrations were recorded at the eastern zone and all the rivers zone. The mean concentrations in zones A, E, F and G were slightly lower compared to the UCC value, 3.09 % by Wedepohl (1995), while sediments from rivers and western zones during both samplings on Dec 2009 and Oct 2010, respectively which close to and exceed the UCC value. From the comparison, the source of Fe in the surficial sediments may come from natural and anthropogenic sources.

Results from European and Asian regions for levels of Fe comparison in gulf of Morbihan sediments are shown in *Table 4–9*. Only a few studies had been conducted in France coastal waters on levels of Fe. Our results are higher compared to Rhône estuary study by Ferrand *et al.* (2012) and much higher than study by Rigollet *et al.* (2004) in the Thau lagoon from France region. However, the levels were comparable to the study by Ruiz and Saiz–Salinas (2000) at Bilbao estuary, Spain.

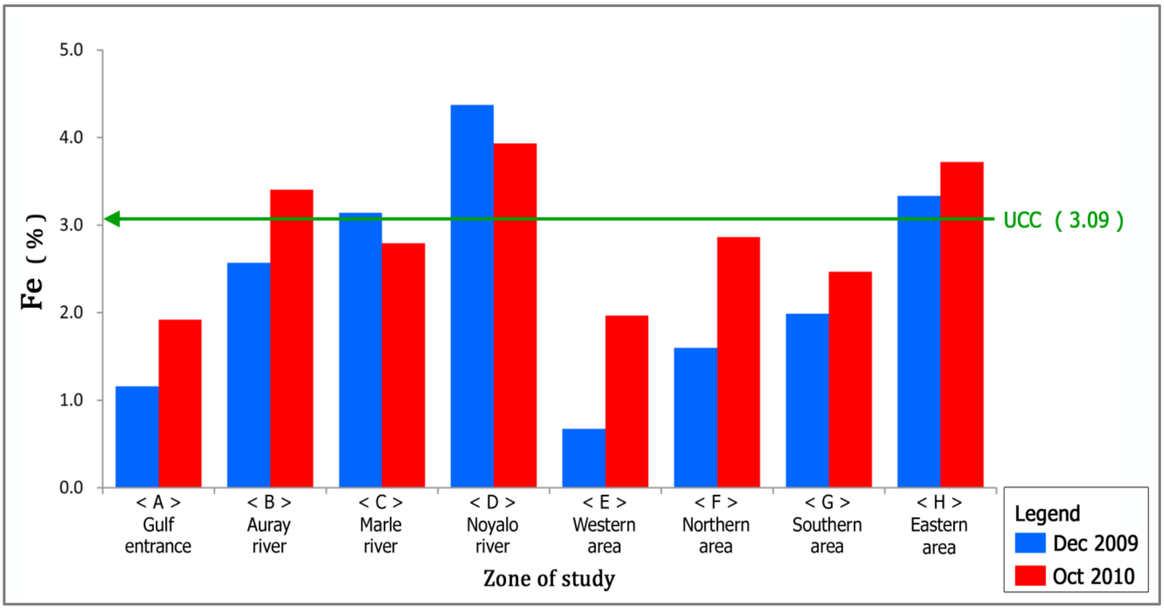

Figure 4–26. *Average concentrations of Fe based on different zone in gulf of Morbihan surficial sediments for both sampling periods.*

Table 4–9. *Comparison of Fe levels in gulf of Morbihan surficial sediments with other studies reported from European and Asian regions.*

Region	Fe (%)	Reference
Gulf of Morbihan	2.73	This study
European region		
Thau lagoon, France	0.61	Rigollet *et al.*, 2004
Rhône estuary, France	2.24	Ferrand *et al.*, 2012
Bilbao estuary, Spain	2.69	Ruiz and Saiz–Salinas, 2000
Ria de Vigo, Spain	3.51	Rubio *et al.*, 2000
Gulf of Finland, Finland	4.5	Leivouri, 1998
Gulf of Venice, Italy	0.01–2.9	Donazzolo *et al.*, 1981
Gulf of Taranto, Italy	3.16	Buccolieri *et al.*, 2006
Gulf of Thermaikos, Greece	3.9	Christophoridis *et al.*, 2009
Asian region		
Gulf of Izmit, Turkey	2.69	Ergin *et al.*, 1991
Gulf of Gemlik, Turkey	4.4	Unlü *et al.*, 2008
Gulf of Suez, Egypt	2.91	Hamed and Emara, 2006
Gulf of Aden, Yemen	1.5	Mostafa *et al.*, 2009
Gulf of Oman, Oman	0.031–2.9	de Mora *et al.*, 2004
Gulf of Mannar, India	1.26	Jonathan *et al.*, 2004
Gulf of Cambay, India	7.5	Tewari *et al.*, 2001
Gulf of Thailand, Thailand	0.49–24.6	Censi *et al.*, 2006

4.4.4 *Concentrations of cobalt in sediments*

Cobalt (Co) is an essential element for marine organisms (Felipe–Satelo *et al*., 2004) and an important micronutrient for marine phytoplankton (Morel *et al*., 1994), in particular the photosynthesis process (Sunda and Huntsman, 1995). The concentrations of Co range between 0.1 and 50 µg g^{-1} for soils (Hamilton, 1994) and between 0.1 and 74 µg g^{-1} for sediments (Bowen, 1979). According to Saito and Moffett (2002), Co has a unique geochemistry; it is neither a typical nutrient nor a scavenged–type element. Additionally, dissolved Co in seawater may be strongly complexed with natural organic ligands (Zhang *et al*., 1990), a process that affects the geochemical cycling, bioavailability and toxicity of this trace element in the marine environment (Ellwood and van den Berg, 2001; Tovar–Sanchez *et al*., 2004).

The sources of Co in the marine environment are both from natural and anthropogenic input. Trace amount of Co occur in rocks, dust, soil, sediments and animal tissues, and they are mobilized in volcanic eruptions, forest fires and biogenic emission (Moreira *et al*., 2002). The man–made or anthropogenic sources are by the products of burning of coal and oil, industrial processes, vehicular exhausts and sewage sludge. This Co and its compounds are used widely in steel and alloys production (Kim *et al*., 2011), electroplating (Manohar *et al*., 2006), agriculture fertilizers (Hala, 2007; Collins and Kinsela, 2011), drier for painting process and coloring pigments (Sayonara *et al*., 2011).

Figure 4–27 shows the comparison isopleth concentration of Co maps between the Quiberon bay and gulf of Morbihan surficial sediments. Generally, the concentrations were higher in the gulf of Morbihan sediments compared to the Quiberon bay for both sampling periods. The statistical analysis, *t*–Test shows that the concentrations were significantly different between the Quiberon bay and gulf of Morbihan for both sampling periods with the *p* value smaller than 0.05.

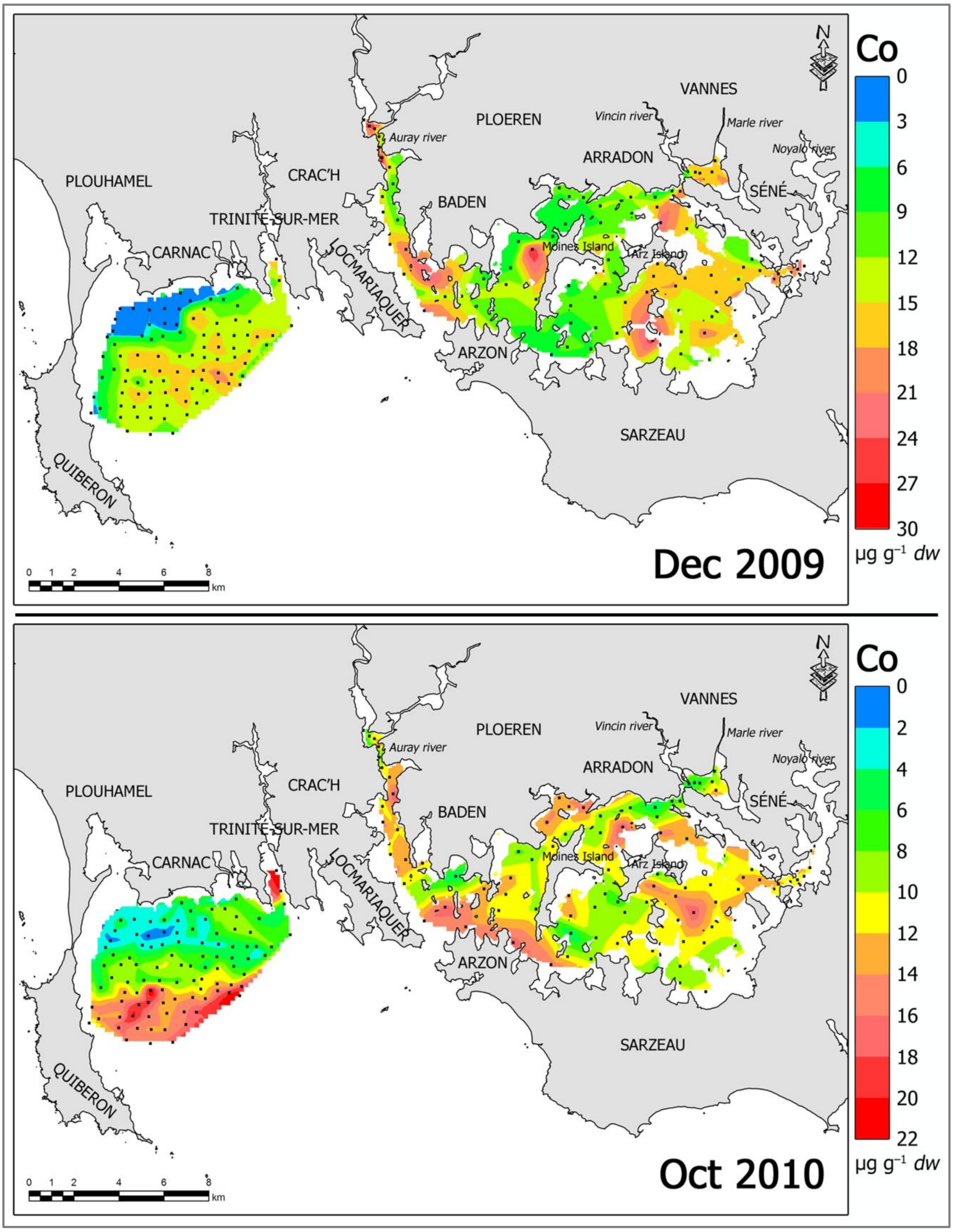

Figure 4–27. *Isopleth maps of Co accumulation in South Brittany waters.*

The mean concentrations of Co in Quiberon bay surficial sediments are shown in *Figure 4–28*. The mean concentrations followed the following pattern: E<B<C<D<A<F, where Trinité–sur–Mer and southern zones had higher mean concentrations compared to the inner zones of the bay area. During Dec 2009 sampling, the mean concentrations in all samples except from western and northern zone were above the UCC value, 11.6 µg g^{-1} *dw*. (Wedepohl, 1995). However, only samples from the southern and Trinité–sur–Mer zones exceed the UCC value during Oct 2010 sampling period. No comparison was established regarding to the N1–N2 value from GEODE since this element is not mentioned in their report. Based on the comparison, the sediments did not greatly pollute by Co compounds in Quiberon bay.

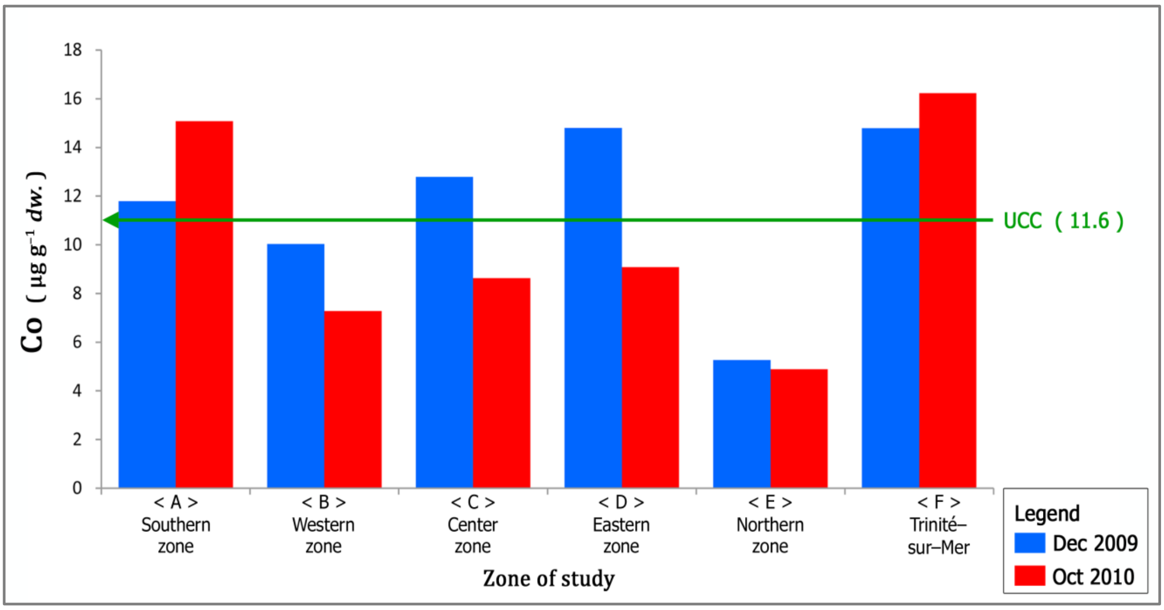

Figure 4–28. *Average concentrations of Co based on different zone in Quiberon bay surficial sediments for both samplings.*

A comparison of the pollution status by Co in Quiberon bay surficial sediments with European and Asian regions were shown in *Table 4–10*. The levels were slightly lower than those measured in Gascogne region, France by N'guessan *et al*. (2009) but two times higher when compared to data from San Simon bay, Spain examined by Alvarez–Iglesias *et al*. (2007).

Table 4–10. *Comparison of Co levels in Quiberon bay surficial sediments with other studies reported from European and Asian regions.*

Region	Co (µg g^{-1} *dw*.)	Reference
Quiberon bay	10.5	This study
European region		
Gascogne region, France	14.4	N'guessan *et al*., 2009
San Simon bay, Spain	5.35	Alvarez–Iglesias *et al*., 2007
Càdiz bay, Spain	5.5–16	Araujo *et al*., 2009
Asian region		
Yellow sea, South Korea	7	Lee *et al*., 2008
North Sulawesi, Indonesia	2.6–20.8	Edinger *et al*., 2008
Masan bay, South Korea	11.5	Hyun *et al*., 2007
Manila bay, Philippines	12.3	Prudente *et al*., 1994
Bengal bay, India	8.1	Muthu Raj and Jayaprakash, 2008
Erdek bay, Turkey	18	Balkis and Cagatay, 2001

The mean concentrations of Co in gulf of Morbihan surficial sediments are shown in *Figure 4–29*. From the figure, the sequence of the mean concentrations follows the decreasing order: D>B>H>C>G>E>F>A, where higher mean concentrations were observed in the rivers and eastern zones of the gulf and lower concentrations were observed at the gulf entrance and western zones. From the comparison graph, it is notable that the mean concentrations during Dec 2009 sampling were comparable and beyond the UCC value (Wedepohl, 1995), 11.6 µg g^{-1} *dw*. In contrast, only samples from zones A, C and G during Oct 2010 sampling were lower than the UCC value whereas the other zones were somewhat above the UCC value. Based on the comparison, higher mean concentrations in some sampling location may be derived from human and mariculture activities surrounding from the gulf area.

A further comparison with published data from European and Asian regions (*Table 4–11*) showed that the levels of Co in gulf of Morbihan sediments were higher than study by Chiffoleau *et al*. (1994) at Seine estuary, Vire estuary by Leleyter and Baraud, 2005 and Rhône estuary by Ferrand *et al*. (2012) studies in France region. However, our levels were slightly lower compared to the gulf of Lion in France Mediterranean sea investigated by Radakovitch *et al*. (2008).

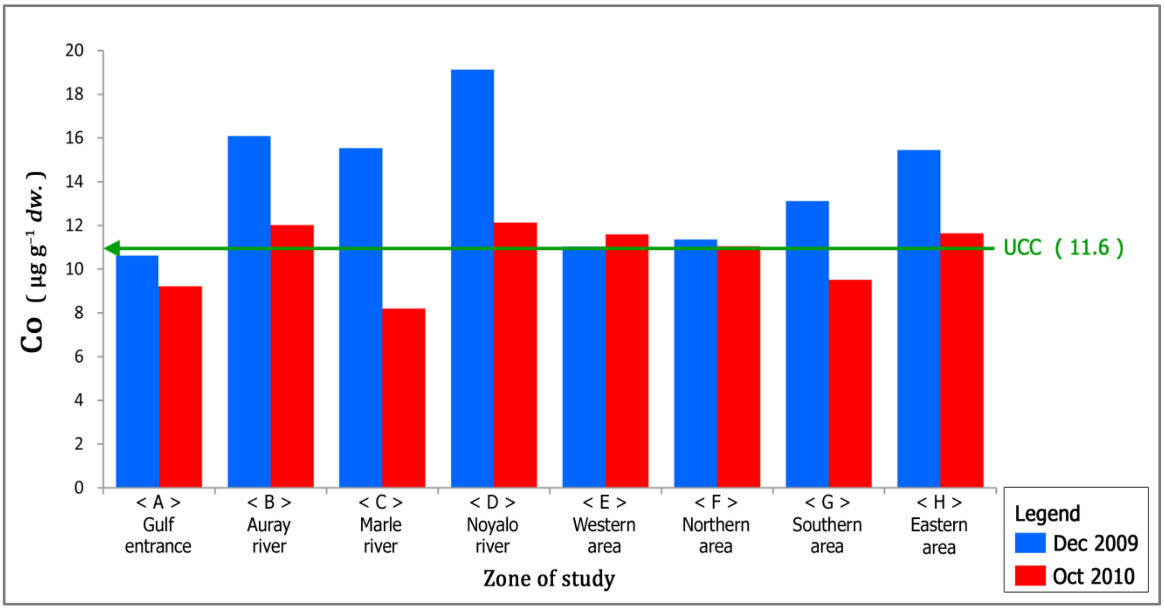

Figure 4–29. *Average concentrations of Co based on different zone in gulf of Morbihan surficial sediments for both samplings.*

Table 4–11. *Comparison of Co levels in gulf of Morbihan surficial sediments with other studies reported from European and Asian regions.*

Region	**Co (µg g^{-1} *dw.*)**	**Reference**
Gulf of Morbihan	12.6	This study
European region		
Seine estuary, France	7.1	Chiffoleau *et al.*, 1994
Vire estuary, France	7	Leleyter and Baraud, 2005
Gulf of Lion, France	14.3	Radakovitch *et al.*, 2008
Rhône estuary, France	6.3	Ferrand *et al.*, 2012
Bilbao estuary, Spain	7	Ruiz *et al.*, 2000
Gulf of Naples, Italy	5.1	Adamo *et al.*, 2005
Gulf of Venice, Italy	6–15	Donazzolo *et al.*, 1981
Ria de Vigo, Spain	11.7	Rubio *et al.*, 2000
Asian region		
Gulf of Aden, Yemen	12.8	Mostafa *et al.*, 2009
Gulf of Cambay, India	26.1	Tewari *et al.*, 2001
Gulf of Gemlik, Turkey	19	Unlu *et al.*, 2008
Gulf of Izmit, Turkey	74	Ergin *et al.*, 1991
Gulf of Mannar, India	15	Jonathan *et al.*, 2004
Gulf of Oman, Oman	0.1–45.2	de Mora *et al.*, 2004
Gulf of Thailand, Thailand	32–715	Censi *et al.*, 2006

4.4.5 Concentrations of copper in sediments

Copper (Cu) is extremely toxic and highly bioaccumulative (Sparling *et al*., 2010; Ciliberti *et al*., 2011) and its presence threatens the water ecological environment. Cu has low solubility in aqueous solution and easily adsorbed on water–borne suspended particles. After a series of natural processes, the water borne Cu finally accumulates in the sediment, and the quantity of Cu contained in the sediment reflect the degree of pollution in the water body (Silvaraj *et al*., 2004). Since Cu is an essential trace nutrient, most marine organisms have evolved mechanisms to regulate concentrations of this metal in their tissues in the presence of variable concentrations in the ambient water, sediments and food (Neff, 2002).

The distribution of Cu in the estuary may also be affected by natural biogeochemical processes such as release from riverine particulate matter (Windom *et al*., 1983), sediment resuspension and pore water intrusion (Ackroyd *et al*., 1986), flocculation of colloidal material (Sholkivitz, 1978), biological scavenging (Flegal *et al*., 1991) and changes in redox conditions (Baeyens *et al*., 1998; Nolting *et al*,. 1999). Changes from conservative behaviour can also be induced by changes in the riverine dissolved Cu concentrations (Cifuentes *et al*., 1990).

There are a number of processes that can lead to the addition and removal of dissolved Cu during estuarine mixing, that result in deviations from the theoretical dilution line through the estuary (Millward and Turner, 1995). Among the addition processes metal releases by tidal sediment disturbance (Ackroyd *et al*., 1986), metal desorption from riverine and/or marine particles (Windom *et al*., 1983) and anthropogenic inputs (Flegal *et al*., 1991); typical removal processes are biological scavenging (Flegal *et al*., 1991), flocculation of colloidal material containing metals (Sholkovitz, 1978) and adsorption onto particles (Turner *et al*. 1993). The extent of dissolved metal sources and sinks will lead to a net addition or removal of dissolved Cu during estuarine mixing in the water column.

Cu is introduced into the aquatic environment through a number of natural methods. The source of Cu in the aquatic organism are minerals in soil and weathered rock from sediment and suspended particles in the water (Hitzman, 2000), biological particles including both living and dead organic material, hydrothermal systems included volcanic actions and deposition from the atmosphere (Lewis, 1995, Li *et al*., 2001). Whereas, elevated of Cu in the marine environment due to anthropogenic activities since it is used in electrical equipment (Baize and Janiec, 1994), antifouling paint for boats hull (Albanis *et al*., 2002), as an algaecide and food preservative (WHO, 1998), construction materials (Donze *et al*., 1990), agriculture activities and municipal wastewater discharges (Järup and Akesson, 2009). In the case of commercial vessels, the toxic properties of paints are further enhanced by adding more Cu (Guerra–Garcia and Garcia Gomez, 2005). Cu is also used for anti–incrusting in these pipelines. These metals may dissolve and become incorporated in the urban sewage effluents as pointed out by Establier (1977) and Phillips *et al*. (1992).

The comparison isopleth maps for concentrations of Cu are shown in *Figure 4–30*. Lower concentrations were observed in the Quiberon bay sediments compared to the gulf of Morbihan. These differences are more significant during Oct 2010 sampling and this was proven by the statistical analysis, t–Test where the calculated value of the p was smaller than 0.05, indicate that the concentrations in the Quiberon bay and gulf of Morbihan were varied significantly.

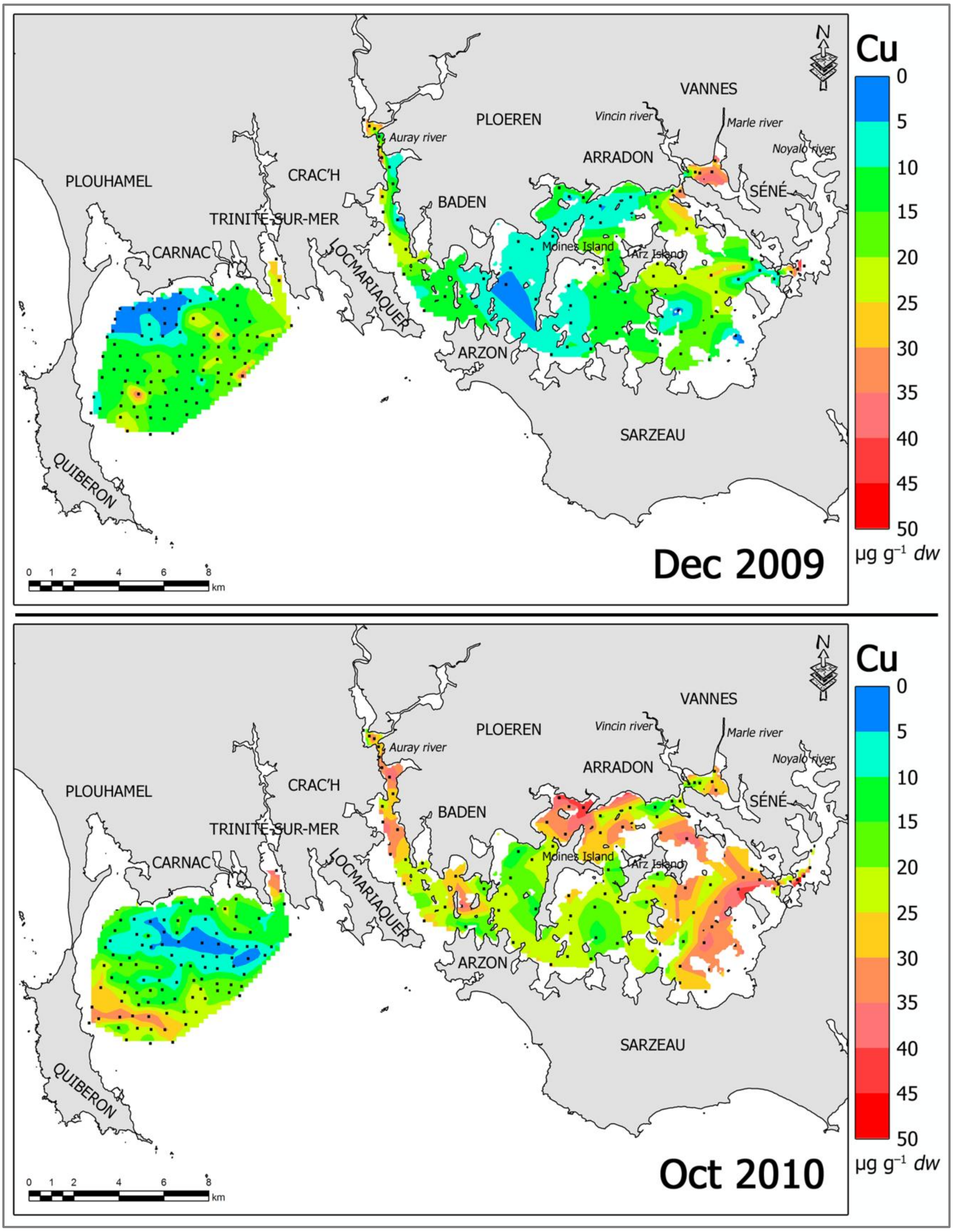

Figure 4–30. *Isopleth maps of Cu accumulation in South Brittany waters.*

The mean concentrations of Cu in different zones from Quiberon bay sediments are shown in *Figure 4–31* and the concentrations followed the order: E<C<B<D<A<F. Higher mean concentrations were observed in Trinité–sur–Mer and southern zones during Dec 2009 sampling, whereas lower concentrations were found in the innermost of the bay compared to the outer of the bay. However, overall the mean concentrations were slightly below the UCC value, 14.3 µg g^{-1} *dw*. (Wedepohl, 1995) and far below compared to N1 classifications by GEODE. Only sediments from Trinité–sur–Mer and southern zones were exceeded the UCC value for both sampling periods. The enrichments at Trinité–sur–Mer zone and southern zone of the Quiberon bay (near Port Haliguen) is considered to be linked to the use of Cu based antifouling paints and the discharge onto nearby the area.

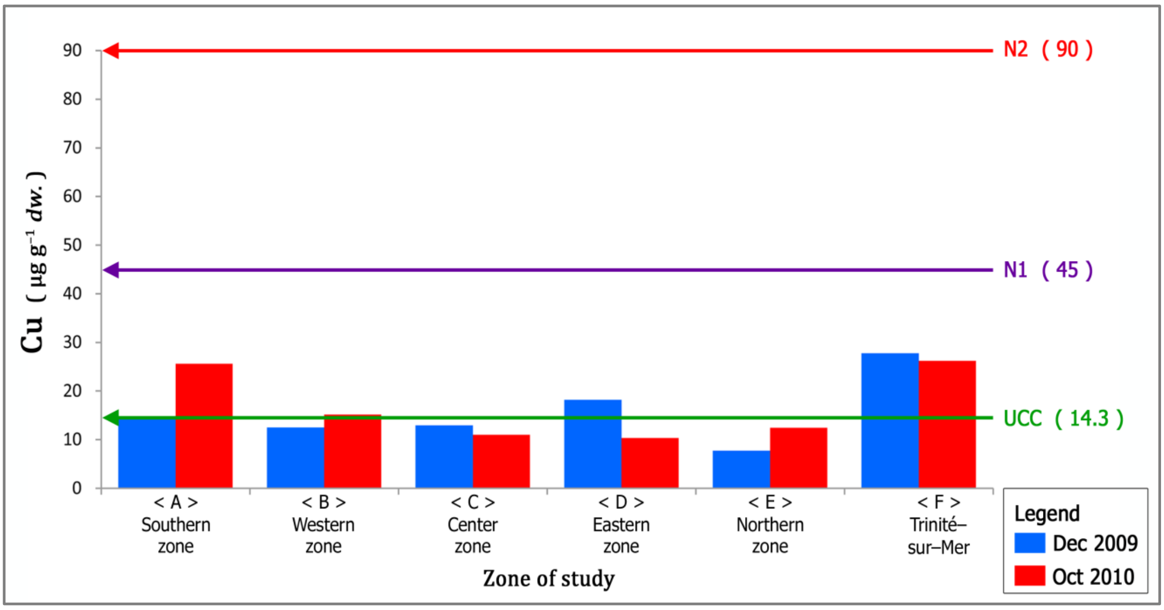

Figure 4–31. *Average concentrations of Cu based on different zone in Quiberon bay surficial sediments for both samplings.*

A comparison of Cu levels in Quiberon bay surficial sediments with other studies from other geographical area from European and Asian regions reveals that levels were quite lower than those from other regions, but two times higher than levels from the San Simon bay in Spain (*Table 4–12*). Similar levels were observed by Strady *et al.* (2011) from Marenne–Oléron bay sediments. The levels from the Quiberon bay was slightly lower than Gascogne coast in France and two to three times lower than Seine bay and southwest coast of France sediments.

Table 4–12. *Comparison of Cu levels in Quiberon bay surficial sediments with other studies reported from European and Asian regions.*

Region	Cu (µg g^{-1} *dw.*)	Reference
Quiberon bay	14.3	This study
European region		
Seine bay, France	38	Fichet *et al.*, 1998
Port–en–Bessin, Seine bay, France	300	Caplat *et al.*, 2005
Marenne Oléron bay, France	2–15	Strady *et al.*, 2011
Southwest coast, France	46–97	Fichet *et al.*, 1999
Gascogne coast, France	18.9	N'guessan *et al.*, 2009
Toulon bay, France	59.9	Tessier *et al.*, 2011
Southern Spain, Spain	30.1	Usero *et al.*, 2005
Càdiz bay, Spain	8.2–130	Araujo *et al.*, 2009
San Simon bay, Spain	6.53	Alvarez–Iglesias *et al.*, 2007
Southwest coast, Spain	41–336	Morillo *et al.*, 2004
Asian region		
Gemlik bay, Turkey	42	Balkis *et al.*, 1999
Bengal bay, India	20	Selvaraj *et al.*, 2004
Jinzhou bay, China	15–400	Wang *et al.*, 2010
Penny bay, Hong Kong	14	Chan *et al.*, 2001
Manila bay, Philippines	47	Prudente *et al.*, 1994
North Sulawesi, Indonesia	10–62.9	Edinger *et al.*, 2008

Figure 4–32 shows the mean concentration of Cu from different zones in gulf of Morbihan surficial sediments. The sequence of mean concentrations follows the decreasing order: D>C>B>H>F>A>G>E, where concentrations of rivers and eastern zones were higher compared to gulf entrance, western and southern zones. The mean concentrations from all the zones were above the UCC value, 14.3 µg g^{-1} *dw.* value suggested by Wedepohl (1995) particularly during Oct 2010 sampling. However, our mean concentrations were far below compared to N1 classification by GEODE. Similarly with the conclusion made for Quiberon bay sediment, some of the sampling area such as rivers zone contain a higher concentration may be due to leakage from antifouling paints to that area.

Comparisons of status of pollution by Cu in gulf of Morbihan surficial sediments are shown in *Table 4–13*. The levels of Cu were comparable to the Gironde estuary investigated by Larrose *et al.* (2010) and slightly lower than those measured in Vire estuary (Leleyter and Baraud, 2005), Loire estuary (Robbe *et al.*, 1985) and the Arcachon basin (Carruesco and Lapaquelleries, 1985) sediments from France coastal waters. In contrast, our levels were higher compared to Rigollet *et al*. (2004) and Ferrand *et al*. (2012) studies at Rhône estuary and Thau lagoon in France Mediterranean sea.

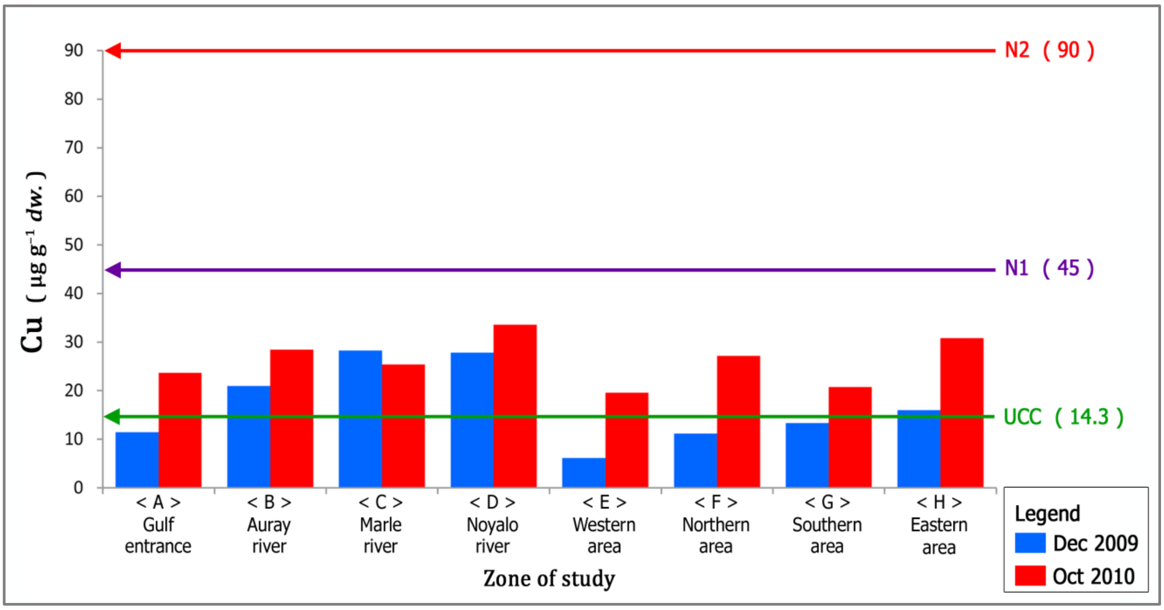

Figure 4–32. *Average concentrations of Cu based on different zone in gulf of Morbihan surficial sediments for both samplings.*

Table 4–13. *Comparison of Cu levels in gulf of Morbihan surficial sediments with other studies reported from European and Asian regions.*

Region	Cu (µg g⁻¹ *dw*.)	Reference
Gulf of Morbihan	21.9	This study
European region		
Vire estuary, France	27	Leleyter and Baraud, 2005
Loire estuary, France	27	Robbe *et al*., 1985
Gironde estuary, France	20.5	Larrose *et al*., 2010
Arcachon basin, France	28	Carruesco and Lapaquellerie, 1985
Gulf of Lion, France	55	Radakovitch *et al*., 2008
Thau lagoon, France	18.7	Rigollet *et al*., 2004
Rhône estuary, France	9.96	Ferrand *et al*., 2012
Bilbao estuary, Spain	118	Ruiz and Saiz–Salinas, 2000
Ria de Vigo, Spain	29.4	Rubio *et al*., 2000
Gulf of Thermaikos, Greece	80	Christophoridis *et al*., 2009
Asian region		
Gulf of Izmit, Turkey	26	Ergin *et al*., 1991
Gulf of Suez, Egypt	7.5	Hamed and Emara, 2006
Gulf of Mannar, India	57	Jonathan *et al*., 2004
Gulf of Thailand, Thailand	7.5–363	Censi *et al*., 2006

4.4.6 *Concentrations of zinc in sediments*

Zinc (Zn), an essential element for terrestrial life and a structural component in numerous enzyme systems, is also associated with sewage pollution (Muniz *et al*., 2004). Higher levels of Zn have environmental and ecological risks even though the source is natural. From an environmental pollution standpoint, Zn is generally considered as toxic element, but very insoluble and very rare (Fortsner and Wittmann, 1983; Alloway, 1990).

A large fraction of the Zn compound entering the oceans of the world is derived from aerial deposition (Neff, 2002) and concentrations of Zn in marine and estuarine sediments vary widely. This may be due to the high amount of suspended organic matter coming from different industrial wastes that precipitate to the bottom and also due to the decrease uptake of zinc by phytoplankton at lower temperature. Zn also used in antifouling paint (Orlic and Tang, 1999). Such paints are used to cover the underwater parts of vessels to protect them from the development of fouling organisms such as algae and barnacles and are based on organic solvents mixed with highly concentrated toxic metals such as Cu and Zn. The analysis of several samples of antifouling paints shows the concentrations of Zn are typically between 15 and 30 % (Orlic and Tang, 1999). Therefore, elevated concentrations of Zn are expected due to the washout of the antifouling paints used for ships in the harbour located in the study area.

Figure 4–33 shows the comparison isopleth maps for concentration of Zn of Quiberon bay and gulf of Morbihan surficial sediments. From both maps, the concentrations were distributed uniformly in both study areas. The *p* value more than 0.05 calculated from statistical analysis, *t*–Test can prove the similarity of the distribution, which suggest that there is no significant different between both study areas.

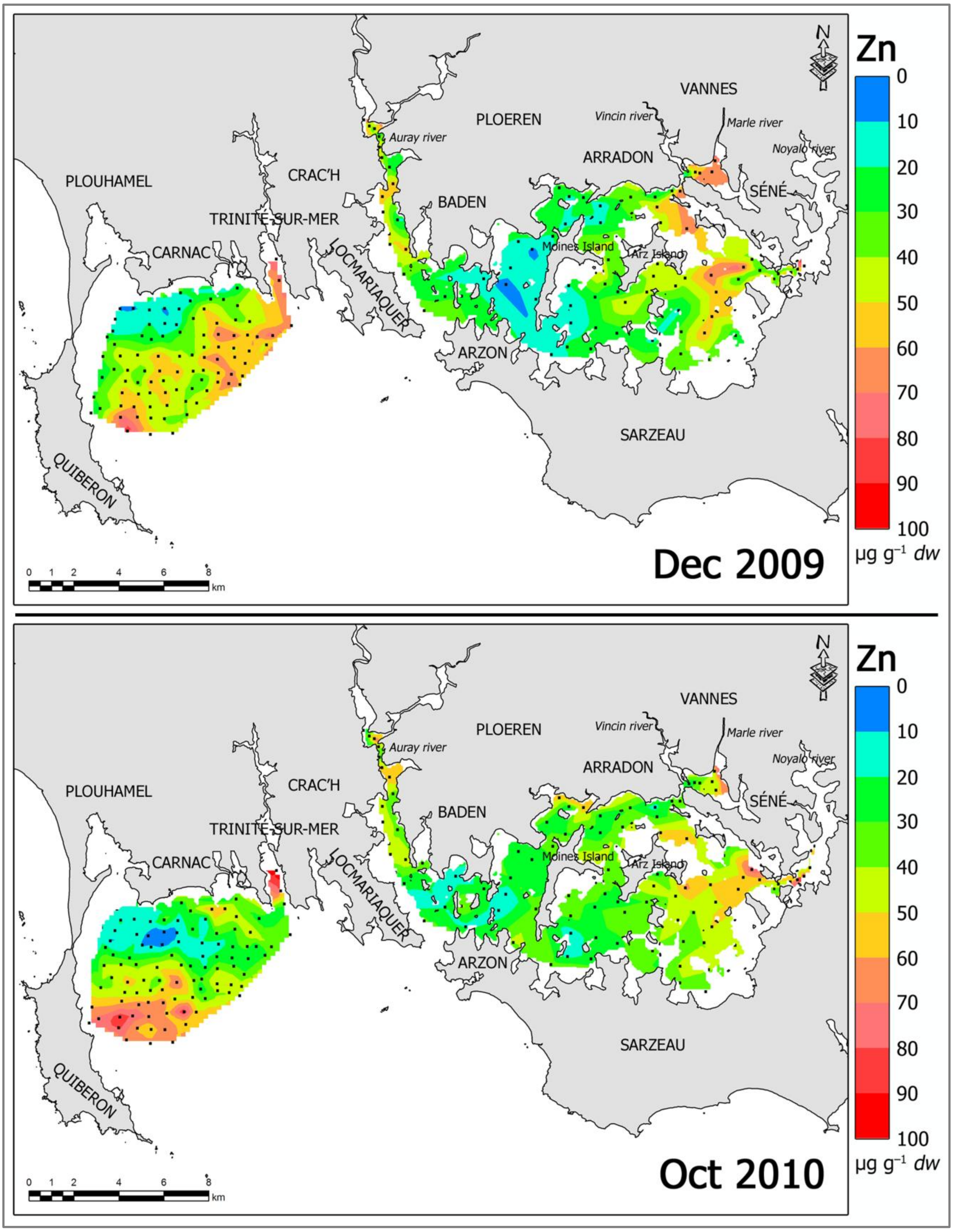

Figure 4–33. *Isopleth maps of Zn accumulation in South Brittany waters.*

The mean concentrations of Zn in Quiberon bay surficial sediments are shown in *Figure 4–34*. The mean concentrations followed the order: E<B<C<D<A<F, where innermost of the bay recorded the lower mean concentrations whereas outer of the bay and Trinité–sur–Mer zone shows the higher mean concentrations. The concentrations in sediments from zone F located in Trinité–sur–Mer area and southern zone were above the UCC value, 52 µg g^{-1} *dw*. suggested by Wedepohl (1995), while sediments from other zones were below the UCC value. When compared to recommendation from GEODE, our levels of Zn were much lower than N1 values. From the data obtained, it can be concluded that Zn interpreted as indicative of crustal origin or natural weathering processes. The high value at Trinité–sur–Mer zone may be derived from the shipyard and shipping activities surrounding the area.

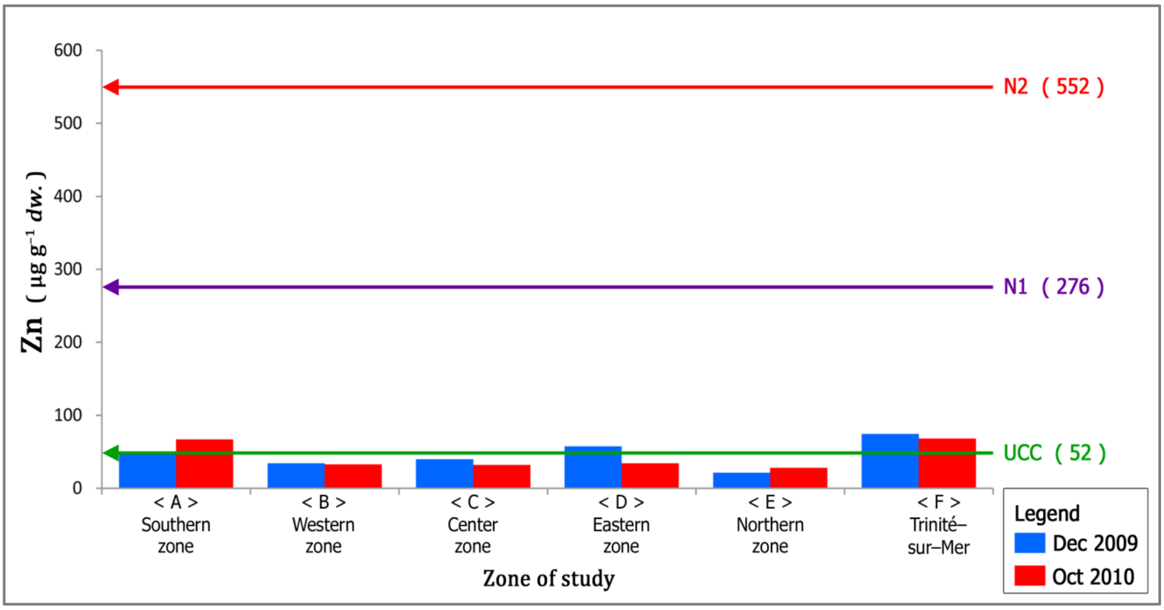

Figure 4–34. *Average concentrations of Zn based on different zone in Quiberon bay surficial sediments for both samplings.*

A comparison of Zn levels with other studies from different geographical areas in European and Asian regions are shown in *Table 4–14*. This comparison reveals that the levels were quite lower than those from other regions. The levels were lower compared to the sediments from the Seine bay (Fichet *et al.*, 1998), Marenne Oléron bay (Strady *et al.*, 2011) and Gascogne coast in France coastal waters. Meanwhile, our levels were far below compared to Port–en–Bessin at France northern coast studied by Caplat *et al*. (2005).

Table 4–14. *Comparison of Zn levels in Quiberon bay surficial sediments with other studies reported from European and Asian regions.*

Region	**Zn (µg g^{-1} *dw*.)**	**Reference**
Quiberon bay	40.7	This study
European region		
Seine bay, France	79	Fichet *et al*., 1998
Port–en–Bessin, Seine bay, France	354	Caplat *et al*., 2005
Marenne Oléron bay, France	25–170	Strady *et al*., 2011
Gascogne coast, France	81.7	N'guessan *et al*., 2009
Toulon bay, France	113.8	Tessier *et al*., 2011
Southern Spain, Spain	173.4	Usero *et al*., 2005
Càdiz bay, Spain	33–170	Araujo *et al*., 2009
San Simon bay, Spain	54.45	Alvarez–Iglesias *et al*., 2007
Southwest coast, Spain	141–649	Morillo *et al*., 2004
Portuguese coastal, Portugal	64	Mil–Homens *et al*., 2006
Asian region		
Gemlik bay, Turkey	175	Balkis *et al*., 1999
Bengal bay, India	127	Muthu Raj and Jayaprakash, 2008
Jiaozhou bay, China	87.2	Dai *et al*., 2007
Bohai bay, China	110.9	Meng *et al*., 2008
Quanzhou bay, China	179.6	Yu *et al*., 2008
Tokyo bay, Japan	106–405	Fukushima *et al*., 1992
Penny bay, Hong Kong	70	Chan *et al*., 2001
Manila bay, Philippines	148	Prudente *et al*., 1994

Figure 4–35 shows the average concentrations of Zn in gulf of Morbihan surficial sediments. From the figure, the sequence of Zn enrichment follows the decreasing order: D>C>B>H>F>G>A>E. The lower mean concentrations were observed at the gulf entrance and western zones, and the concentrations were lower than UCC value 52 µg g^{-1} *dw*. suggested by Wedepohl (1995). On the other hand, while higher mean concentrations were found in rivers and eastern zone of the gulf, and these concentrations were closed to UCC value. However, all the mean concentrations were relatively lower than

the N1 values by GEODE. Similarly with the observation made for Quiberon bay sediments, the sediments from the gulf of Morbihan also did not greatly polluted with Zn.

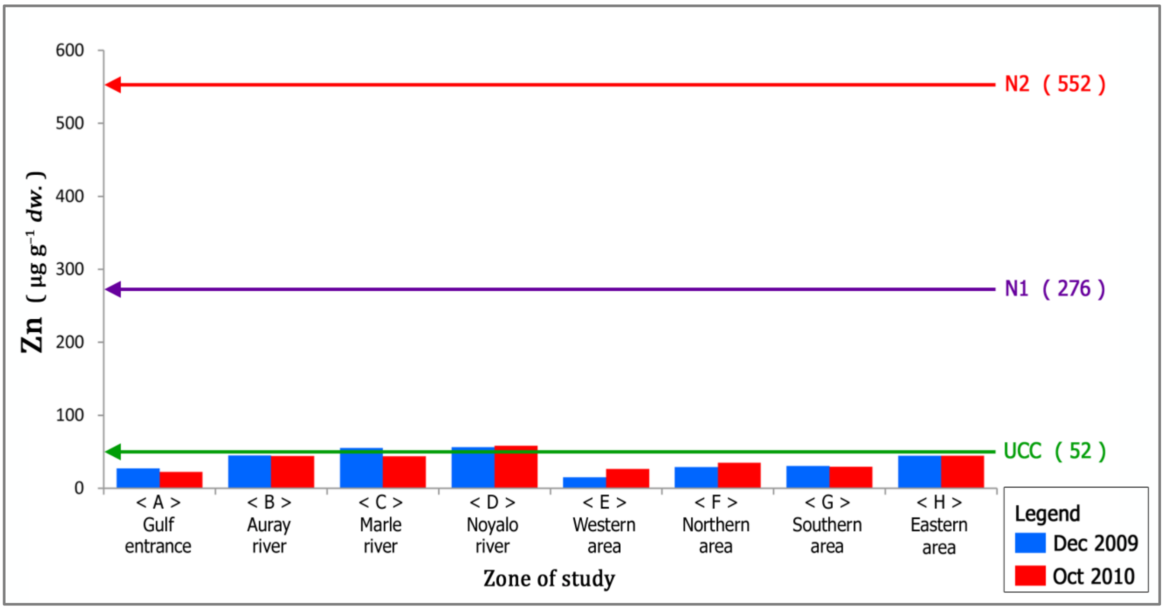

Figure 4–35. *Average concentrations of Zn based on different zone in gulf of Morbihan surficial sediments for both samplings.*

Furthermore, *Table 4–15* reveals that Zn levels in this study were comparable with study from the Thau lagoon in France (Rigollet *et al*., 2004), but relatively lower with those reported from the Seine estuary by Chiffoleau *et al*. (1994) and Vire estuary (Leleyter and Baraud, 2005) at France northern coast; Rhône estuary (Ferrand *et al*., 2012) and gulf of Lion (Radakovitch *et al*., 2008) at France Mediterranean sea; three times lower than Loire estuary (Robbe *et al*., 1985), Gironde estuary (Larrose *et al*., 2010) and Arcachon basin (Carruesco and Lapaquellerie, 1985) located at the western coast.

Table 4–15. *Comparison of Zn levels in gulf of Morbihan surficial sediments with other studies reported from European and Asian regions.*

Region	Zn (µg g^{-1} *dw.*)	Reference
Gulf of Morbihan	38.4	This study
European region		
Seine estuary, France	222	Chiffoleau *et al.*, 1994
Vire estuary, France	135	Leleyter and Baraud, 2005
Loire estuary, France	176.8	Robbe *et al.*, 1985
Gironde estuary, France	150	Larrose *et al.*, 2010
Arcachon basin, France	142	Carruesco and Lapaquellerie, 1985
Gulf of Lion, France	189	Radakovitch *et al.*, 2008
Thau lagoon, France	36.1	Rigollet *et al.*, 2004
Rhône estuary, France	61.3	Ferrand *et al.*, 2012
Bilbao estuary, Spain	646	Ruiz and Saiz–Salinas, 2000
Ria de Vigo, Spain	105	Rubio *et al.*, 2000
Gulf of Finland, Finland	43	Leivouri, 1998
Gulf of Taranto, Italy	47.4	Buccolieri *et al.*, 2006
Gulf of Venice, Italy	2–450	Donazzolo *et al.*, 1981
Gulf of Thermaikos, Greece	184	Christophoridis *et al.*, 2009
Asian region		
Gulf of Izmit, Turkey	75	Ergin *et al.*, 1991
Gulf of Gemlik, Turkey	41	Unlü *et al.*, 2008
Gulf of Oman, Oman	1.57–52.2	de Mora *et al.*, 2004
Gulf of Suez, Egypt	42.9	Hamed and Emara, 2006
Gulf of Mannar, India	73	Jonathan *et al.*, 2004
Gulf of Cambay, India	50.6	Tewari *et al.*, 2001
Gulf of Thailand, Thailand	26–1454	Censi *et al.*, 2006

4.4.7 Concentrations of arsenic in sediments

Arsenic (As) is a ubiquitous element, which occurs in the environment naturally, as well as due to human activities (Baeyens *et al.*, 2007). Due to the toxic and carcinogenic effects of As to humans, it is regarded as a contaminant and has received a high public concern. The adverse health impacts of acute or chronic levels of arsenic are; dermal changes, respiratory, cardiovascular, reproductive, mutagenic and carcinogenic effects (Mandal and Suzuki, 2002). The higher levels of As are also toxic to marine organisms (Cutter and Cutter, 1995). The accumulation or release of trace elements in wetland sediments is largely controlled by their geochemistry, where the redox behaviour plays a particularly important role (Fox and Doner, 2003). As is redox sensitive; the redox potential controls the chemical partitioning, and the solubility and mobility of arsenic (Signes–Pastor *et al*., 2007). The accumulations of As as well as other toxic elements in soils and sediments are influenced by the presence of silicates and other naturally adsorbing oxides. Besides the oxides, As sorption phenomena are also influenced by other naturally occurring components such as organic matter and pyrite content (Pikaray *et al*., 2005).

The As in the environment originates from natural enrichments and is intensified by anthropogenic activities. The most common sources of As in the natural environment are volcanic rocks, specifically their weathering products and ash, marine sedimentary rocks, hydrothermal ore deposits and associated geothermal waters, and fossil fuels, including coals and petroleum (Korte and Fernando, 1991; Smedley and Kinniburgh, 2002). Natural sources of As in water has been attributed to several natural geochemical processes, including oxidation of As–bearing sulfides, desorption of As from (hydro)oxides (e.g., iron, aluminum and manganese oxides), reductive dissolution of As–bearing iron (hydro)oxides, release of As from geothermal water, and evaporative concentration (Bennett and Dudas, 2003), as well as leaching of As from sulfides by carbonates (Kim *et al*., 2000).

The main anthropogenic activities that may release As into the environment include nonferrous metal mining and smelting, fossil fuel processing and combustion, wood preserving, pesticide production and application, and disposal and incineration of municipal and industrial wastes (Popovic *et al*., 2001; Prosun *et al*., 2002), and use of pesticide and herbicides in the agricultural activities (Donze *et al*., 1990). Most anthropogenic releases of As are to land or soil, primarily in the form of pesticides or solid wastes.

During Dec 2009 sampling, As were well scattered in Quiberon bay and gulf of Morbihan surficial sediments (*Figure 4–36*). However, higher concentrations of As were observed in gulf of Morbihan sediment compared to Quiberon bay. Then again, statistical analysis, *t*–Test shows that there is a significant difference between the two study areas as the *p* value slighter than 0.05.

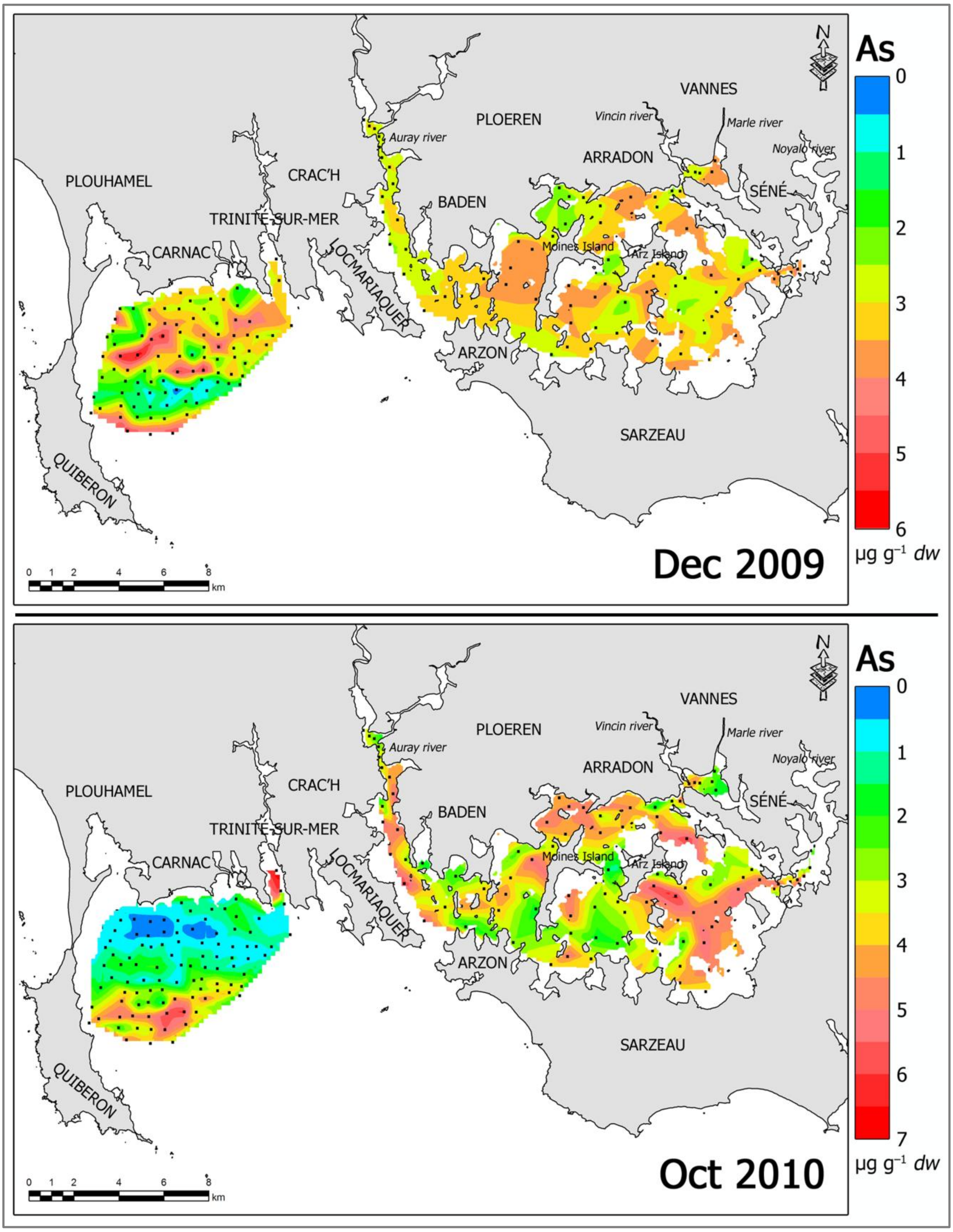

Figure 4–36. *Isopleth maps of As accumulation in South Brittany waters.*

Figure 4–37 shows the mean concentrations of As based on the zone division in Quiberon bay surficial sediments. The sequence of the mean concentrations follows the increasing order: E<B<C<D<A<F. Lower mean concentrations occurred at innermost of the bay, while Trinité–sur–Mer zone had higher mean concentrations. The mean concentrations were higher compared to the UCC value, 2.0 µg g^{-1} *dw*. by Wedepohl (1995) specifically during Oct 2010 sampling. In comparison with the values by GEODE, our mean concentrations were much lower than the N1 values. Based on the comparison, it can be concluded that As enters the sediments by natural weathering process and from anthropogenic input.

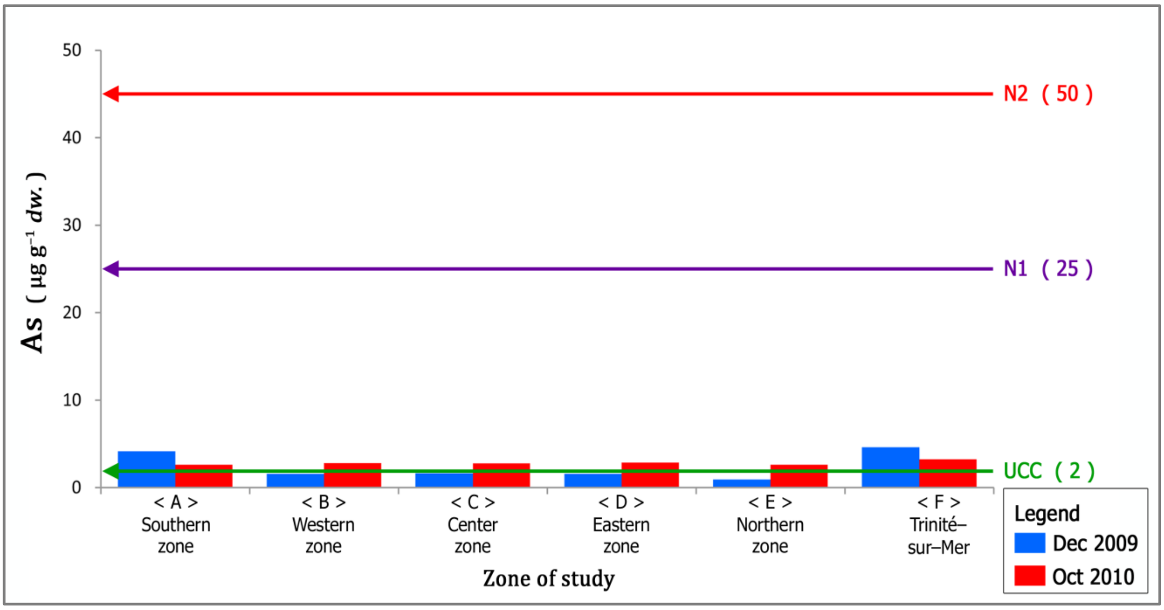

Figure 4–37. *Average As concentrations based on different zone in Quiberon bay surficial sediments for both samplings.*

Comparison of status of pollution by As in Quiberon bay surficial sediments are shown in *Table 4–16*. There are few data from European and Asian regions for comparison of the As levels since not many studies have been conducted in this region. The levels were relatively lower than those measured in Marenne Oléron bay sediment analyzed by Strady *et al*. (2011), N'guessan *et al*. (2009) at Gascogne coast and Tessier *et al*. (2011) at Toulon bay from France region.

Table 4–16. *Comparison of As levels in Quiberon bay surficial sediments with other studies reported from European and Asian regions.*

Region	**As (µg g^{-1} *dw.*)**	**Reference**
Quiberon bay	2.38	This study
European region		
Marenne Oléron bay, France	4–22	Strady *et al.*, 2011
Gascogne coast, France	15.14	N'guessan *et al.*, 2009
Toulon bay, France	19.6	Tessier *et al.*, 2011
San Simon bay, Spain	9	Alvarez–Iglesias *et al.*, 2007
Southern Spain, Spain	34.2	Usero *et al.*, 2005
Liverpool bay, UK	5.1	Camacho–Ibar *et al.*, 1992
Asian region		
Bohai bay, China	6.4	Meng *et al.*, 2008
Quanzhou bay, China	21.7	Yu *et al.*, 2008
Yellow sea, South Korea	8.5	Luo *et al.*, 2010
North Sulawesi, Indonesia	5–275.4	Edinger *et al.*, 2008

The mean concentrations of As in gulf of Morbihan surficial sediments are shown in *Figure 4–38*. From the figure, the sequence of As contamination follows the decreasing order: B<F<C<A<G<E<H<D, where higher mean concentrations were observed in the Noyalo river and eastern zone of the gulf. Lower mean concentrations were recorded at the Auray river zone. In comparison with the UCC value, 2.0 µg g^{-1} *dw*. by Wedepohl (1995), all the mean concentrations were beyond the value for both sampling periods, Dec 2009 and Oct 2010. Conversely, the mean concentrations were far lower compared to N1 values set by GEODE. Based on the comparison data, gulf of Morbihan sediments was slightly polluted with As compound.

A comparison of status of pollution by As in gulf of Morbihan surficial sediments with European and Asian regions are shown in *Table 4–17*. The levels were quite lower than those measured, such as from Larrose *et al*. (2010) at Gironde estuary in France coastal except slightly higher than the result from Ruiz and Saiz–Salinas (2000) at Bilbao estuary in Spain.

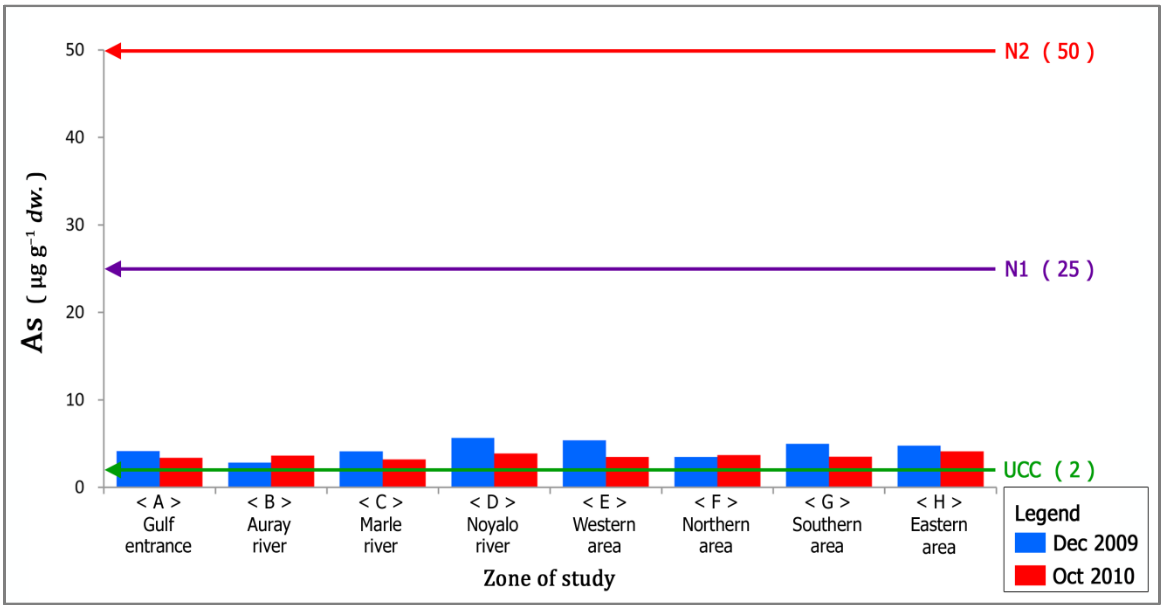

Figure 4–38. *Average concentrations of As based on different zone in gulf of Morbihan surficial sediments for both samplings.*

Table 4–17. *Comparison of As levelns in gulf of Morbihan surficial sediments with other studies reported from European and Asian regions.*

Region	As (µg g^{-1} *dw.*)	Reference
Gulf of Morbihan	3.97	This study
European region		
Gironde estuary, France	16.9	Larrose *et al.*, 2010
Bilbao estuary, Spain	1.72	Ruiz and Saiz–Salinas, 2000
Gulf of Bothnia, Finland	23.9	Leivouri, 1998
Gulf of Finland, Finland	16	Leivouri, 1998
Gulf of Naples, Italy	15.7	Adamo *et al.*, 2005
Asian region		
Gulf of Oman, Oman	0.7–9.6	de Mora *et al.*, 2004

4.4.8 Concentrations of cadmium in sediments

Cadmium (Cd) is one of the most toxic metals measured in this study (McLeese, 1981; Neff, 2002) and relatively rare metal. Cd has no essential biological functions and is highly toxic to plants and animals. Cd can be toxic to aquatic organisms as well as to humans who eat fish contaminated with it (Capelli *et al.*, 1983). The major hazard to human health from Cd is its chronic accumulation in kidneys (Alloway 1990). Previous studies have shown that the amount of Cd in the sediment is related to the amount leached into the water

(Neff, 2002). Thus much of the input of Cd to the estuary may be of anthropogenic origin. The relatively homogeneous distribution of dissolved Cd in major water bodies is usually explained by the formation of Cd chloro–complexes in the marine environment (Elbaz–Poulichet *et al*., 1987; Ahrland, 1988; Pempkowiak *et al*., 2000), which can easily be transported by currents to the entire water mass of any water body.

Referring to Cd, its compounds are also used in areas such as pigments or stabilizers in plastics, in alkaline batteries such anthropogenic inputs will contribute to increased levels of Cd in the environment. Cd is used in pigments or stabilizers in plastics and in alkaline batteries, which would contribute to elevating its concentration in marine sediments (Sin *et al*., 2001). The river traffic and periodical dredging of local harbors may also contribute to Cd release by mixing up and oxidizing anoxic sediments. Cd element in anoxic environments is initially presented in insoluble forms and became progressively more soluble by aerobic exposure (Stephens *et al*., 2001).

Figure 4–39 show the comparison of Cd concentrations in surficial sediments between Quiberon bay and gulf of Morbihan. There again, the concentrations in the Quiberon bay were lower compared to the gulf of Morbihan particularly during Oct 2010 sampling. This is also supported by the statistical analysis, *t*–Test where the calculated *p* value was smaller than 0.05.

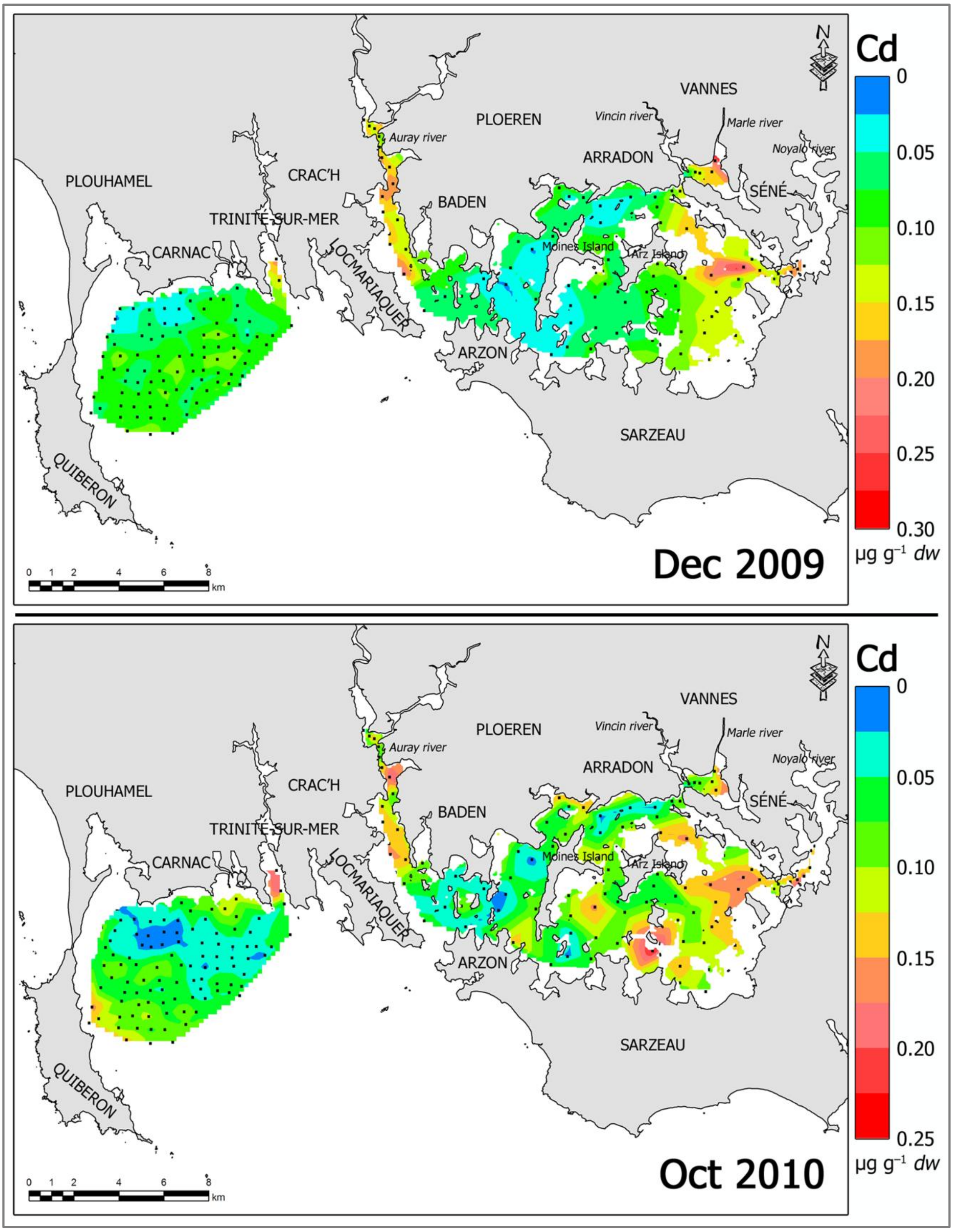

Figure 4–39. *Isopleth maps of Cd accumulation in South Brittany waters.*

The mean concentrations of Cd in Quiberon bay surficial sediments are shown in *Figure 4–40*. The mean concentrations followed the following pattern: E<C<D<B<A<F, where Trinité–sur–Mer zone had higher mean concentrations compared to the zones within the bay area. The mean concentrations were closed to the UCC value, 0.102 µg g^{-1} *dw*. (Wedepohl, 1995), whereas the mean concentrations in Trinité–sur–Mer sediments were exceeded the UCC value for both samplings, Dec 2009 and Oct 2010. Despite the high contents of Cd in the sediments of the study area, the mean concentrations were far below compared to the N1 values by GEODE. Therefore, the Cd compound in the Quiberon bay can be concluded to derive from natural weathering sources and anthropogenic processes dominate the distribution of Cd in the sediments.

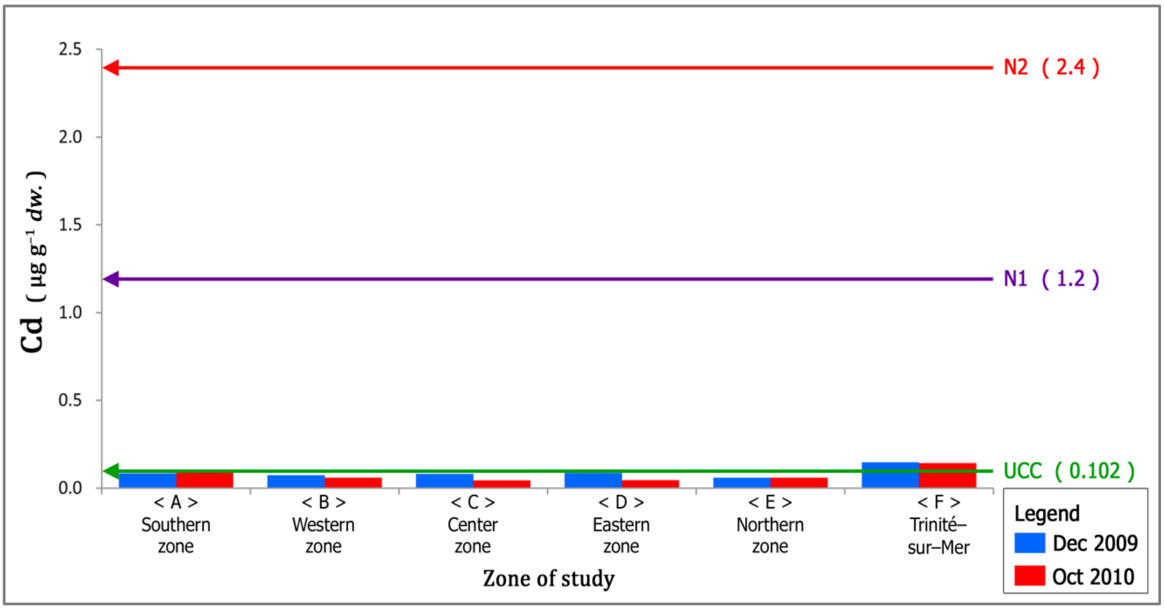

Figure 4–40. *Average concentrations of Cd based on different zone in Quiberon bay surficial sediments for both samplings.*

Table 4–18 shows the comparison of Cd levels in Quiberon bay surficial sediments with other studies conducted in European and Asian regions. The levels in our study were relatively lower compared to those reported. In comparison with the levels in sediments from the Seine bay (Fichet *et al.*, 1998) and Toulon bay (Tessier *et al.*, 2011) in France coastal, our results were two times lower than their study and four times lower than the study by Fichet *et al.* (1999) and N'guessan *et al.* (2009) from southwest coast and the Gascogne coast in France western coast.

Table 4–18. *Comparison of Cd levels in Quiberon bay surficial sediments with other studies reported from European and Asian regions.*

Region	Cd (µg g^{-1} *dw.*)	Reference
Quiberon bay	0.07	This study
European region		
Seine bay, France	0.13	Fichet *et al.*, 1998
Marenne Oléron bay, France	0.1–0.45	Strady *et al.*, 2011
Southwest coast, France	0.29–1.91	Fichet *et al.*, 1999
Gascogne coast, France	0.3	N'guessan *et al.*, 2009
Toulon bay, France	0.15	Tessier *et al.*, 2011
Southern Spain, Spain	0.38	Usero *et al.*, 2005
Càdiz bay, Spain	0.14–0.56	Araujo *et al.*, 2009
Southwest coast, Spain	0.19–2.5	Morillo *et al.*, 2004
Asian region		
Quanzhou bay, China	0.4	Yu *et al.*, 2008
Jinzhou bay, China	1.2–6.4	Wang *et al.*, 2010
Jiaozhou bay, China	0.76	Dai *et al.*, 2007
Xiamen bay, China	0.33	Zhang *et al.*, 2007
Masan bay, South Korea	1.24	Hyun *et al.*, 2007
Youngil bay, South Korea	1.5	Lee *et al.*, 2008
Tokyo bay, Japan	0.5–1.4	Fukushima *et al.*, 1992
Manila bay, Philippines	1.92	Prudente *et al.*, 1994

Figure 4–41 shows the mean concentration values of Cd in gulf of Morbihan surficial sediments in different zones. The sediment Cd enrichment followed the order: A>E>F>G>H>C>B>D. Also, higher mean concentrations were observed in rivers and eastern zones while the lower mean concentrations were found in the gulf entrance and western zones of the gulf. In comparison with UCC value, 0.102 µg g^{-1} *dw*. by Wedepohl (1995), concentrations from rivers and eastern zones sediments were closed and above the value for both sampling periods, Dec 2009 and Oct 2010. However when compared to N1 values by GEODE, our results were far below the level. Similar in Quiberon bay sediments, natural and anthropogenic process dominant the distribution of Cd in gulf of Morbihan sediments.

A comparison of Cd levels in surficial sediments with other reported from different geographical areas from European and Asian regions is shown in *Table 4–19*. The comparison table reveals that the levels were much lower than those from other regions; slightly lower than study by Carruesco and Lapaquellerie (1985) in Arcachon basin, France; three to four times lower than Thau lagoon examined by

Rigollet *et al.* (2004), Loire estuary (Robbe *et al.*, 1985) and Gironde estuary (Larrose *et al.*, 2010). In contrast, the levels in Rhône estuary analyzed by Ferrand *et al.* (2012) were lower compared to the gulf of Morbihan levels.

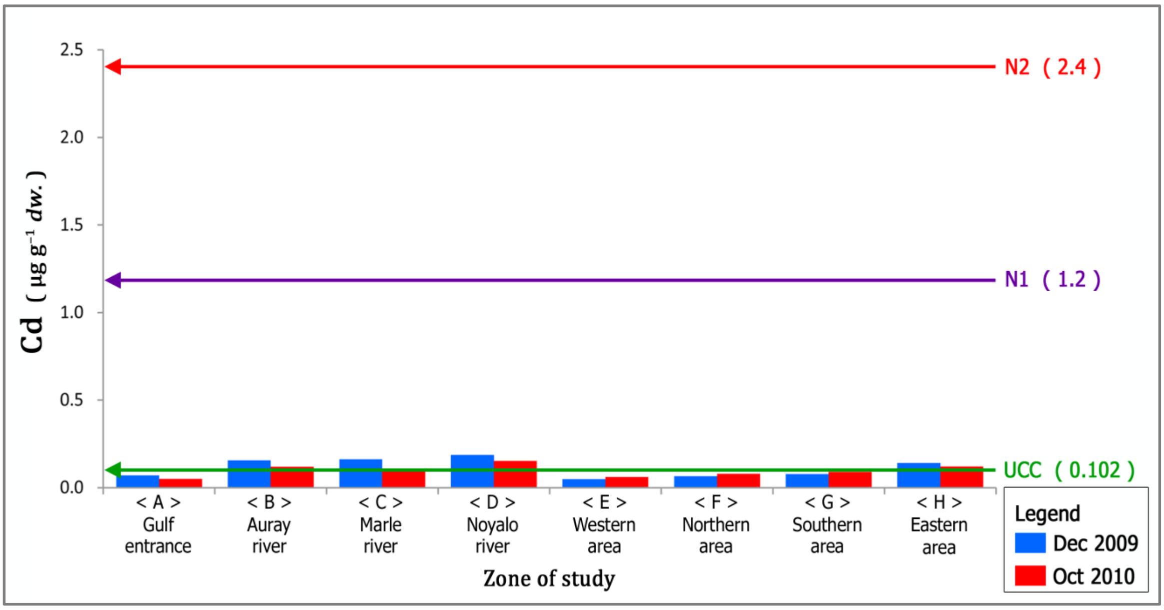

Figure 4–41. *Average concentrations of Cd based on different zone in gulf of Morbihan surficial sediments for both samplings.*

Table 4–19. *Comparison of Cd levels in gulf of Morbihan surficial sediments with other studies reported from European and Asian regions.*

Region	**Cd (µg g^{-1} *dw.*)**	**Reference**
Gulf of Morbihan	0.11	This study
European region		
Seine estuary, France	2.2	Chiffoleau *et al.*, 1994
Loire estuary, France	0.34	Robbe *et al.*, 1985
Vire estuary, France	1	Leleyter and Baraud, 2005
Gironde estuary, France	0.45	Larrose *et al.*, 2010
Arcachon basin, France	0.16	Carruesco and Lapaquellerie, 1985
Gulf of Lion, France	0.6	Radakovitch *et al.*, 2008
Thau lagoon, France	0.28	Rigollet *et al.*, 2004
Rhône estuary, France	0.08	Ferrand *et al.*, 2012
Bilbao estuary, Spain	4	Ruiz and Saiz–Salinas, 2000
Gulf of Finland, Finland	1.06	Leivouri, 1998
Gulf of Naples, Italy	0.9	Adamo *et al.*, 2005
Gulf of Venice, Italy	0.5–4.0	Donazzolo *et al.*, 1981
Asian region		
Gulf of Suez, Egypt	2.8	Hamed and Emara, 2006
Gulf of Oman, Oman	0.02–0.21	de Mora *et al.*, 2004
Gulf of Mannar, India	0.16	Jonathan *et al.*, 2004
Gulf of Cambay, India	0.31	Srinivasa *et al.*, 2005

4.4.9 Concentrations of mercury in sediments

Mercury (Hg) has become of increasing concern due to its toxicity and its contamination in the environment. Hg emitted from anthropogenic sources is widely dispersed and has produced elevated Hg deposition rates around the world. The signal of Hg pollution has been found worldwide in various archives such as sediments, peat bogs and glacier ice. Hg is not an essential element and, because of its ability to bio–accumulate in the adipose tissues of living organisms, it is a potential problem for human health. In fact, Hg is not easily eliminated by humans and animals (Eisler, 1981), has adverse effects on the central nervous system (Fitzgerald and Clarkson, 1991), and causes teratogenic damage during the early stage of development (Clarkson, 1990; USEPA, 1997).

Since the beginning of the industrial age, increasing amounts of Hg have been mobilized and released into the environment (Mason *et al*., 1994). Industrial production of NaOH and plastic, illegal dumping of industrial rubbish, waste incineration, fossil fuel burning (Donze *et al*., 1990), mining activities (Lin *et al*., 2010) and metal smelting are the major sources of Hg contamination to the aquatic environment. Polluted rivers and discharges from industrial facilities can carry Hg compound along the coasts. Particularly, installation of industrial chlor–alkali plants has been recognized to be responsible for persistent contamination of various ecosystems worldwide (Hissler and Probst, 2006). This is a broad phenomenon in Europe, where discharges from chlor–alkali plants constitute 14 % of the total anthropogenic Hg emissions (Biester *et al*., 2002).

The comparison of Hg concentration in isopleth maps pattern between the Quiberon bay and gulf of Morbihan surficial sediments are shown in *Figure 4–42*. The concentrations were not differed significantly during Dec 2009 sampling, but during the Oct 2010 sampling, the concentrations in the gulf of Morbihan were higher compared to the Quiberon bay. However, statistical analysis, *t*–Test shows that there is a significant difference between the both study areas with the *p* value smaller than 0.05.

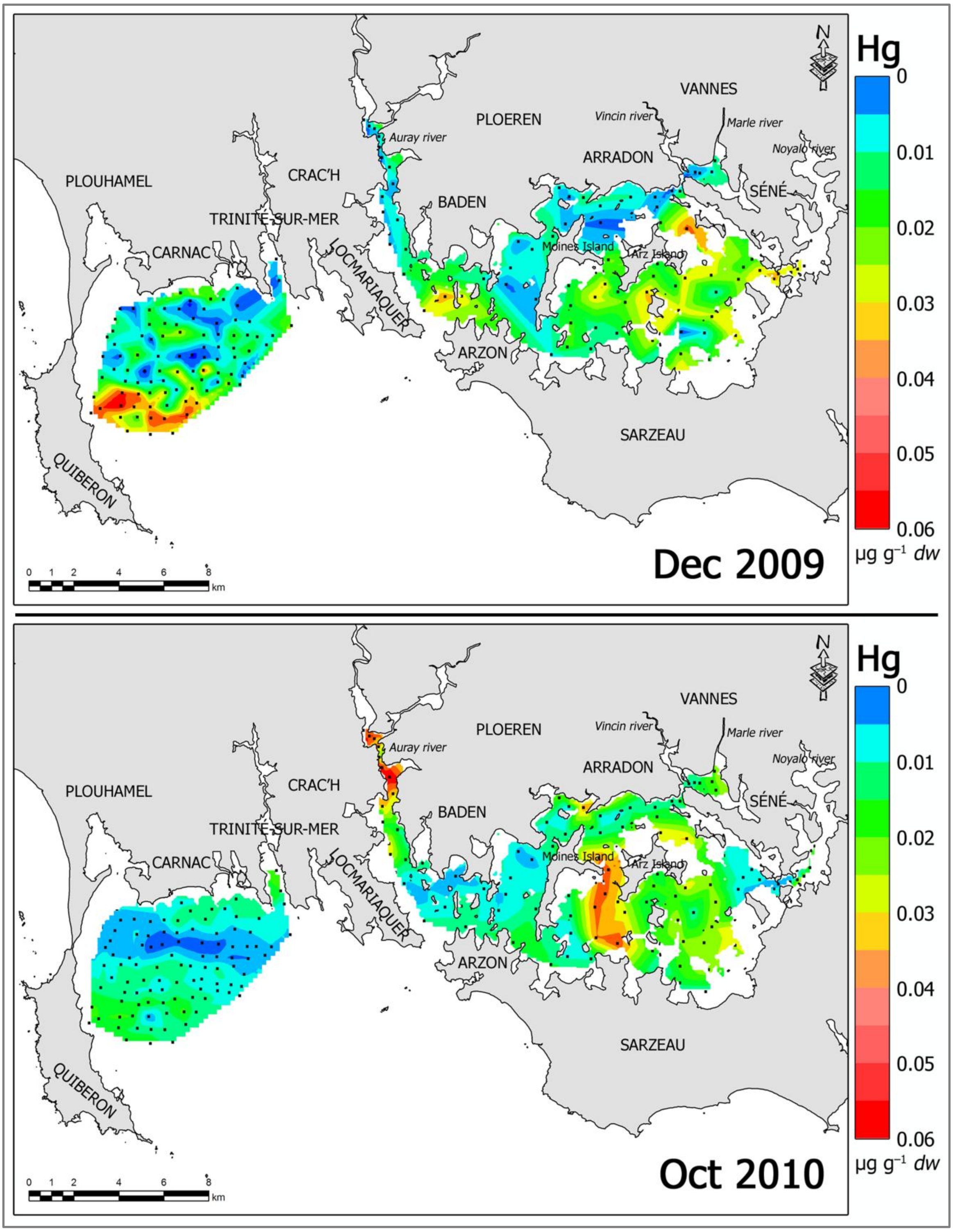

Figure 4–42. *Isopleth maps of Hg accumulation in South Brittany waters.*

The mean concentrations of Hg in Quiberon bay surficial sediments are shown in *Figure 4–43*. The mean concentrations of Hg followed the following pattern: A>B>C>F>E>D, where southern zone located at outer bay had higher mean concentrations of Hg compared to the innermost of the bay area. Despite the high concentration in the sediments of the study area, the mean concentrations were below the UCC value, 0.056 µg g^{-1} *dw* (Wedepohl, 1995) and much lower than the N1 values set by GEODE. Only the mean concentrations in Oct 2010 sediments at the southern zone were closed to the UCC values. Based on the observation, the sediments did not pollute by Hg compounds in this region, and non–anthropogenic process dominant the distribution of Hg in the sediments.

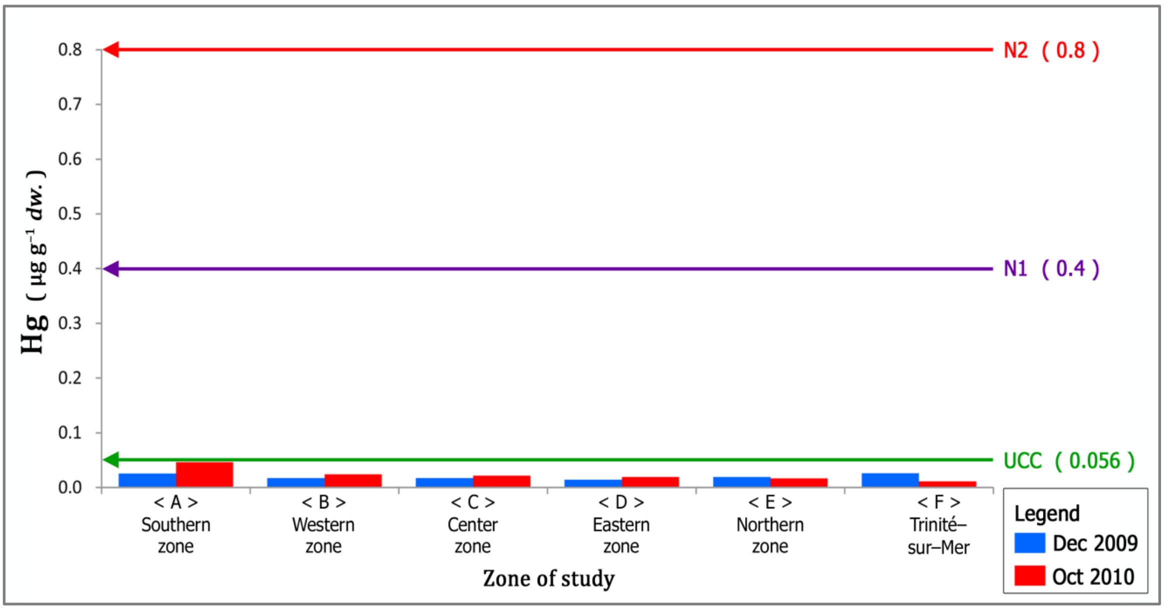

Figure 4–43. *Average concentrations of Hg based on different zone in Quiberon bay surficial sediments for both samplings.*

Table 4–20 shows the comparison of Hg levels in Quiberon bay surficial sediments with other studies from European and Asian regions. Generally, the levels in our study were relatively lower compared to those reported from European and Asian regions. In comparison with sediment from the Marenne Oléron bay investigated by Strady *et al*. (2011) and Toulon bay by Tessier *et al*. (2011), our results were lower than their findings.

Table 4–20. *Comparison of Hg levels in Quiberon bay surficial sediments with other studies reported from European and Asian regions.*

Region	**Hg (µg g^{-1} *dw*.)**	**Reference**
Quiberon bay	0.02	This study
European region		
Marenne Oléron bay, France	0.01–0.13	Strady *et al.*, 2011
Toulon bay, France	0.19	Tessier *et al.*, 2011
Southern coast, Spain	0.2	Usero *et al.*, 2005
Càdiz bay, Spain	0.09–0.97	Araujo *et al.*, 2009
North coast, Belgium	<0.005–0.636	Alsenoy *et al.*, 1993
Liverpool bay, UK	0.116	Camacho–Ibar *et al.*, 1992
Asian region		
Erdek bay, Turkey	0.499	Balkis & Çağatay, 2001
Yellow sea, South Korea	0.028	Luo *et al.*, 2010
Xiamen bay, China	0.091	Chen *et al.*, 1992
Quanzhou bay, China	0.4	Yu *et al.*, 2008
Bohai bay, China	0.25	Meng *et al.*, 2008

Figure 4–44 shows the mean concentrations of Hg in gulf of Morbihan surficial sediments in different zones. The sediments Hg enrichment followed the order: E<C<F<A<B<G<H<D. Higher mean concentrations were observed in Noyalo river and eastern zones while the lower mean concentrations were found in the western zone. In comparison with background value, 0.056 µg g^{-1} dw by Wedepohl (1995), our findings were relatively lower, but when compared to N1 values by GEODE, our results were far below the level. Similar to Quiberon bay observation, non–anthropogenic or natural weathering process were dominating the distribution of Hg in the gulf of Morbihan surficial sediments.

The comparison the Hg levels in the gulf of Morbihan surficial sediments and other studies reported from European and Asian regions are shown in *Table 4–21*. The comparison table reveals that the levels were much lower than those from other regions; far below than the levels in the Seine estuary analyzed by Mikac *et al.* (1999), Gironde estuary by Larrose *et al.* (2010) and Arcachon basin by Carruesco and Lapaquellerie (1985) and slightly lower with study by Stoichev *et al.* (2004) at Adour estuary and Ferrand *et al.* (2012) at Rhône estuary from France coastal waters.

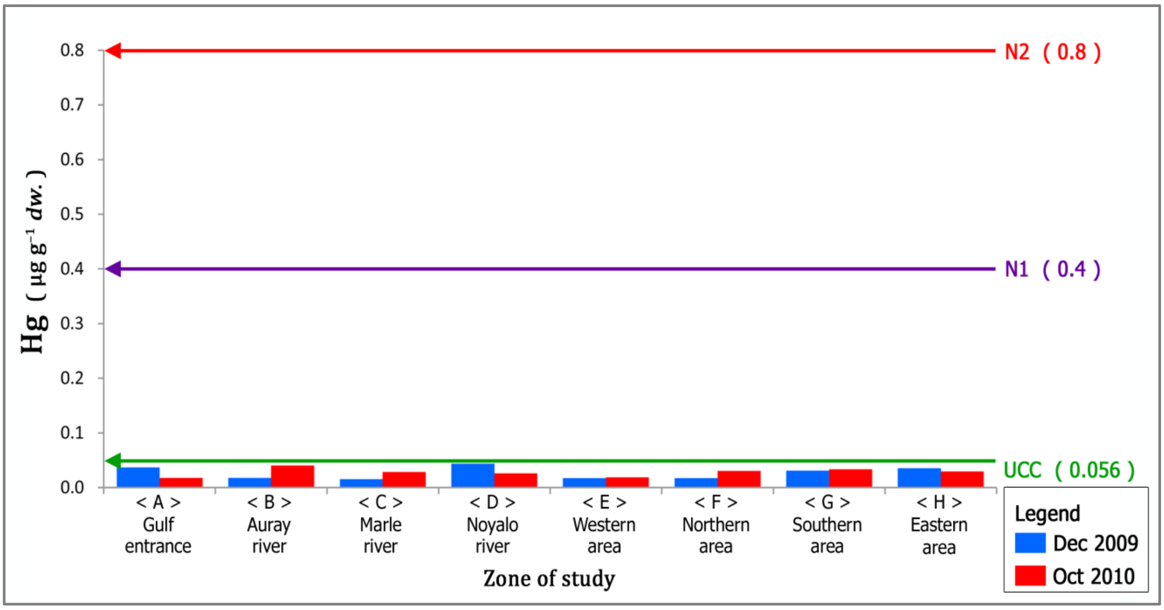

Figure 4–44. *Average concentrations of Hg based on different zone in gulf of Morbihan surficial sediments for both samplings.*

Table 4–21. *Comparison of Hg levels in gulf of Morbihan surficial sediments with other studies reported from European and Asian regions.*

Region	Hg (µg g^{-1} *dw.*)	Reference
Gulf of Morbihan	0.03	This study
European region		
Seine estuary, France	0.46	Mikac *et al.*, 1999
Gironde estuary, France	0.114	Larrose *et al.*, 2010
Arcachon basin, France	0.12	Carruesco and Lapaquellerie, 1985
Adour estuary, France	0.05	Stoichev *et al.*, 2004
Rhône estuary, France	0.05	Ferrand *et al.*, 2012
Gulf of Taranto, Italy	0.12	Buccolieri *et al.*, 2006
Gulf of Venice, Italy	0.1–3.0	Donazzolo *et al.*, 1981
Gulf of Finland, Finland	0.13	Leivouri, 1998
Gulf of Bothnia, Finland	0.27	Leivouri, 1998
Asian region		
Gulf of Oman, Oman	<0.0001–0.22	de Mora *et al.*, 2004
Gulf of Persian, Iran	0.05	Dehghan *et al.*, 2009

4.4.10 Concentrations of lead in sediments

Lead (Pb) is also a highly toxic metal for plants and animals (Alloway 1990; Kennish 1992; Routh and Ikramuddin 1996). The solubility of Pb is controlled principally by $PbCO_3$, and low–alkalinity and low–pH waters can have higher Pb concentrations (Gowd *et al*., 2010). Pb, like the other metals discussed above, is a natural component of marine ecosystems. It is present at low concentrations in clean seawater, sediments and in the tissues of marine plants and animals (Neff, 2002). It is well known that this trace metal has contaminated the troposphere, mostly during the 19th century by human activities related to gasoline combustion and metal processing (Nriagu and Pacyna, 1988).

Pb was elevated to higher levels in the environment due to the use of leaded petrol in ships, boats, automobiles and car batteries as well as spillage during shipment and other operations result. Besides these contributions, atmospheric deposition of Pb from vehicle emissions is well documented (Matthai and Birch, 2001). The elevated Pb concentration in sediment may also be caused by the road run–off of Pb containing dust originated from leaded petroleum, as the traffic in the vicinity is heavy. Emissions from automobiles consuming leaded petrol are the major source of atmospheric Pb (Huntzincker *et al*., 1975; Martin *et al*., 1989) and the atmospheric pathway may represent a major source of Pb to marine sediments. The importance of the volume of traffic as a source of Pb has been recently reported in the north–eastern coast of Spain (Lopez–Sanchez *et al*., 1996). Previous studies also have indicated elevated levels of Pb in aquatic systems receiving effluents from urban areas (El Nemr, 2003; Kishe and Machiwa, 2003).

Figure 4–45 shows the comparison isopleth maps of Pb concentrations in Quiberon bay and gulf of Morbihan surficial sediments. The concentrations were differed significantly between the two study areas for both sampling periods, Dec 2009 and Oct 2010. This is also supported by the statistical analysis, *t*–Test where the calculated *p* value were slighter than 0.05.

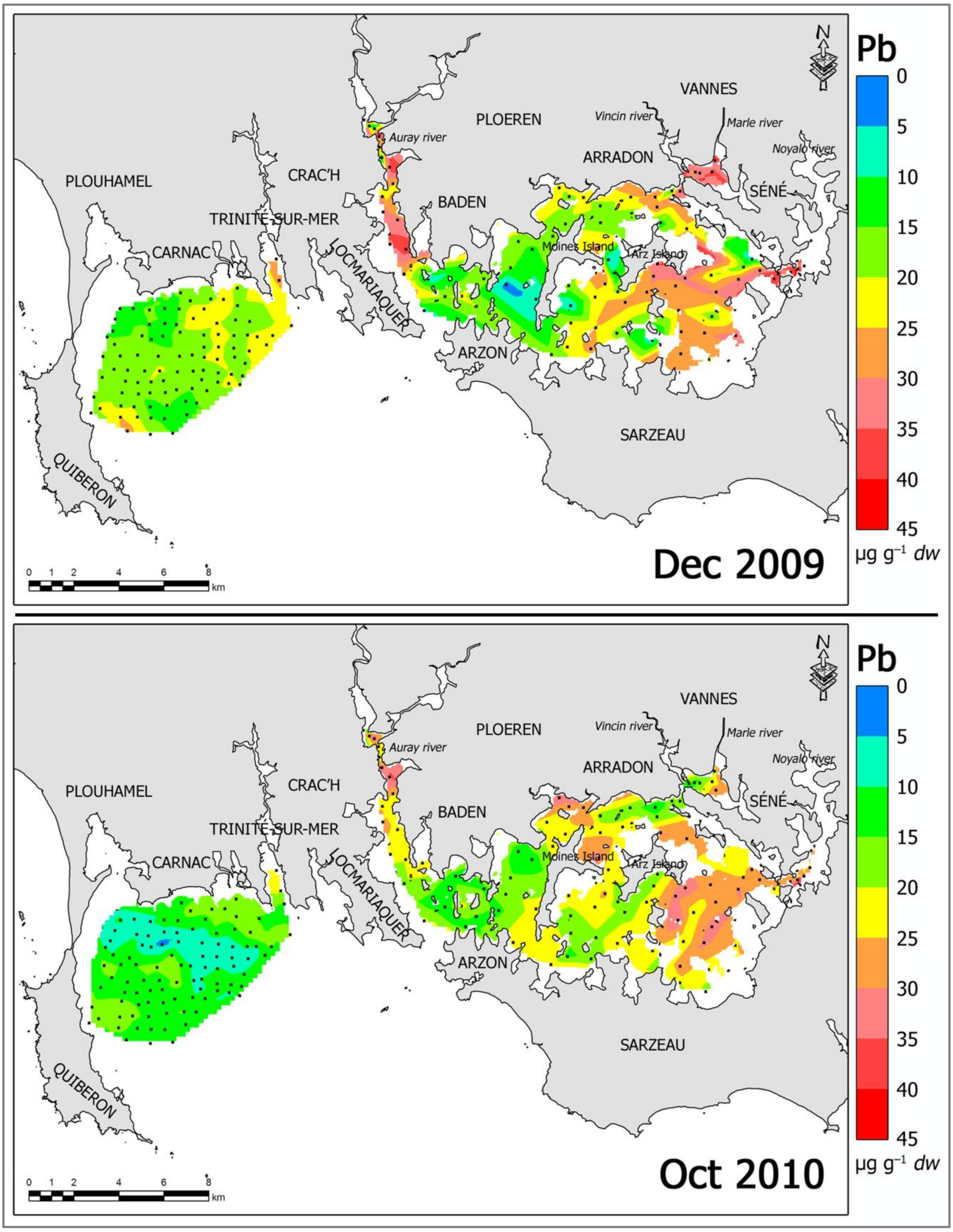

Figure 4–45. *Isopleth maps of Pb accumulation in South Brittany waters.*

Mean concentrations of Pb in Quiberon bay surficial sediments based on zone classification are shown in *Figure 4–46*. The sequence of Pb contaminations follows the increasing order: C<B<D<E<A<F. Again, the mean concentrations were higher at

zone F, Trinité–sur–Mer area compared to the other zones in the bay area and the concentrations exceed the UCC value, 17 µg g^{-1} *dw.* suggested by Wedepohl (1995) for both sampling periods, Dec 2009 and Oct 2010. Meanwhile, it can be noted that, all the mean concentrations particularly during Dec 2009 sampling were close to the UCC value. However, when compared to the N1 levels by GEODE, our result was relatively lower than the values. Despite the high concentrations in the sediments of the study area, it can be concluded that the Pb accumulation resulting from a combination of natural and anthropogenic factors.

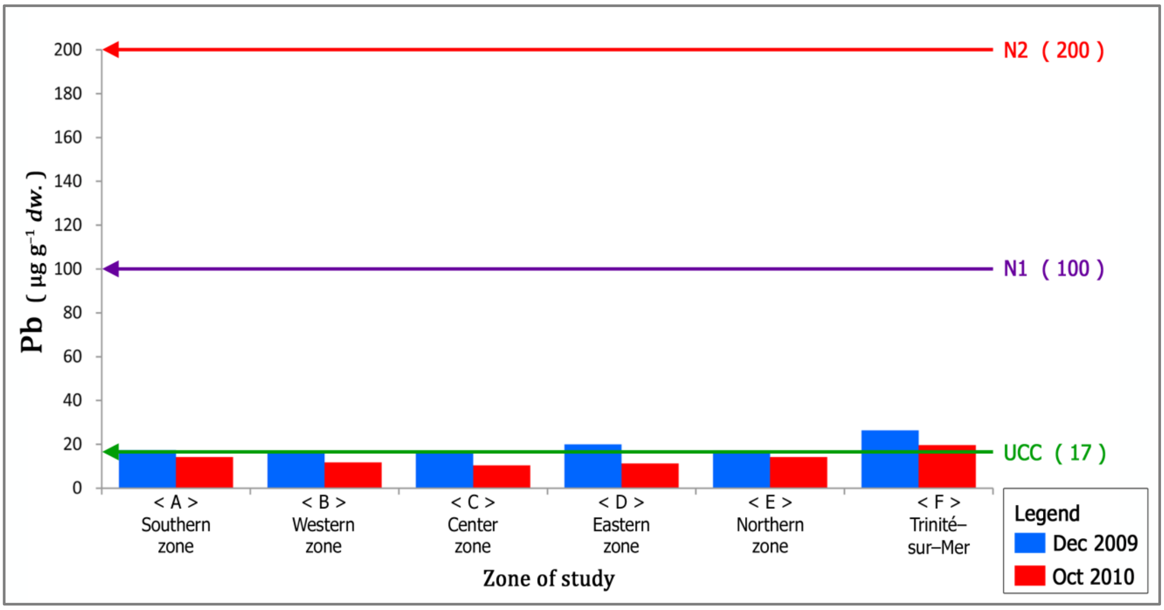

Figure 4–46. *Average concentrations of Pb based on different zone in Quiberon bay surficial sediments for both samplings.*

Table 4–22 shows the comparison of Pb levels in the gulf of Morbihan surficial sediments with other studies conducted from European and Asian regions. The levels in our study were relatively lower compared to those reported and comparable to the study by Usero *et al*. (2005) at the southern coast in Spain and Mil–Homens *et al*. (2006) in Portuguese coastal, Portugal. In comparison with the concentrations in sediment from Seine bay analyzed by Caplat *et al*. (2005), Strady *et al*. (2011) at Marenne Oléron bay, Gascogne coast by N'guessan *et al*. (2009) and Toulon bay by Tessier *et al*. (2011) at France coastal waters, our results were far below than their study.

Table 4–22. *Comparison of Pb levels in Quiberon bay surficial sediments with other studies reported from European and Asian regions.*

Region	**Pb (µg g^{-1} *dw*.)**	**Reference**
Quiberon bay	15.0	This study
European region		
Seine bay, France	166	Caplat *et al.*, 2005
Marenne Oléron bay, France	10–95	Strady *et al.*, 2011
Southwest coast, France	44.6	Fichet *et al.*, 1999
Gascogne coast, France	24.9	N'guessan *et al.*, 2009
Toulon bay, France	73.3	Tessier *et al.*, 2011
Southern coast, Spain	16.1	Usero *et al.*, 2005
Càdiz bay, Spain	12–230	Araujo *et al.*, 2009
San Simon bay, Spain	566.3	Alvarez–Iglesias *et al.*, 2007
Southwest coast, Spain	20–197	Morillo *et al.*, 2004
Portuguese coastal, Portugal	17.3	Mil–Homens *et al.*, 2006
Asian region		
Gemlik bay, Turkey	43	Balkis *et al.*, 1999
Bengal bay, India	32.4	Muthu Raj and Jayaprakash, 2008
Jiaozhou bay, China	28.8	Dai *et al.*, 2007
Bohai bay, China	17.9	Meng *et al.*, 2008
Quanzhou bay, China	67.7	Yu *et al.*, 2008
Youngil bay, South Korea	36.3	Lee *et al.*, 2008
Tokyo bay, Japan	25–58	Fukushima *et al.*, 1992
Penny bay, Hong Kong	28	Chan *et al.*, 2001
Manila bay, Philippines	60	Prudente *et al.*, 1994

Figure 4–47 shows the mean concentrations of Pb in gulf of Morbihan surficial sediments based on different zones. The enrichment of Pb can be classified according to following orders: A<E<F<G<C<H<B<D. Sediments from the gulf entrance and western zones show the lower mean concentrations compared to the rivers and eastern zones, which exhibit the higher mean concentrations. As shown in the figure, all the mean concentrations exceed the UCC value, 17 µg g^{-1} *dw*. suggested by Wedepohl (1995) except zones with lower mean concentration, gulf entrance and western zones which were close to the UCC value. Therefore, the concentrations above the background value can be illustrated as a broken line and considered to be the effect of pollution, suggesting that the contaminations of Pb were present in the gulf of Morbihan sediments, with accumulations resulting

from a combination of natural and anthropogenic factors. However, our values were far below than N1–N2 value by GEODE.

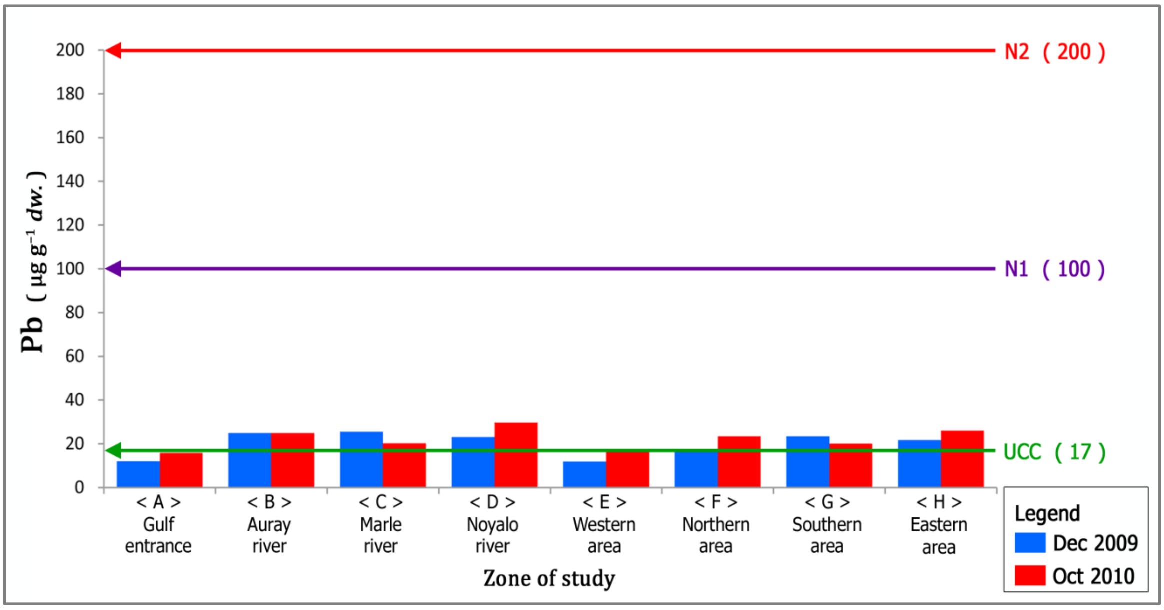

Figure 4–47. *Average concentrations of Pb based on different zone in gulf of Morbihan surficial sediments for both samplings.*

In order to gain information about the status of Pb levels, values from the gulf of Morbihan surficial sediments were compared to other studies from European and Asian regions and the comparisons are shown in *Table 4–23*. From the observation, our levels were higher compared to Thau lagoon studied by Rigollet *et al*. (2004) and Rhône estuary by Ferrand *et al*. (2012) in France Mediterranean sea. In contrast, the levels in sediments from the Seine estuary (Chiffoleau *et al*., 1994) and Vire estuary (Leleyter and Baraud, 2005) at northern coast and the Loire estuary (Robbe *et al*., 1985), Gironde estuary (Larrose *et al*., 2010) and the Arcachon basin (Carruesco and Lapaquellerie, 1985) at the western coast in France coastal were higher than the levels of this study area. Overall, although the levels in the gulf of Morbihan were slightly exceeded the UCC value, the levels were still below the values from other areas from European and Asian regions.

Table 4–23. *Comparison of Pb levels in gulf of Morbihan surficial sediments with other studies reported from European and Asian regions.*

Region	**Pb (μg g^{-1} *dw*.)**	**Reference**
Gulf of Morbihan	22.8	This study
European region		
Seine estuary, France	80.8	Chiffoleau *et al*., 1994
Vire estuary, France	40	Leleyter and Baraud, 2005
Loire estuary, France	52.4	Robbe *et al*., 1985
Gironde estuary, France	41.8	Larrose *et al*., 2010
Arcachon basin, France	36	Carruesco and Lapaquellerie, 1985
Thau lagoon, France	13.8	Rigollet *et al*., 2004
Gulf of Lion, France	49.3	Radakovitch *et al*., 2008
Rhône estuary, France	14.6	Ferrand *et al*., 2012
Bilbao estuary, Spain	126	Ruiz and Saiz–Salinas, 2000
Ria de Vigo, Spain	51.3	Rubio *et al*., 2000
Gulf of Finland, Finland	50	Leivouri, 1998
Gulf of Taranto, Italy	57.8	Buccolieri *et al*., 2006
Gulf of Venice, Italy	10.0–68.0	Donazzolo *et al*., 1981
Gulf of Naples, Italy	123	Adamo *et al*., 2005
Gulf of Thermaikos, Greece	77	Christophoridis *et al*., 2009
Asian region		
Gulf of Izmit, Turkey	36	Ergin *et al*., 1991
Gulf of Gemlik, Turkey	29	Unlü *et al*., 2008
Gulf of Suez, Egypt	29.3	Hamed and Emara, 2006
Gulf of Oman, Oman	0.43–99	de Mora *et al*., 2004
Gulf of Mannar, India	16	Jonathan *et al*., 2004
Gulf of Cambay, India	30.2	Tewari *et al*., 2001

4.5 Factor controlling metallic trace elements in surficial sediments

4.5.1 Correlation between metallic trace elements and types of sediment

Typically, metallic trace elements (MTE) adsorption increases with decreasing grain sizes of the sediment. This reflects the tendency for MTEs to be preferentially adsorbed on the large surface area of fine grained sediments rich in clay minerals (Horowitz, 1991; Green *et al.*, 2001). As a result, clay rich muddy sediments play an important role in the entrapment and deposition of chemical contaminants through sediment surface adsorption. Furthermore, the organic contaminants released into the aquatic ecosystem also tend to be fine particles and they are transported and deposited along with naturally occurring fine grained sediments. This process leads to the proposal that fine grained sediments can act as sinks for organic pollutants (Bell *et al.* 1997; Birch 2000) released into the surrounding catchments (Summerhayes *et al.* 1985). In contrast, coarse grained quartz and shell rich sediments particularly sediment from the Quiberon bay tends to dilute the MTEs concentrations in bulk sediments (Deely, 1991; Lin and Chen, 1996).

It is well established that granulometry of the sediment is a significant controlling factor in the abundance of MTEs (Zhang *et al*., 2007; Caeiro *et al*., 2009; Satheeshkumar and Senthilkumar, 2011). Fine grain sediments tend to have relatively high MTE contents, due in part to the high specific surface of the smaller particles. This enrichment is mainly due to the surface adsorption and ionic attraction (McCave, 1984; Horowitz and Elrick, 1987), also, coatings of organic matter are prevalent in fine grain sediments, and these coatings bind a variety of MTEs (Wangersky, 1986; Keil *et al*., 1994).

To further evaluate potential relationships between MTEs and clay fraction, a matrix of Pearson correlation coefficients relationship was used and illustrated in *Table 4–24*. The correlation values given in *r* were calculated by SPSS statistic software and the correlation graphs are given in *Figure 4–48*.

Table 4–24. *Value of correlations (r) with strength of relationship.*

Correlation coefficients (r)	Strength of relationship
< 0.20	Very negligible relationship
0.20 – 0.40	Low correlation; definite but weak related
0.40 – 0.70	Moderate correlation; substantial related
0.70 – 0.90	High correlation; marked relationship
> 0.90	Very high correlation; very reliable relationship

From the figure, all MTEs show a positive correlation toward grain size with the positive *r* values. Moderate correlation exist between Zn (r = 0.419), Fe (r = 0.406) and Cd (r = 0.401) and grain sizes, while the other MTEs studied show a low correlation toward grain size, Cr (r = 0.361); Pb (r = 0.292); Co (r = 0.287); Cu (r = 0.214); Hg (r = 0.203); As (r = 0.201) and Mn (r = 0.184).

Although some MTEs have a low correlation toward grain sizes, this may suggest that all the MTEs studied are significantly associated with clay minerals and/or silt/clay size constituents of the surficial sediments. These granulometric relations showed that correlation occurred consistently when increasing MTEs concentrations and decreasing grain size. It is obvious that the coarser grained sediments had a dilution effect on most MTEs concentration (Axtmann and Luoma, 1991; Loring and Rantala, 1992; Angelidis and Aloupi, 2000; Lin *et al*., 2002), as supported by the significant negative correlation between sand content and MTE concentrations.

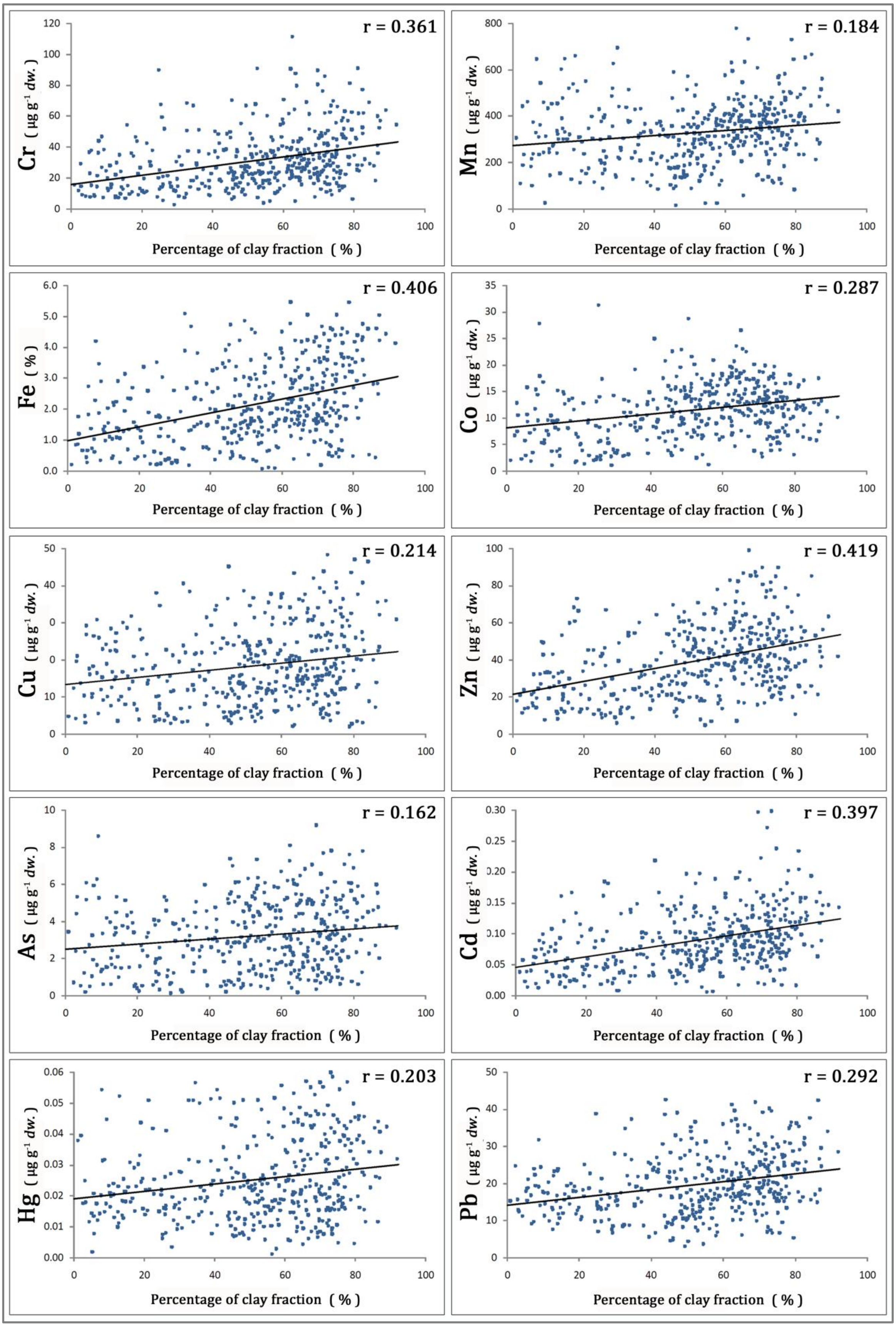

Figure 4–48. *Correlation between MTEs concentration and percentage clay fraction in surficial sediments from Quiberon bay and gulf of Morbihan.*

4.5.2 Correlation between metallic trace elements and total organic carbon content

MTEs resulting from anthropogenic contamination are either associated with organic matter that present in the thin fraction of the sediments, or adsorbed on Fe/Mn hydrous oxides, or precipitated as hydroxides, sulphides and carbonates (Saulnier and Mucci, 2000). The correlation between the MTE concentrations and the organic matter contents in the sediments has been published by various research teams (Suzuki *et al.*, 1979; Rubinstein *et al.*, 1983; Duzzin *et al.*, 1988; Martincic *et al.*, 1990). Although most adsorbed pollutants in the sediments are not readily available for aquatic organisms, the variation of some physical and chemical characteristics (pH, salinity, redox potential and the content of organic chelators) of the overlying water may provoke the release of the elements back to the aqueous phase, hence under changing environmental conditions, the sediments may become themselves important pollution sources (Soares *et al.*, 1999; Upadhyay *et al*., 2006; Sayadi *et al*., 2010).

Significant positive correlation coefficients were also observed between TOC contents and MTEs studied in the Quiberon bay and gulf of Morbihan (*Figure 4–49*). Only Fe shows a high correlation with TOC contents (r = 0.702) and moderate correlations exist between Cd (r = 0.637), Pb (r = 0.625), Cr (r = 0.608), Cu (r = 0.478) and TOC contents. Low positive correlation among As (r = 0.350), Co (r = 0.332), Hg (r = 0.324), Zn (r = 0.292), Mn (r = 0.171) and with TOC contents were clearly observed in the figure. This might suggest that these MTEs contaminants have a considerable association with organic matter, and they probably have a common origin or source and the MTEs have been introduced into the Quiberon bay and gulf of Morbihan environment attached to the organic materials. The obtained results endorsed that the sediment organic matter acts as a metal carrier and also their complexation with organic matter plays an important role in their distribution patterns as reviewed by Ray *et al*. (2006) and Yu *et al*. (2008) in their study.

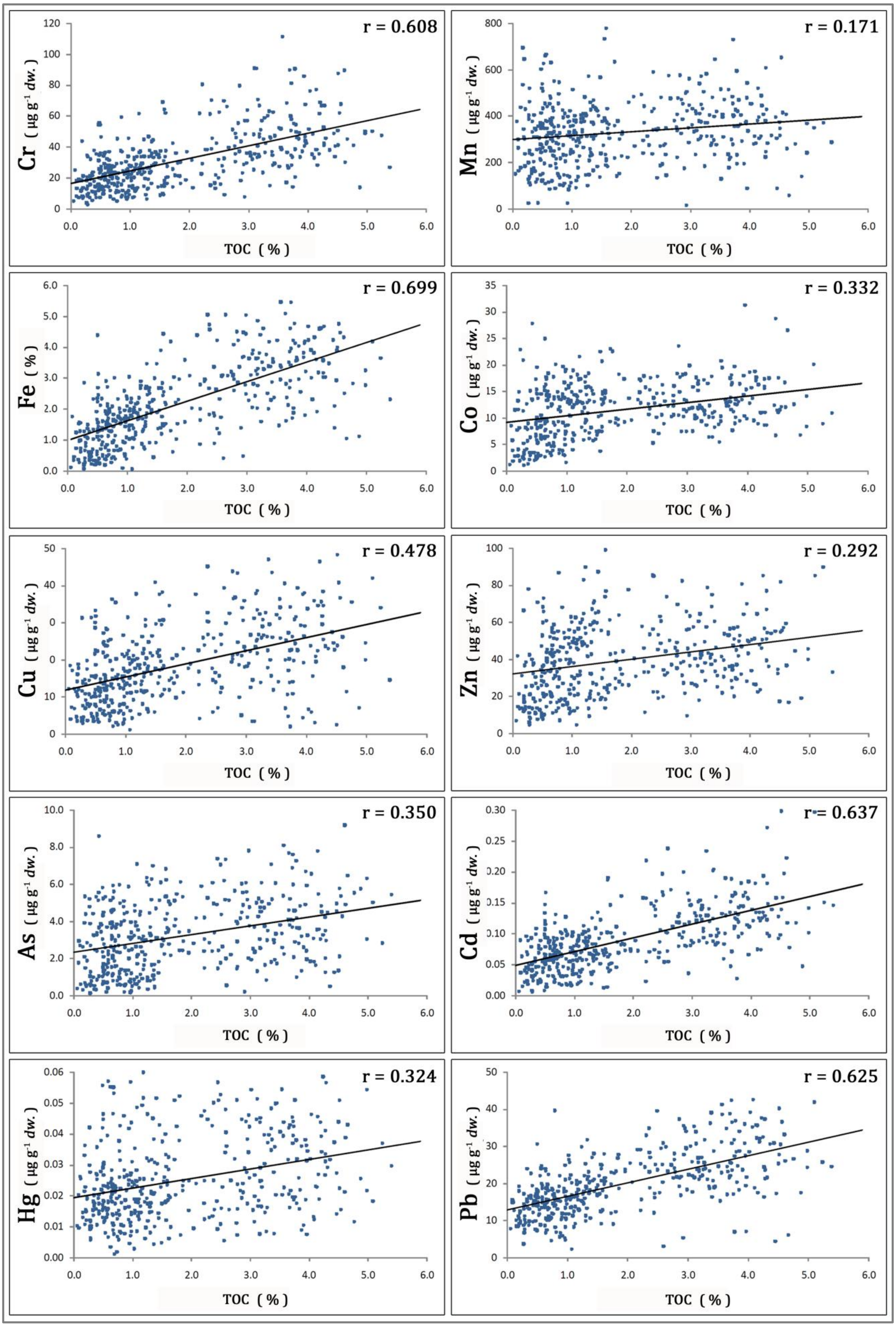

Figure 4–49. *Correlation between MTEs concentration and total organic carbon contents in surficial sediment from Quiberon bay and gulf of Morbihan.*

The results from this study demonstrated that these MTEs (especially Fe, Cr, Cu, Cd and Pb) are bound closely with the organic matter. This is consistent with the classical sediment geochemical and environmental studies that TOC contents are also commonly used to explain the enrichment besides the association with grain sizes in order to better interpret MTE contaminations in sediments (Windom *et al.*, 1991; Church and Scudlark, 1998; Lin *et al.*, 2002). TOC contents have been shown as an important metalsorption phase in both aerobic and anaerobic sediment horizons (Luoma, 1990). Sediments from open system such as the Quiberon bay region have lower TOC contents, similar to values reported by other investigators (Voutsinou–Taliadouri and Varnavas, 1995; Del Valls and Chapman, 1998; Del Valls *et al.*, 1998; Angelidis and Aloupi, 2000), while the higher TOC contents were observed in the gulf of Morbihan region. The greatest TOC contents were associated with the greatest concentration of the MTEs studied.

Concise conclusions based on the results indicate that TOC contents were relatively more important than grain sizes in controlling the distribution of MTEs for the studied sediments. The above observations might suggest that the sorption mechanism of MTEs in the Quiberon bay and gulf of Morbihan surficial sediments is mainly controlled by chemical adsorption, rather than physical or deposition of elements with organic matter on the top of the sediments. MTEs can associate with the ligands through the several functional groups such as –OH, $-NH_2$, –COOH of the organic matters in the sediment and generate stable organic metals (Riffaldi *et al.*, 1983; Gao *et al.*, 2010). These organic–metals can attract the metallic ions while flowing into the bay and gulf from the upstream rivers and then release the metallic ions into the water column upon the benthic decomposition of organics. The organic–metals seem to be stable and accumulate to a high concentration in the vicinity of the study area particularly in the closed system, e.g. gulf of Morbihan region. The stable organic–metals decomposition rates might be far smaller than their formation rates and this mechanism leads to easy accumulation of the metal ions in the sediment and difficult to release the contaminant back to the water environment (Yu *et al.*, 2008).

4.5.3 *Co–association of metallic trace elements concentration*

In order to explore the possible associations between variables of MTE, a simple statistical analysis on the measured data were performed by the SPSS software. Pearson's correlation coefficient for Cr, Mn, Fe, Co, Cu, Zn, As, Cd, Hg and Pb in the surficial sediments from the Quiberon bay and gulf of Morbihan are depicted in *Table 4–25*.

The matrix summarizes the strength of the linear relationship between each pair of variables. When the correlation coefficients belonging to the MTEs were determined, it was well realized that there was a good positive correlation between all MTEs studied even some MTEs particularly Hg, show a low correlation coefficient (Mn–Co; Mn–As; Mn–Hg; Co–Hg; Cu–Hg; Zn–Hg; Zn–As; Hg–As and Hg–Pb).

Table 4–25. *Correlation coefficient of total MTE concentrations in surficial sediments from Quiberon bay and gulf of Morbihan.*

	Cr	**Mn**	**Fe**	**Co**	**Cu**	**Zn**	**As**	**Cd**	**Hg**
Mn	0.501	1							
Fe	0.815	0.578	1						
Co	0.475	0.259	0.514	1					
Cu	0.665	0.457	0.809	0.420	1				
Zn	0.618	0.459	0.737	0.574	0.709	1			
As	0.402	0.189	0.369	0.407	0.322	0.257	1		
Cd	0.814	0.391	0.826	0.486	0.700	0.765	0.304	1	
Hg	0.405	0.224	0.375	0.200	0.236	0.247	0.254	0.314	1
Pb	0.772	0.428	0.852	0.365	0.593	0.523	0.384	0.758	0.217

On the other hand, strong relationship among the MTEs content, Cr–Cd (r = 0.814), Cr–Pb (r = 0.772), Cu–Zn (r = 0.709), Cu–Cd (r = 0.700), Zn–Cd (r = 0.765), Cd–Pb (r = 0.758) in the surficial sediments indicate that their existence and similarity among them. This situation showed that the same geochemical processes a played role (Rubio *et al*., 2000; Kurun *et al*., 2007; Usha and Seshan, 2010) in the accumulation of these MTEs in Quiberon bay and gulf of Morbihan surficial sediments.

Notably, the correlation and geochemical associations of MTEs reveal a significant source of contamination reflecting a common origin of similar nature existing from the anthropogenic effluents. Apparently, this strong correlation also indicating that those heavy metals were released from the same source (Turner, 2000). Meanwhile, low correlation for As and Hg with others MTEs, suggesting that As and Hg might have different anthropogenic and natural sources in the Quiberon bay and gulf of Morbihan surficial sediments.

Fe shows a good correlation with other oxides which have a higher affinity with most elements, especially for MTEs (Stumm and Morgan, 1996), and that the organic matter contents are important for controlling factors in the abundance of trace metals (Rubio *et al.*, 2000). As a consequence, the geochemistry of Fe and organic matter could affect the geochemical behaviour of trace metals in the aquatic environment by involved in redox processes associated with the enrichment of a number of trace metals (Jarvis and Higgs, 1987; Pruysers *et al.*, 1991). One of the evidences is that concentrations of Fe and TOC often correlate (r = 0.702) with concentrations of other metals in the marine environment (Zwolsman *et al.*, 1996; Basaham and El–Sayed, 1998).

Here, Fe compound (hydroxides, oxides, carbonates, sulphides) played the most important roles in metals fractionation (Bodur and Ergin, 1994) and controlled others heavy metal mobility through related sorption processes. This phenomenon can probably be ascribed to the high stability constants for these Cr–Fe, Cu–Fe, Zn–Fe and Pb–Fe binding forms (Ramos *et al.*, 1999; Kelderman and Osman, 2007). Hence, these findings could suggest that Fe compounds in the sediments of the study area are very effective scavengers of other heavy metals. This is supported in earlier experiments by other geochemists (Calvert and Price, 1977; Feely *et al.*, 1983; Salomons and Foèrstner, 1984).

4.6 Multivariate assessment of surficial sediments contamination

4.6.1 Assessment 1 – Enrichment factors with Li as a reference element

To reduce the metallic trace elements (MTEs) variability caused by the grain sizes and mineralogy of the sediments, and to identify anomalous MTEs contribution, geochemical normalization has been used with various degrees of success by employing conservative elements (Emmerson *et al*., 1997; Lee *et al*., 1998). Various elements have been proposed in the literatures to be clay mineral indicators and hence to have the potential for the environmental studies. Some of them are lithium, Li (Loring, 1990; Aloupi and Angelidis, 2001; Soto–Jiménez and Paez–Osuna, 2001); aluminium, Al (Tuncel *et al*., 2007; Tessier *et al*., 2011); scandium, Sc (Grousset *et al*., 1995); cesium, Cs (Ackerman, 1980; Roussiez *et al*., 2005); cobalt, Co (Matthai and Birch, 2001); and thorium, Th (Larrose *et al*., 2010; Strady *et al*., 2011). Among above conservative elements, Li and Al have been widely applied in estuarine and coastal studies (Din, 1992; Tam and Yao, 1998; Schiff and Weisberg, 1999).

Li also has been proposed by Loring (1990) as an alternative for Al in high latitude areas in Western Europe and North America. Alternatively, Li meets the basic criteria for use as a normalizing element for MTEs (Loring, 1990) because of several factors, namely:

(1) it is a lattice component of fine–grained major trace–metal–bearing minerals such as the phyllosilicates and clay minerals,
(2) it reflects the granular variability of its host mineral component, and
(3) it is a conservative element

On the other hand, the suitability of Li and Al as the geochemical normalizer was tested in the Quiberon bay and gulf of Morbihan surficial sediments. The values of Pearson's correlation between Li and Al coefficients versus MTEs are shown in *Table 4–26*. The stronger positive covariance of all studied MTEs with Li over that with Al shows that Li is a better normalizer for the assessment of contamination in Quiberon bay and gulf of Morbihan surficial sediments.

Table 4–26. *Comparison correlation coefficient of MTEs with Li and Al in surficial sediments from Quiberon bay and gulf of Morbihan.*

MTEs	**Cr**	**Mn**	**Fe**	**Co**	**Cu**	**Zn**	**As**	**Cd**	**Hg**	**Pb**
Li	0.586	0.468	0.626	0.415	0.396	0.582	0.263	0.457	0.155	0.501
Al	0.213	0.234	0.178	0.119	0.180	0.092	0.181	0.228	0.117	0.292

In addition, the reference element must be strongly correlated to the fine fraction sediments and not dependent on the anthropogenic inputs (Rubio *et al*., 2000; Mil–Homens *et al.*, 2006; Garcia *et al*., 2009). The concentrations of Li in Quiberon bay and gulf of Morbihan surficial sediments have a good agreement with sediment grain sizes with the *r* value = 0.652 (substantial related) compared to Al, *r* = 0.379 (weak related) (*Figure 4–20*) which satisfied with the qualification demand in this contamination status assessment in Quiberon bay and gulf of Morbihan.

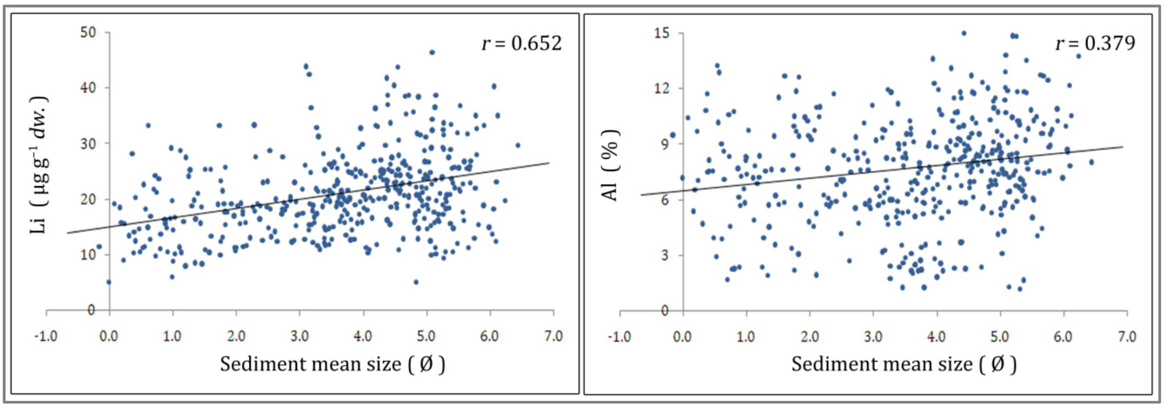

Figure 4–50. *Relationships between concentrations of Li and Al with sediment mean size in Quiberon bay and gulf of Morbihan.*

Therefore after several analyses and considerations, we chose to use Li as a reference element in the enrichment factors (EF) calculation in order to gain more information regarding the degree of pollution or environmental contamination in Quiberon bay and gulf of Morbihan surficial sediments. The EF of the MTEs was calculated according to the following formula:

$$Enrichment\ factors = \frac{(MTE/Li\ )_{sediment}}{(MTE/Li)_{background}}$$

which is the observed MTE/normalize ratio in the sample divided by the MTE/normalize ratio reported for a reference background. Since we do not have MTEs background values for our study area, we adopt the element abundance from average upper continental crust (UCC) abundance data reviewed by Wedepohl (1995), which gives 35 µg g^{-1} *dw.* (Cr), 527 µg g^{-1} *dw.* or (Mn), 3.09 % (Fe), 11.6 µg g^{-1} *dw.* (Co), 14.3 µg g^{-1} *dw.* (Cu), 52 µg g^{-1} *dw.* (Zn), 2.0 µg g^{-1} *dw.* (As), 0.102 µg g^{-1} *dw.* (Cd), 0.056 µg g^{-1} *dw.* (Hg) and 17 µg g^{-1} *dw.* (Pb).

Based on the researches by several geochemists (Jiang and Li, 2002; Zhang and Liu, 2002; Valdés *et al.*; 2005), if an EF value is between 0 and 1.5, it is suggested that the heavy metals may be entirely from crustal materials or natural weathering processes. If an EF is greater than 1.5, it is suggested that a significant portion of heavy metals to have arisen from non–crustal sources or anthropogenic pollution (Feng *et al.*, 2004; Strady *et al.*, 2011).

More precisely, five degrees of sediment contamination categories are recognized on the basis of the EF (Sutherland, 2000; Loska and Wiechula, 2003):

Table 4–27. *Sediment contamination categories based on EF value*

EF range	Contamination category
EF < 2	Deficiency to minimal enrichment
2 < EF < 5	Moderately enrichment
5 < EF < 20	Significant enrichment
20 < EF < 40	Very high enrichment
EF > 40	Extremely high enrichment

Table 4–28 and *Table 4–29* present the average, minimum and maximum EF values of the MTEs studied with respect to the UCC average (Wedepohl, 1995). The distribution of EF values in Quiberon bay and gulf of Morbihan sediments were depicted through the interpolation analysis computed by ArcGIS 9.3 software. *Figure 4–51* to *Figure 4–70* shows the isopleth maps of EF value for both study locations. The sequences of EF follow the increasing order:

Fe<Hg<As<Cu<Mn<Co<Zn<Cd<Cr<Pb for Dec 2009 sampling period and Hg<As<Fe<Mn<Cr<Co<Cd<Zn<Cu<Pb for Oct 2010 sampling period in the Quiberon bay surficial sediments and Hg<Mn<Fe<Zn<Cu<As<Cr<Co<Cd<Pb for Dec 2009 sampling period and Hg<Zn<Mn<Co<As<Cd<Fe<Cr<Cu<Pb for Oct 2010 sampling period in the gulf of Morbihan surficial sediments.

Table 4–28. *Enrichment factor values for Quiberon bay surficial sediments.*

	Dec 2009		**Oct 2010**		**Contamination category**
	Mean	**Min – Max**	**Mean**	**Min – Max**	
Cr	0.85	0.42 – 2.03	0.67	0.12 – 1.26	Deficiency to minimal enrichment
Mn	0.76	0.28 – 2.78	0.65	0.09 – 2.65	Moderate enrichment
Fe	0.48	0.06 – 0.87	0.52	0.05 – 0.93	Deficiency to minimal enrichment
Co	0.82	0.17 – 1.91	0.67	0.11 – 1.78	Deficiency to minimal enrichment
Cu	0.72	0.23 – 2.35	0.81	0.16 – 2.01	Moderate enrichment
Zn	0.84	0.25 – 1.55	0.81	0.16 – 1.65	Deficiency to minimal enrichment
As	0.63	0.04 – 2.09	0.43	0.03 – 1.17	Deficiency to minimal enrichment
Cd	0.85	0.23 – 1.42	0.67	0.10 – 2.24	Moderate enrichment
Hg	0.50	0.03 – 1.17	0.38	0.12 – 0.83	Deficiency to minimal enrichment
Pb	1.32	0.75 – 2.71	0.96	0.44 – 2.33	Moderate enrichment

Table 4–29. *Enrichment factor values for gulf of Morbihan surficial sediments.*

	Dec 2009		**Oct 2010**		**Contamination category**
	Mean	**Min – Max**	**Mean**	**Min – Max**	
Cr	1.13	0.23 – 3.35	1.23	0.29 – 2.34	Deficiency to minimal enrichment
Mn	0.59	0.04 – 1.54	0.89	0.28 – 2.77	Moderate enrichment
Fe	0.84	0.03 – 1.61	1.13	0.24 – 1.95	Deficiency to minimal enrichment
Co	1.15	0.47 – 3.62	0.91	0.38 – 2.63	Moderate enrichment
Cu	0.96	0.06 – 3.30	1.60	0.54 – 3.57	Moderate enrichment
Zn	0.86	0.18 – 2.31	0.88	0.27 – 1.87	Moderate enrichment
As	1.03	0.06 – 2.82	0.97	0.17 – 2.54	Moderate enrichment
Cd	1.22	0.26 – 3.79	1.12	0.21 – 2.36	Moderate enrichment
Hg	0.55	0.09 – 1.42	0.63	0.20 – 1.30	Deficiency to minimal enrichment
Pb	1.87	0.32 – 3.93	1.87	0.92 – 4.15	Moderate enrichment

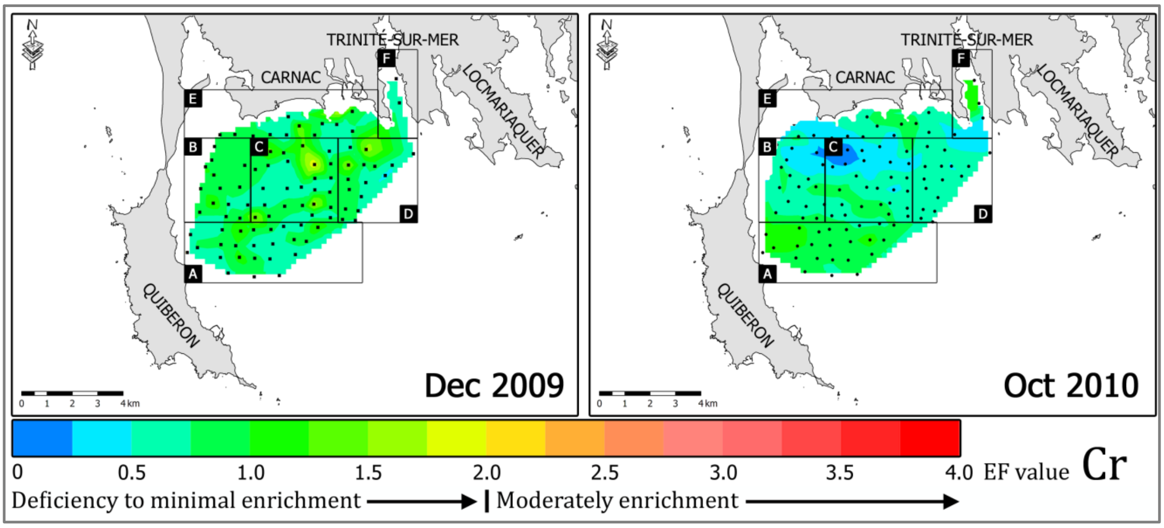

Figure 4–51. *Contamination category based on EF values for Cr in Quiberon bay surficial sediments for both samplings.*

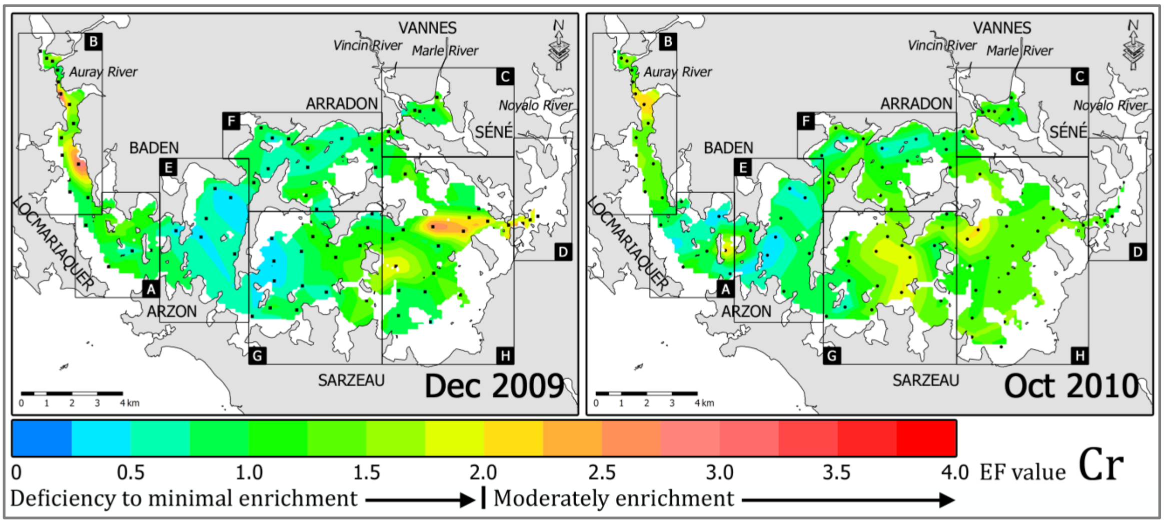

Figure 4–52. *Contamination category based on EF values for Cr in gulf of Morbihan surficial sediments for both samplings.*

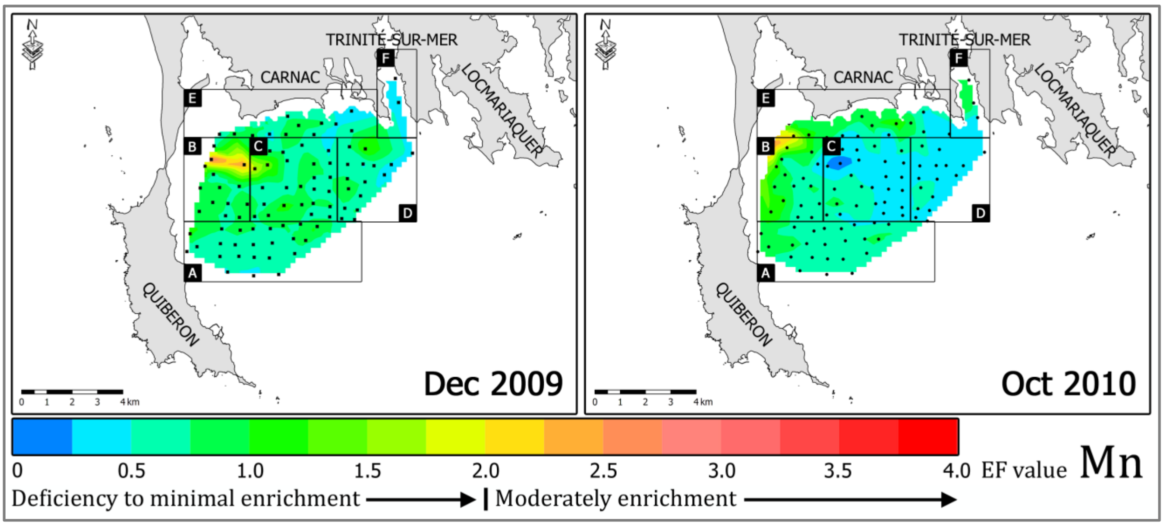

Figure 4–53. *Contamination category based on EF values for Mn in Quiberon bay surficial sediments for both samplings.*

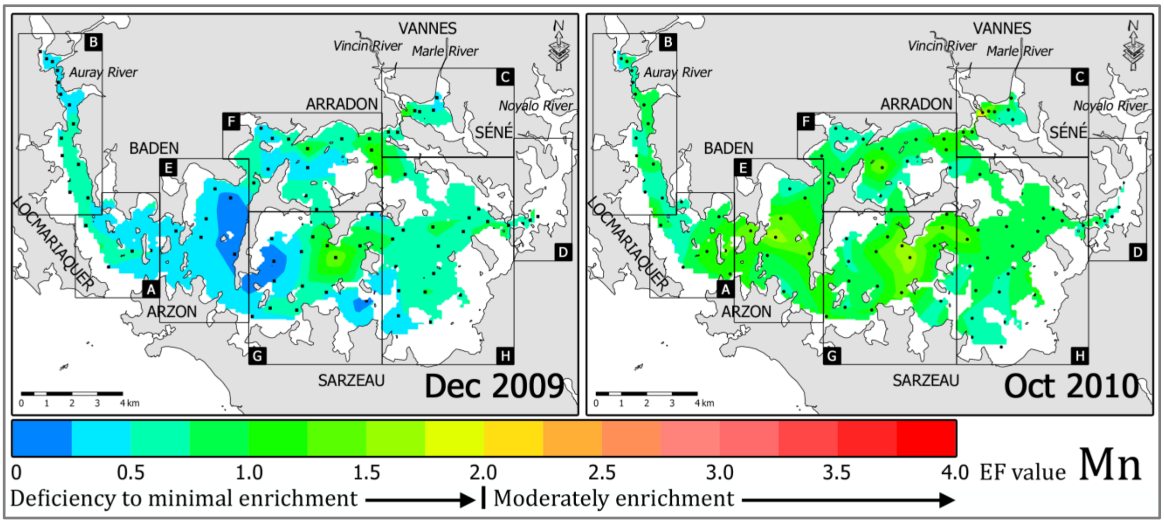

Figure 4–54. *Contamination category based on EF values for Mn in gulf of Morbihan surficial sediments for both samplings.*

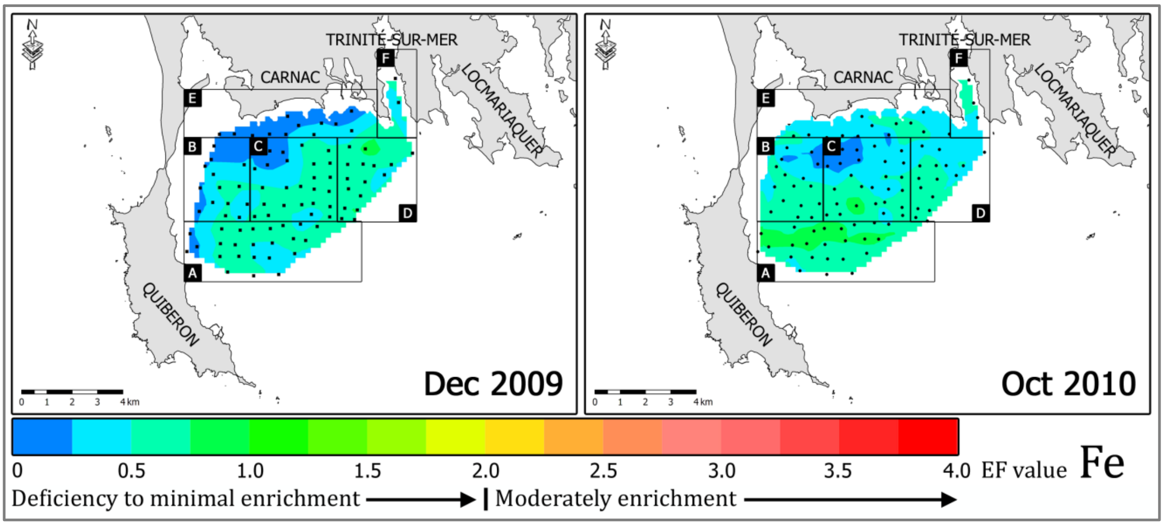

Figure 4–55. *Contamination category based on EF values for Fe in Quiberon bay surficial sediments for both samplings.*

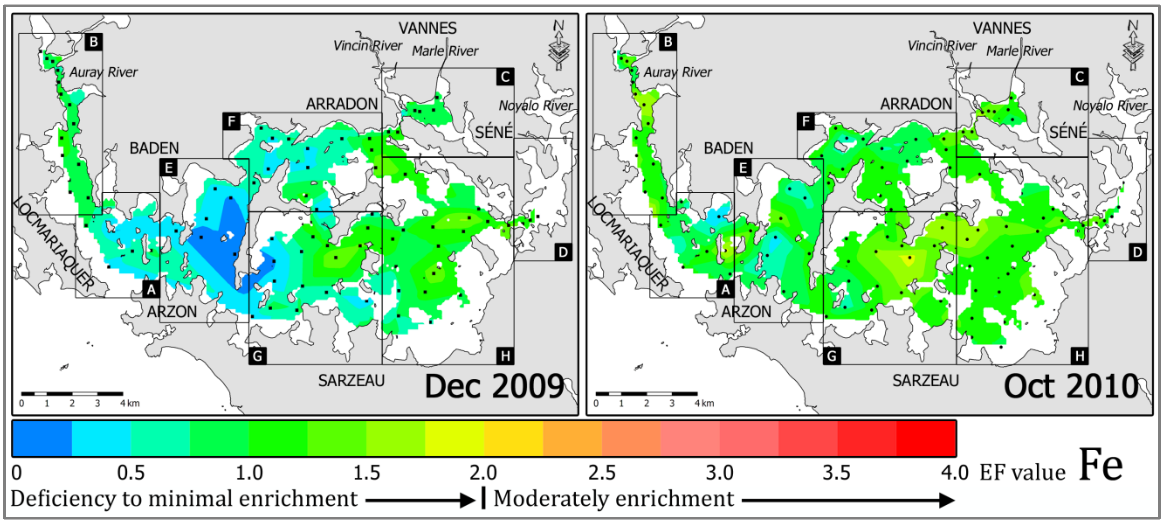

Figure 4–56. *Contamination category based on EF values for Fe in gulf of Morbihan surficial sediments for both samplings.*

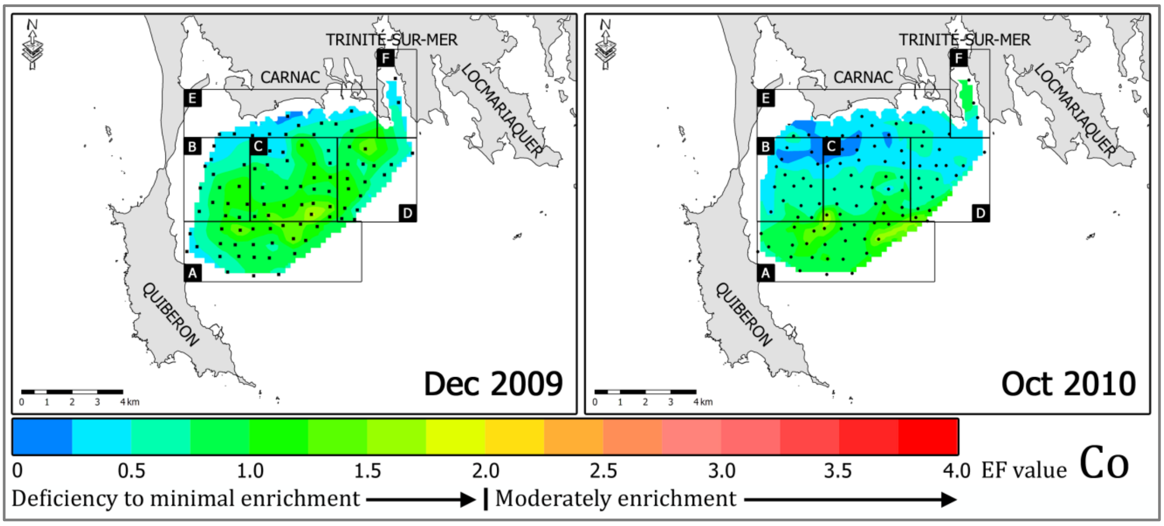

Figure 4–57. *Contamination category based on EF values for Co in Quiberon bay surficial sediments for both samplings.*

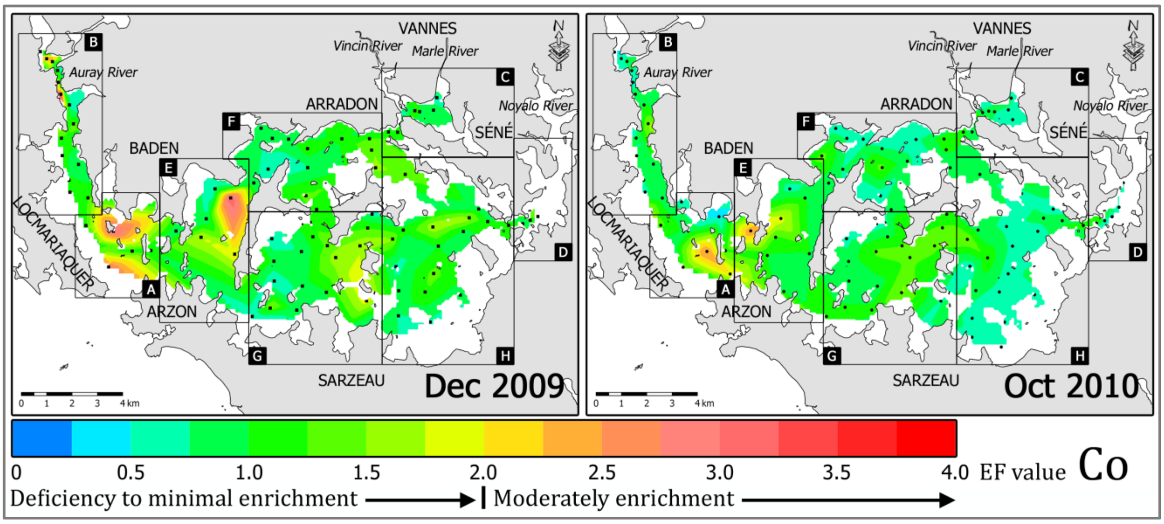

Figure 4–58. *Contamination category based on EF values for Co in gulf of Morbihan surficial sediments for both samplings.*

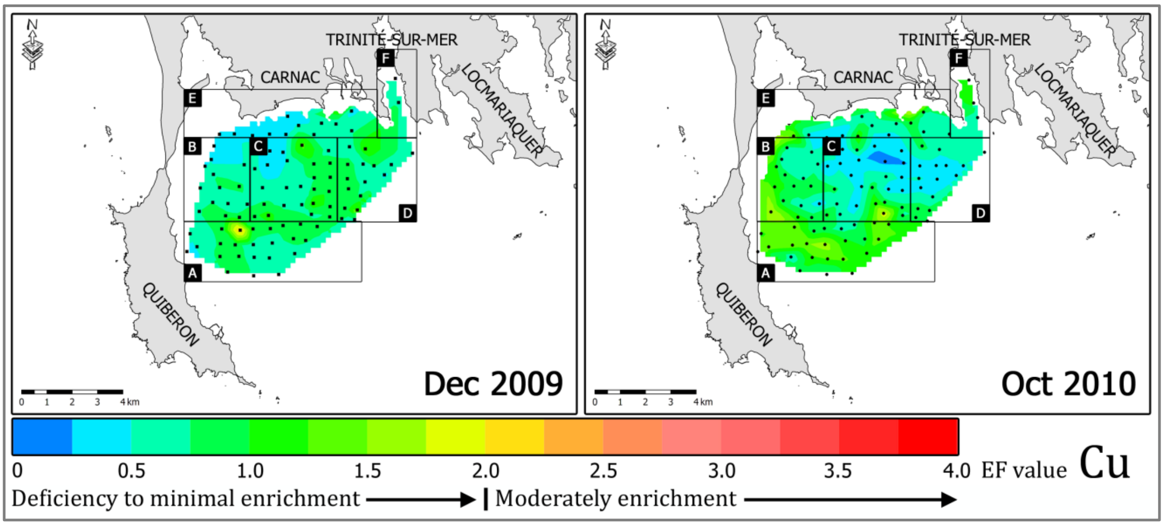

Figure 4–59. *Contamination category based on values for Cu in Quiberon bay surficial sediments for both samplings.*

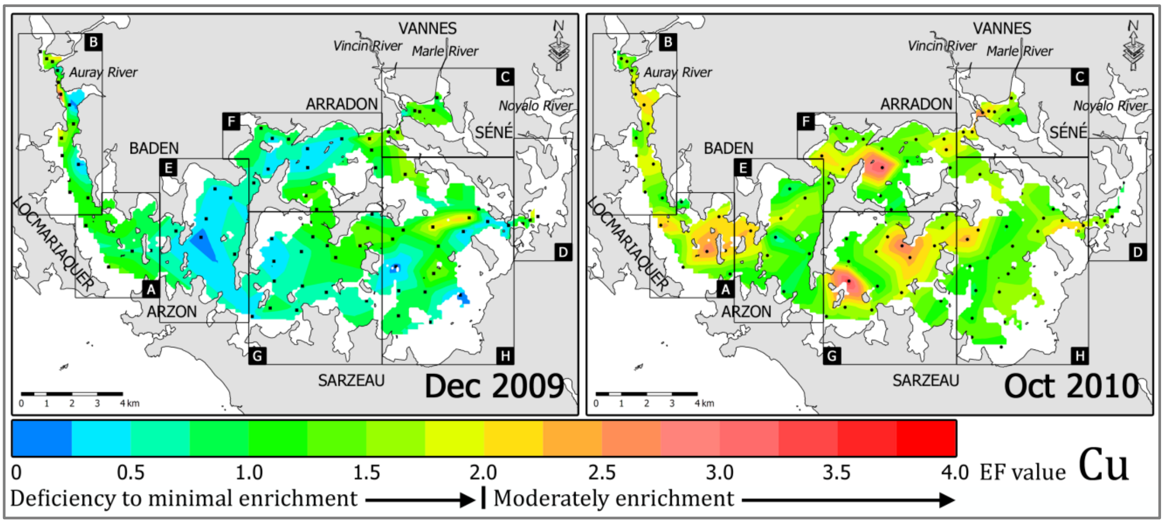

Figure 4–60. *Contamination category based on EF values for Cu in gulf of Morbihan surficial sediments for both samplings.*

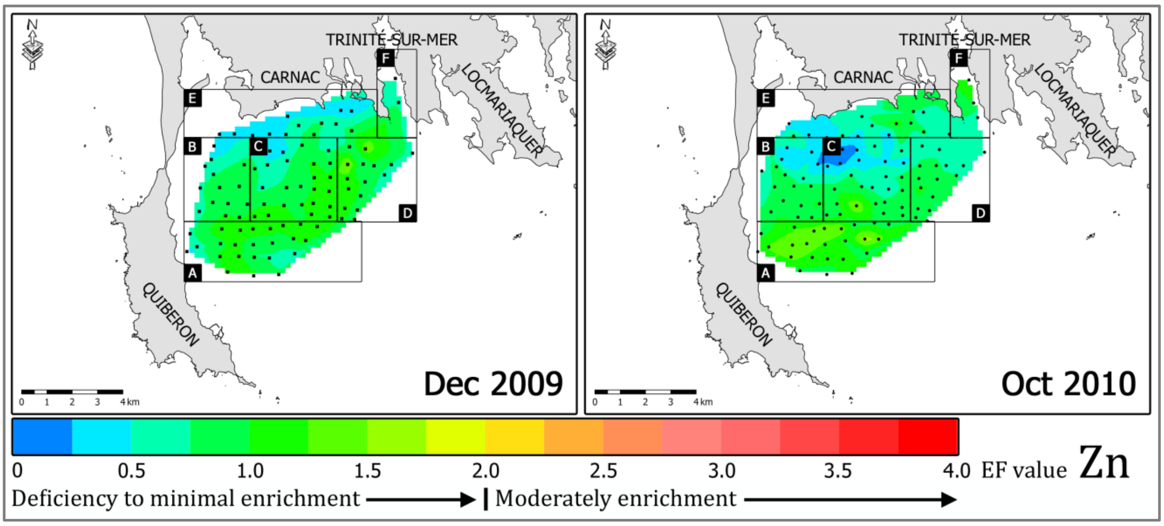

Figure 4–61. *Contamination category based on EF values for Zn in Quiberon bay surficial sediments for both samplings.*

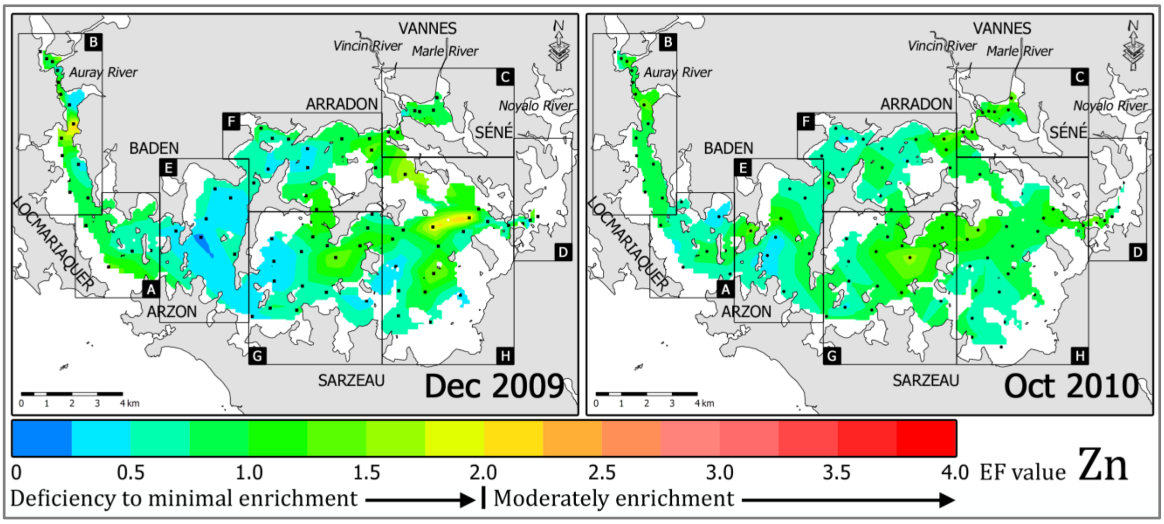

Figure 4–62. *Contamination category based on EF values for Zn in gulf of Morbihan surficial sediments for both samplings.*

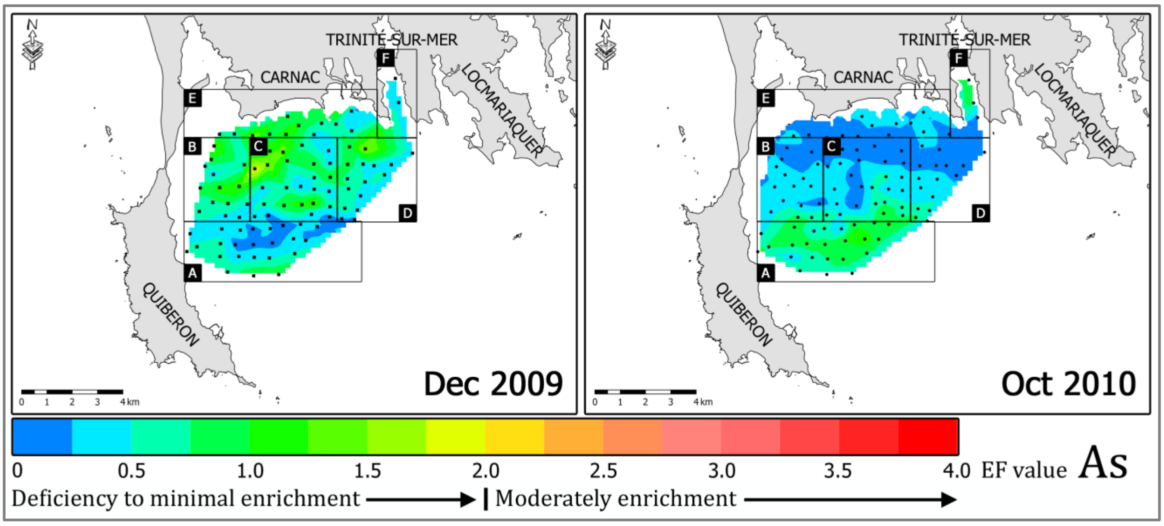

Figure 4–63. *Contamination category based on EF values for As in Quiberon bay surficial sediments for both samplings.*

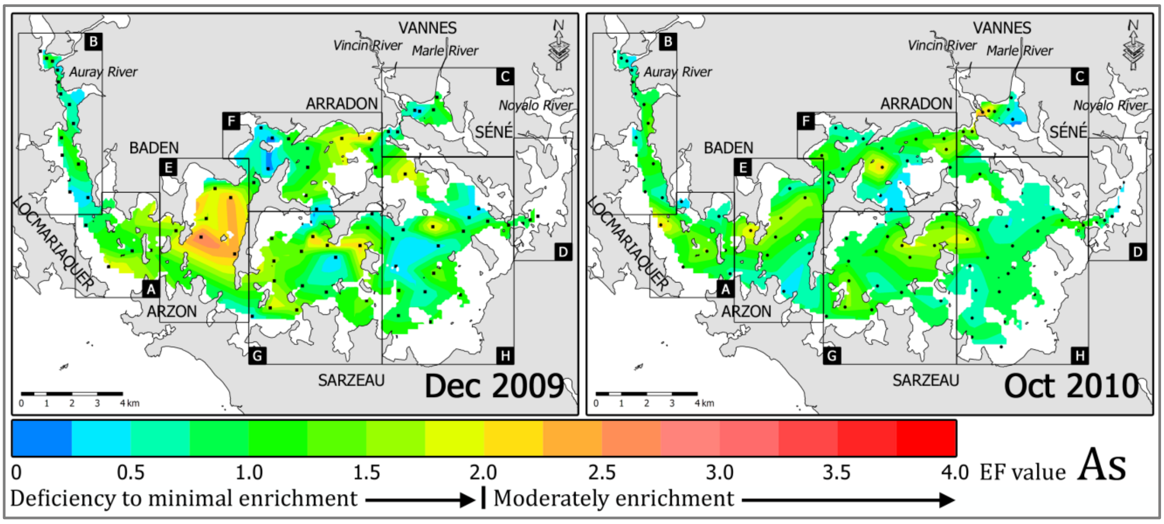

Figure 4–64. *Contamination category based on EF values for As in gulf of Morbihan surficial sediments for both samplings.*

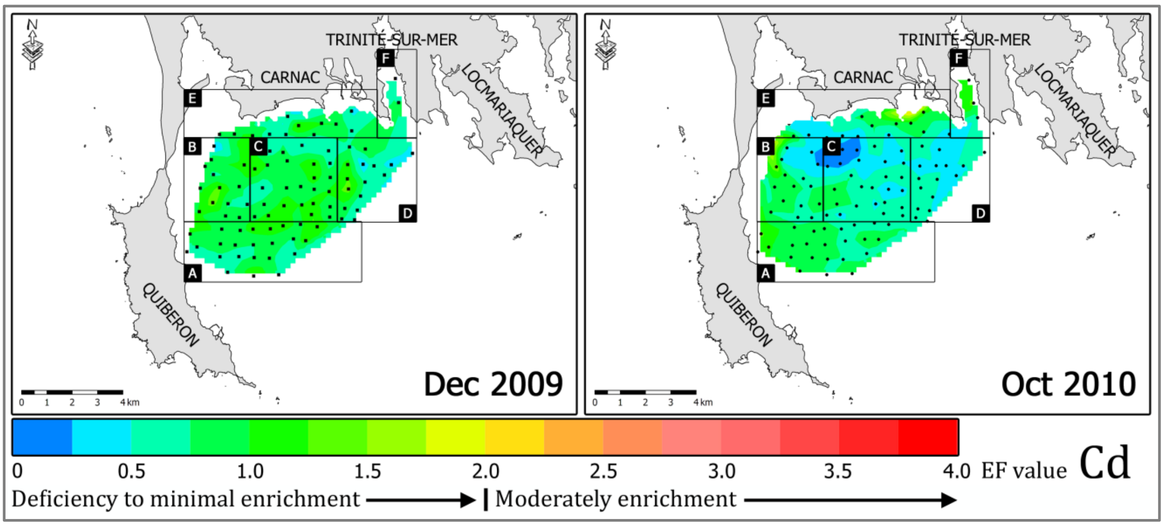

Figure 4–65. *Contamination category based on EF values for Cd in Quiberon bay surficial sediments for both samplings.*

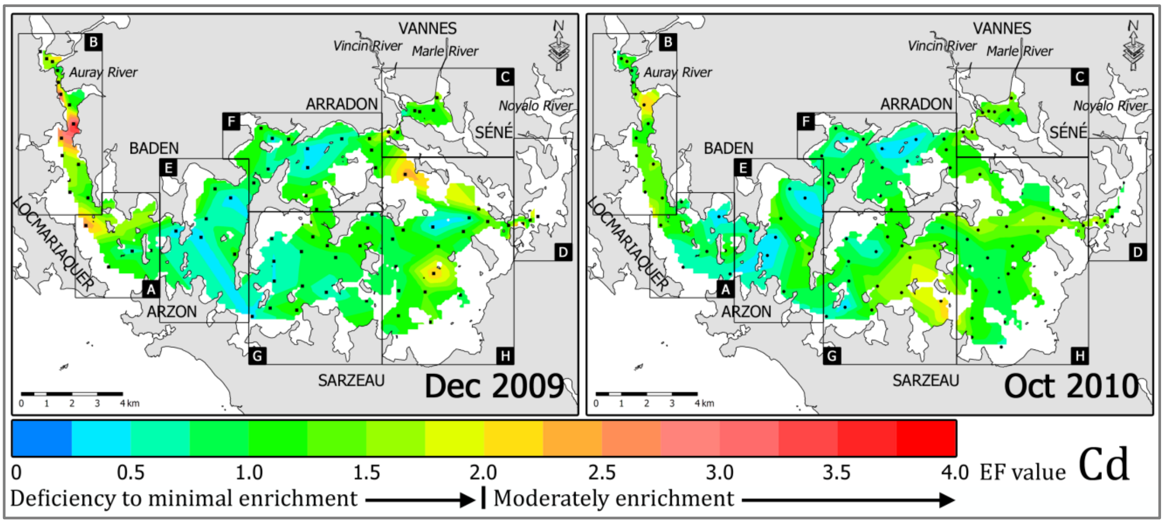

Figure 4–66. *Contamination category based on EF values for Cd in gulf of Morbihan surficial sediments for both samplings.*

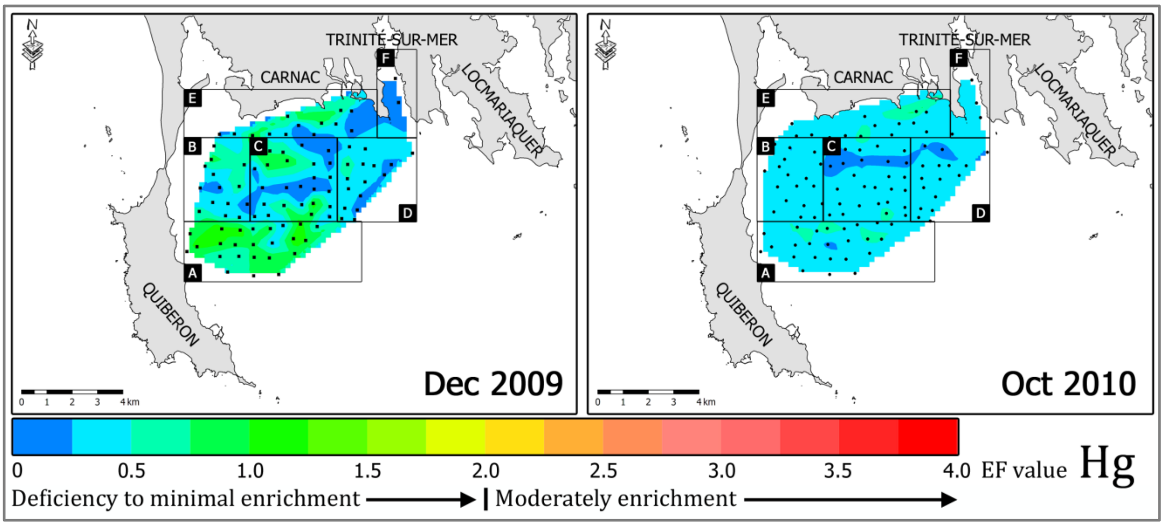

Figure 4–67. *Contamination category based on EF values for Hg in Quiberon bay surficial sediments for both samplings.*

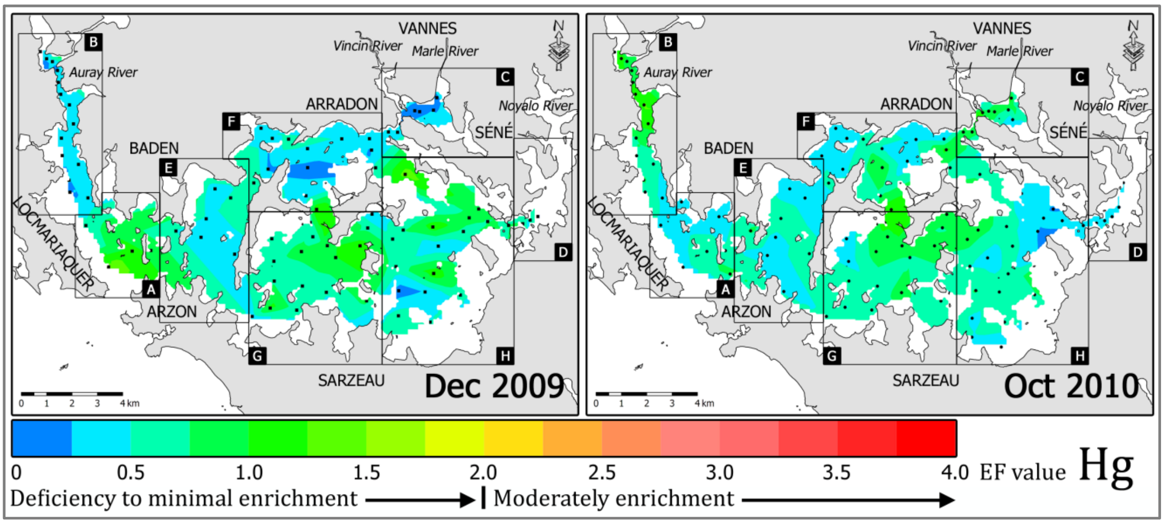

Figure 4–68. *Contamination category based on EF values for Hg in gulf of Morbihan surficial sediments for both samplings.*

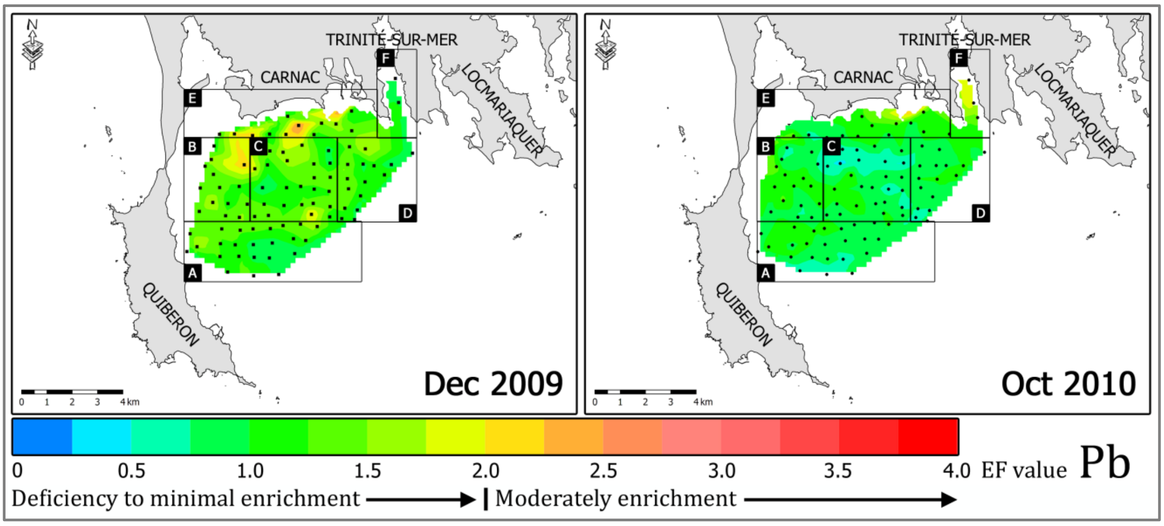

Figure 4–69. *Contamination category based on EF values for Pb in Quiberon bay surficial sediments for both samplings.*

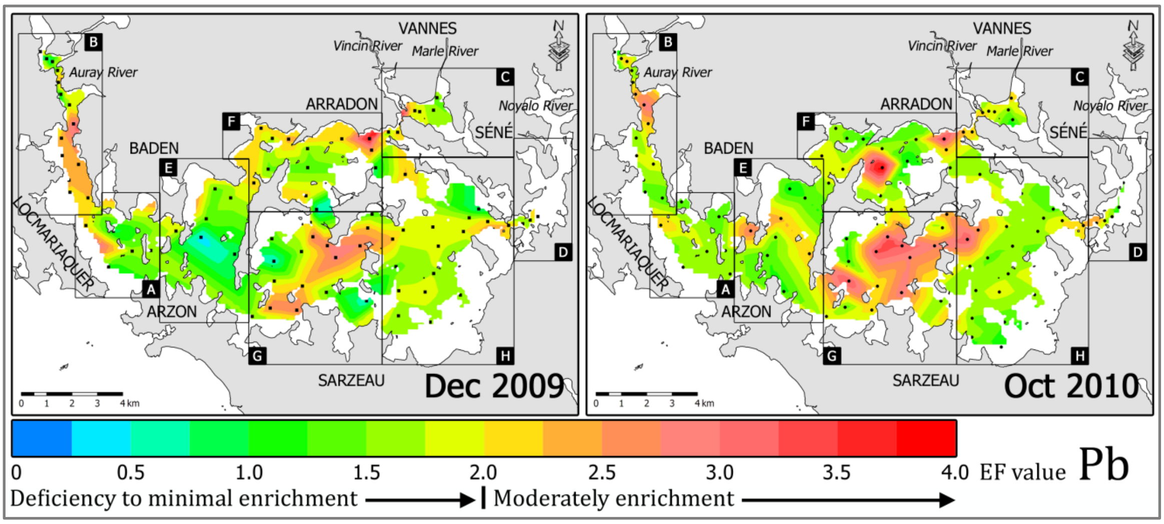

Figure 4–70. *Contamination category based on EF values for Pb in gulf of Morbihan surficial sediments for both samplings.*

Generally, the average of EF values for all the MTEs studied were below than 1.5 and fell within the natural background level, except Pb for both sampling periods in gulf of Morbihan which was greater than 1.5, i.e. above the average mean sediment value illustrated as a broken line and considered to be the effect of pollution (Zhang and Liu, 2002). It is suggested that a significant portion of Pb is delivered from non–crustal or natural weathering processes and provided by other sources into the gulf system (Feng *et al.*, 2004).

Compared to contamination category by Sutherland (2000), Cr, Fe, Co, Zn, As and Hg in Quiberon bay surficial sediment were categorized as deficiency to minimal enrichment, while Mn, Cu, Cd and Pb were categorized as moderate enrichment but some areas fell within the minimal enrichment category. In contrast, in gulf of Morbihan surficial sediments, only Cr, Fe and Hg were classified as deficiency to minimal enrichment. Rest of the MTEs (Mn, Co, Cu, Zn, As, Cd and Pb) were graded to moderate enrichment, and similar to the Quiberon bay sediment, some areas also fell within the minimal enrichment category.

Overall, the average EF of all MTEs studied including Pb are found to be less than 2, suggesting that these MTEs contaminations are currently not a major concern although moderate enrichment of these metals are found in few localized area.

4.6.2 Assessment 2 – Index of geoaccumulation

Another commonly used criterion to evaluate the MTEs pollution in sediments is the index of geoaccumulation (*I*geo) originally introduced by Müller (1969) in order to determine and define MTEs contamination in sediments by comparing current concentrations with MTEs background levels. Similar to metal enrichment factor, index of geoaccumulation can be used as a reference to estimate the extent of metal pollution in Quiberon bay and gulf of Morbihan sediments. The index of geoaccumulation (*I*geo) is defined by the following equation:

$$Index\ of\ geoaccumulation = \ log_2(\frac{C_n}{1.5B_n})$$

where C_n is the measured concentration of the examined element (n) in the our sediment and B_n is the geochemical background concentration of the element (n). Factor 1.5 is the background matrix correction factor due to the lithogenic effects (Müller, 1969). The upper continental crust values of the MTEs of interest are the same as those used in the aforementioned enrichment factor calculation (Wedepohl, 1995).

Müller (1969) has distinguished seven classes of the *I*geo from Class 0 to Class 6 (*Table 4–30*). The highest class (Class 6) reflects at least 100–fold enrichment above the background values. *Table 4–31* and *Table 4–32* shows the mean, minimum and maximum *I*geo value for Quiberon bay and gulf of Morbihan surficial sediment evaluation for both sampling periods, Dec 2009 and Oct 2010. This *I*geo value give similarity information as the aforementioned EF values where both study areas were slightly enriched with Pb.

As shown in *Table 4–31*, no enrichment is noted for all studied MTEs in Quiberon bay, thus surficial sediments in the Quiberon bay can be categorized as class 0 or practically uncontaminated although some areas such as Trinité–sur–Mer were classified with slightly contaminated with Cr, Cu, Zn, Cd and Pb based on their maximum values which somewhat exceed the class 0 classification.

Table 4–30. *Sediment contamination categories based on* I*geo value*

Class	Value	Sediment quality
0	*I*geo ≤ 0	Practically uncontaminated
1	0 < *I*geo < 1	Slightly contaminated
2	1 < *I*geo < 2	Moderately contaminated
3	2 < *I*geo < 3	Moderately to heavily contaminated
4	3 < *I*geo < 4	Heavily contaminated
5	4 < *I*geo < 5	Heavily to extremely contaminated
6	*I*geo > 5	Extremely contaminated

Meanwhile, based on the mean values, all MTEs studied except Pb were ranked as practically uncontaminated (*Table 4–32*) in surficial sediments from the gulf of Morbihan. Nevertheless, Pb was clearly enriched in almost all sediments and fell into class 1 or slightly contaminated although some areas were classified as practically uncontaminated. For Cr, Cu, Zn and Cd, some maximum *I*geo value also exceed 0 especially at the eastern zone and rivers (Auray, Marle and Noyalo) zones indicate that these locations also received insufficient of anthropogenic or non–crustal pollutant.

Table 4–31. I*geo values for Quiberon bay surficial sediments.*

	Dec 2009		Oct 2010		Contamination category and sediment quality
	Mean	Min / Max	Mean	Min / Max	
Cr	−1.02	−2.62 / 0.24	−1.51	−4.16 / 0.39	Class 0 (Practically uncontaminated)
Mn	−1.21	−2.76 / −0.24	−1.60	−4.94 / −0.02	
Fe	−2.03	−4.67 / −0.02	−1.89	−5.72 / −0.24	
Co	−1.15	−3.41 / −0.19	−1.63	−4.34 / 0.03	
Cu	−1.29	−3.12 / 0.45	−1.31	−3.55 / 0.33	
Zn	−1.05	−3.12 / 0.16	−1.26	−4.08 / 0.34	
As	−1.68	−5.58 / −0.33	−2.39	−5.99 / −0.14	
Cd	−1.01	−2.97 / 0.01	−1.58	−4.58 / 0.32	
Hg	−2.11	−6.10 / −0.49	−2.27	−4.14 / −1.33	
Pb	−0.36	−1.34 / 0.32	−0.95	−2.64 / 0.10	

Table 4–32. *Igeo values for gulf of Morbihan surficial sediments.*

	Dec 2009		Oct 2010		Contamination category and sediment quality
	Mean	**Min / Max**	**Mean**	**Min / Max**	
Cr	−0.84	−3.27 / 1.09	−0.69	−2.96 /0.44	Class 0 (Practically uncontaminated)
Mn	−1.74	−5.58 / −0.11	−1.12	−2.63 / −0.28	
Fe	−1.27	−6.59 / 0.24	−0.76	−3.22 / 0.14	
Co	−0.75	−2.26 / 0.48	−1.11	−2.59 / −0.29	
Cu	−1.21	−4.64 / 0.69	−0.26	−1.89 / 0.65	
Zn	−1.24	−4.03 / 0.13	−1.14	−3.09 / 0.21	
As	−1.15	−5.29 / 0.29	−1.12	−2.56 / −0.25	
Cd	−0.67	−3.21 / 0.93	−0.83	−3.50 / 0.62	
Hg	−1.92	−3.90 / −0.67	−1.61	−2.90 / −0.48	
Pb	0.03	−3.21 / 0.92	0.04	−2.56 / 0.75	Class 1 (Slightly contaminated)

To obtain *I*geo isopleth maps, data were visualized using ArcGIS software. The kriging interpolations of the *I*geo value were expressed in *Figure 4–71* to *Figure 4–89*.

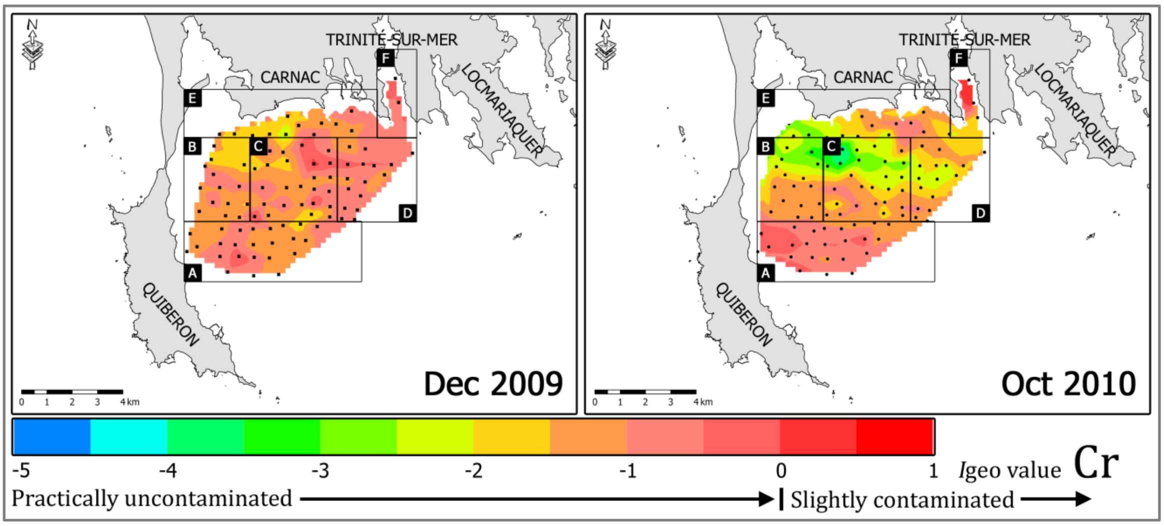

Figure 4–71. *Contamination category based on Igeo values for Cr in Quiberon bay surficial sediments for both samplings.*

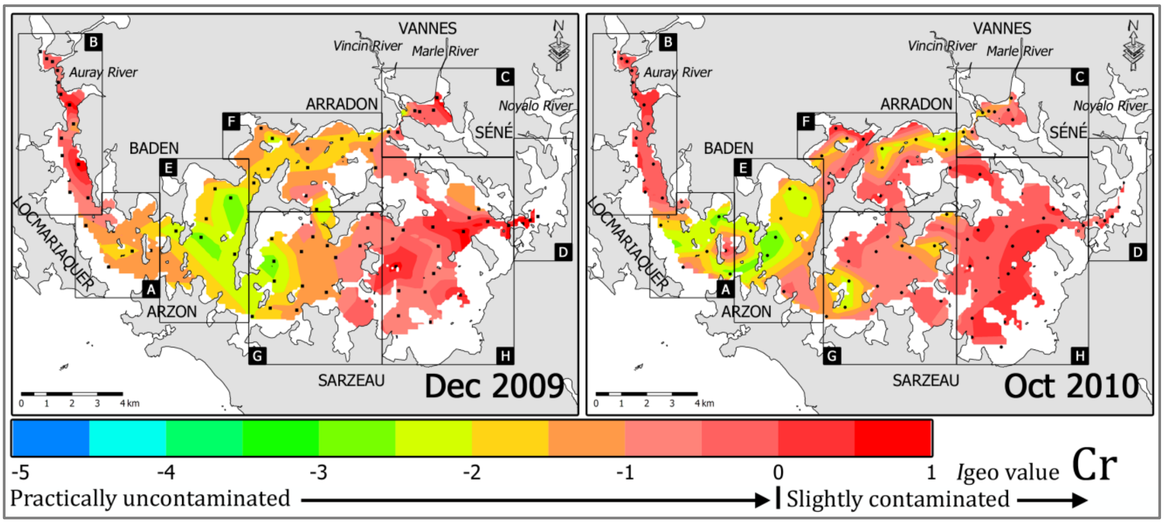

Figure 4–72. *Contamination category based on Igeo values for Cr in gulf of Morbihan surficial sediments for both samplings.*

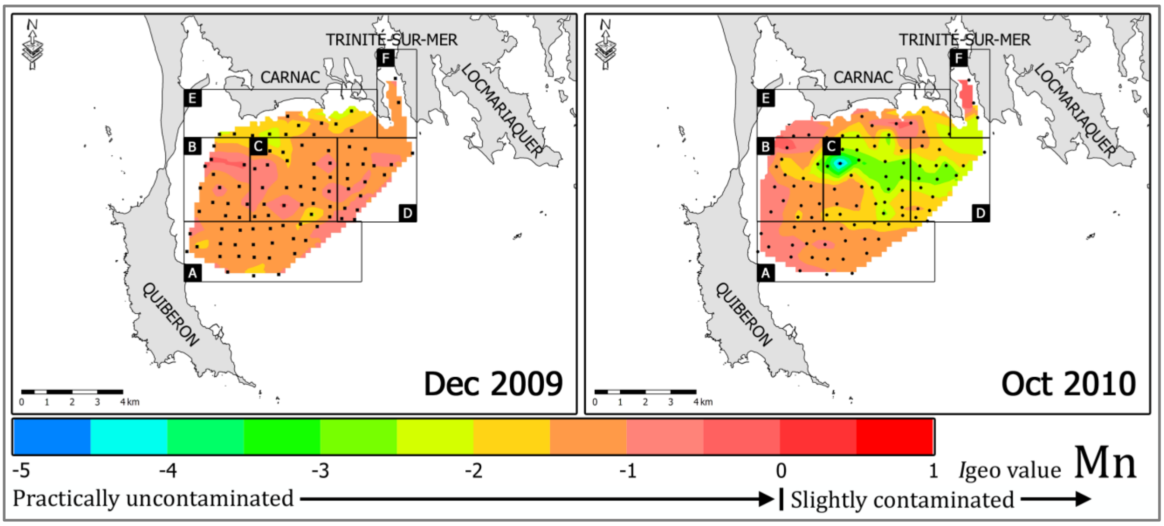

Figure 4–73. *Contamination category based on Igeo values for Mn in Quiberon bay surficial sediments for both samplings.*

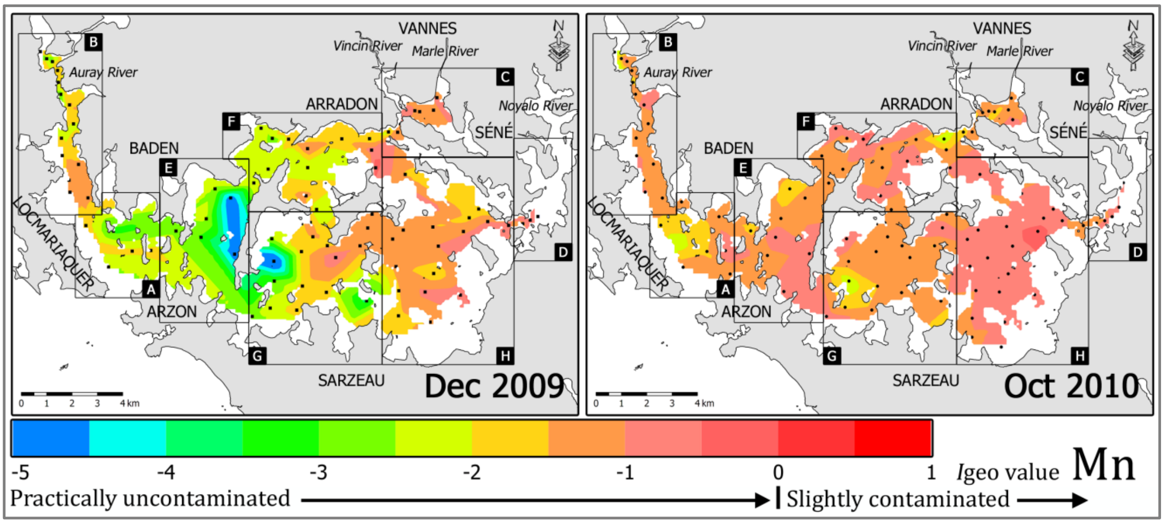

Figure 4–74. *Contamination category based on Igeo values for Mn in gulf of Morbihan surficial sediments for both samplings.*

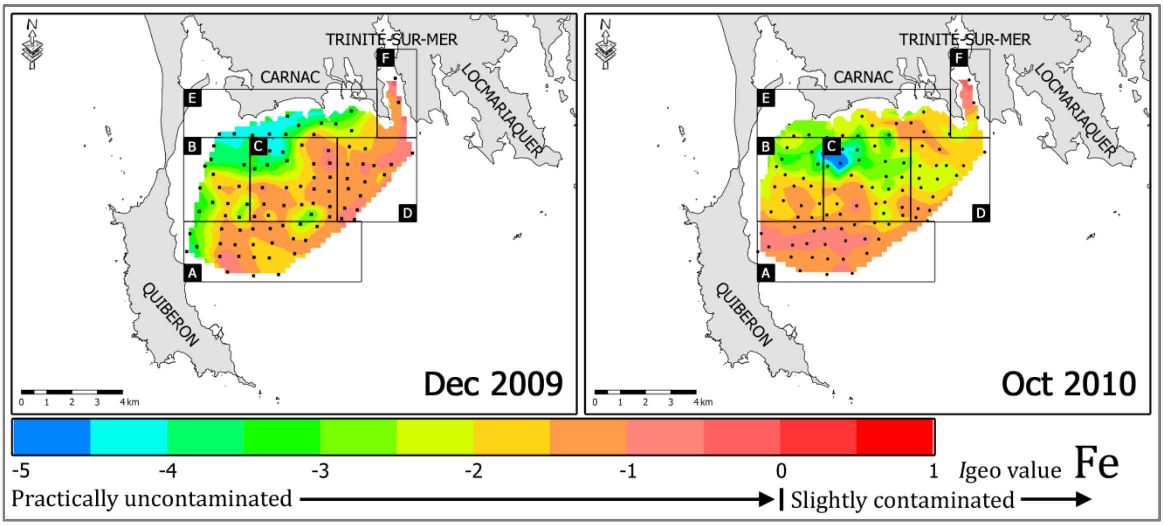

Figure 4–75. *Contamination category based on Igeo values for Fe in Quiberon bay surficial sediments for both samplings.*

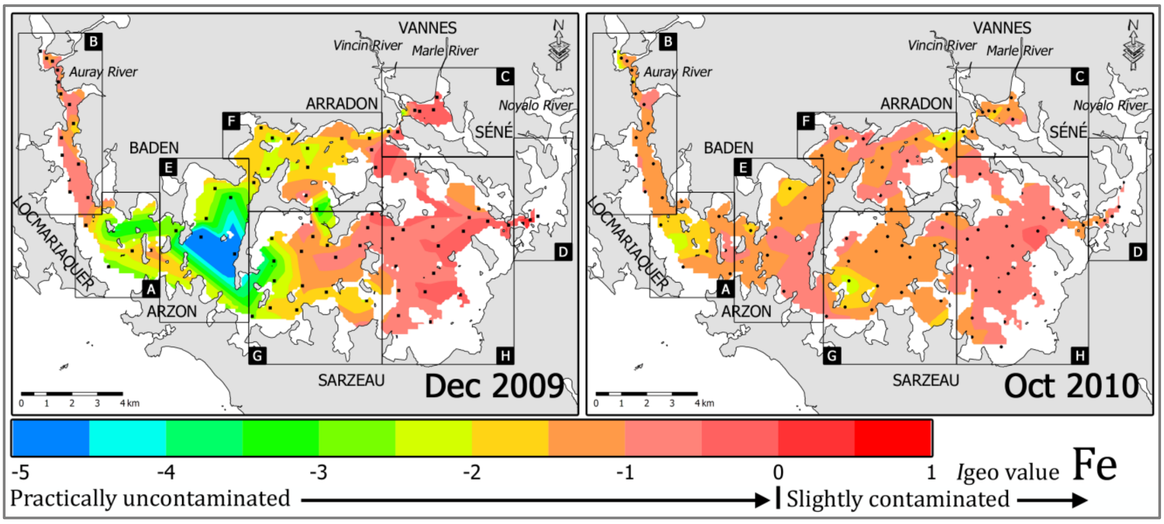

Figure 4–76. *Contamination category based on Igeo values for Fe in gulf of Morbihan surficial sediments for both samplings.*

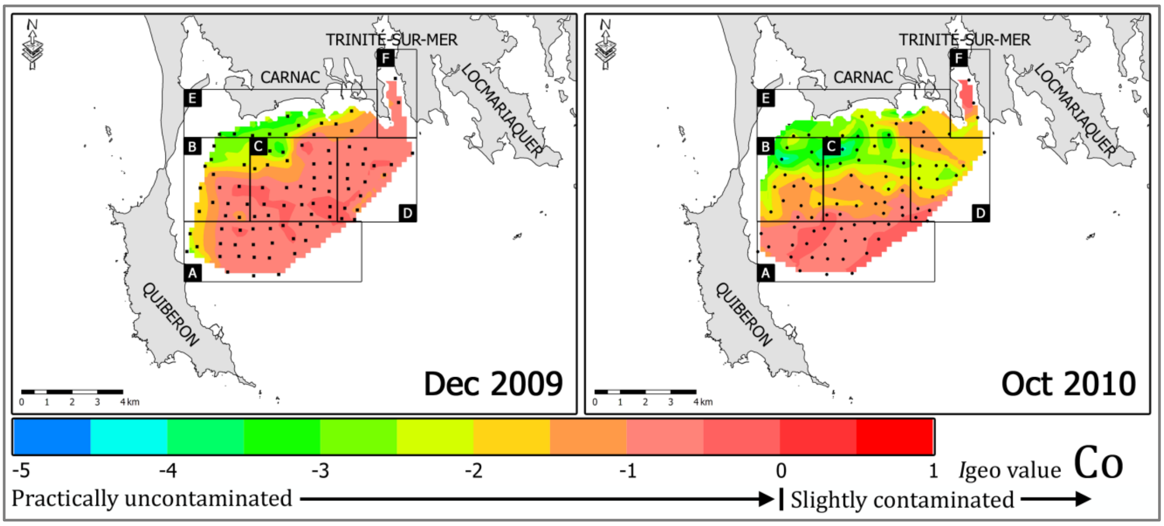

Figure 4–77. *Contamination category based on Igeo values for Co in Quiberon bay surficial sediments for both samplings.*

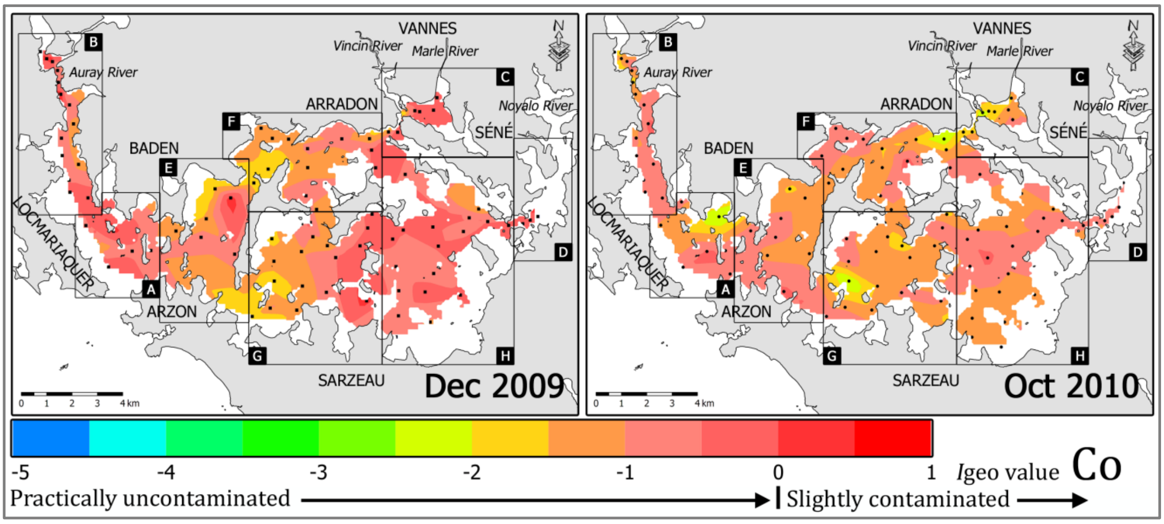

Figure 4–78. *Contamination category based on Igeo values for Co in gulf of Morbihan surficial sediments for both samplings.*

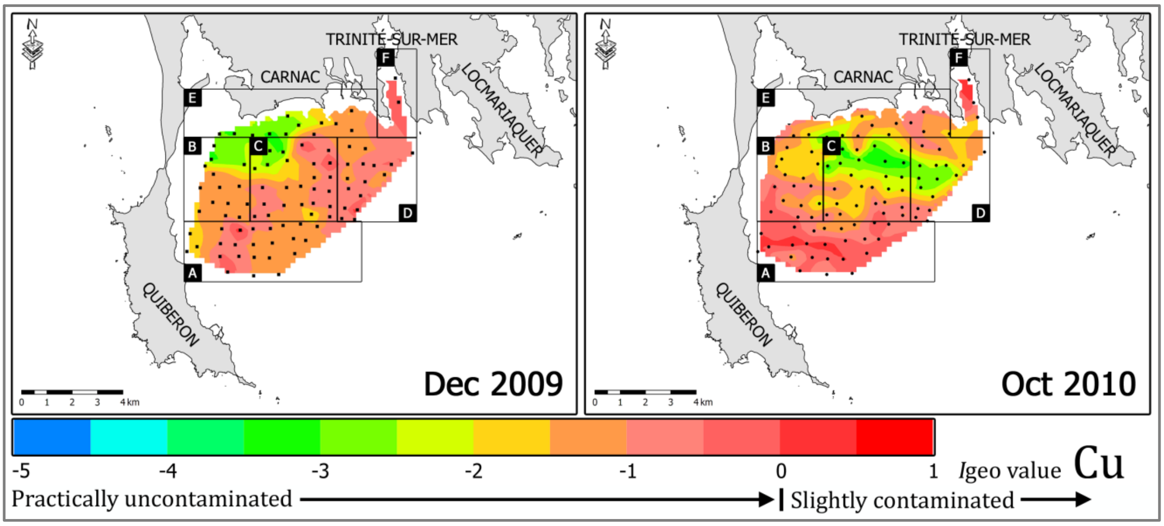

Figure 4–79. *Contamination category based on Igeo values for Cu in Quiberon bay surficial sediments for both samplings.*

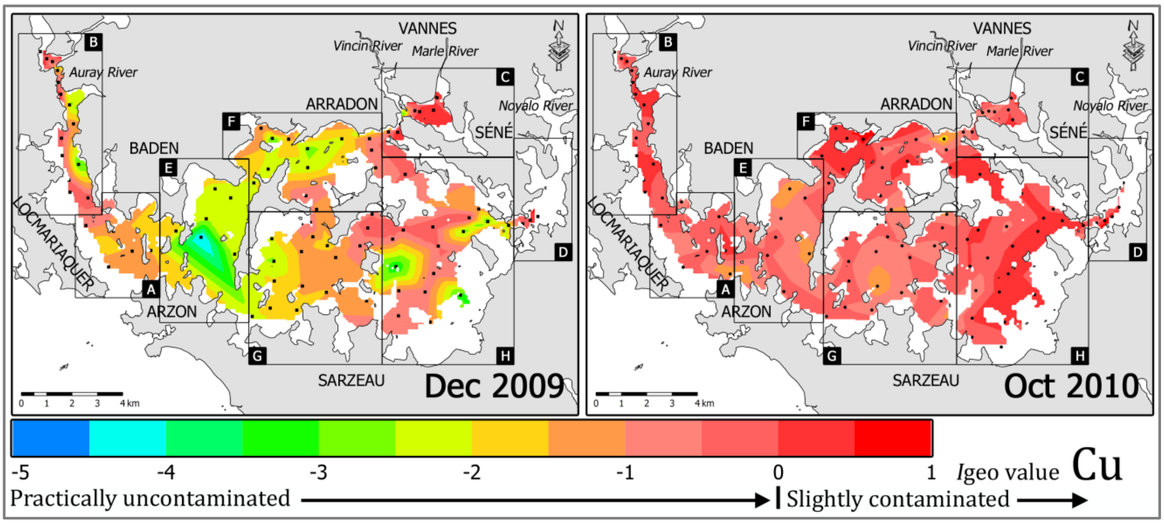

Figure 4–80. *Contamination category based on Igeo values for Cu in gulf of Morbihan surficial sediments for both samplings.*

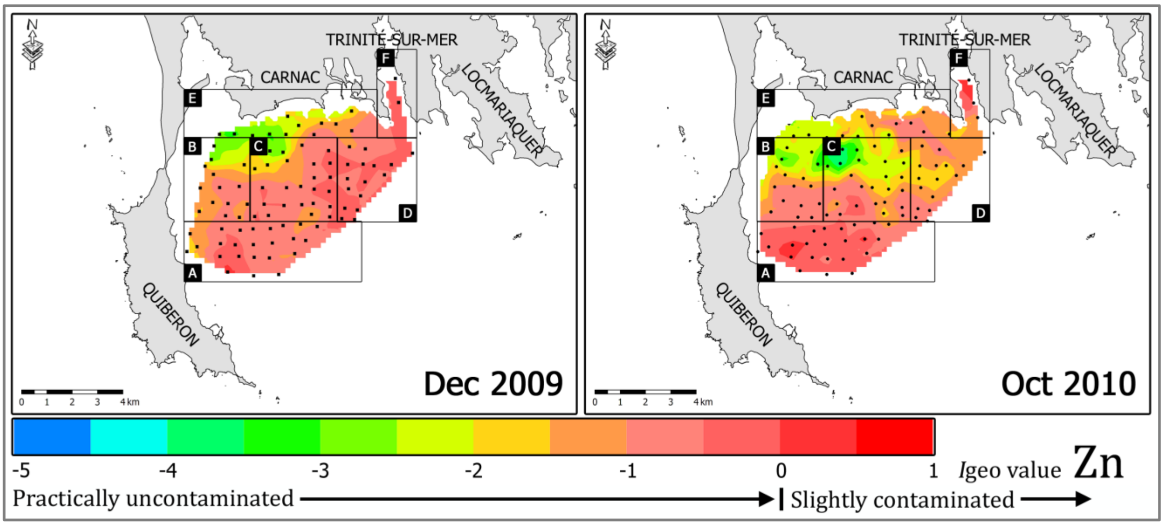

Figure 4–81. *Contamination category based on Igeo values for Zn in Quiberon bay surficial sediments for both samplings.*

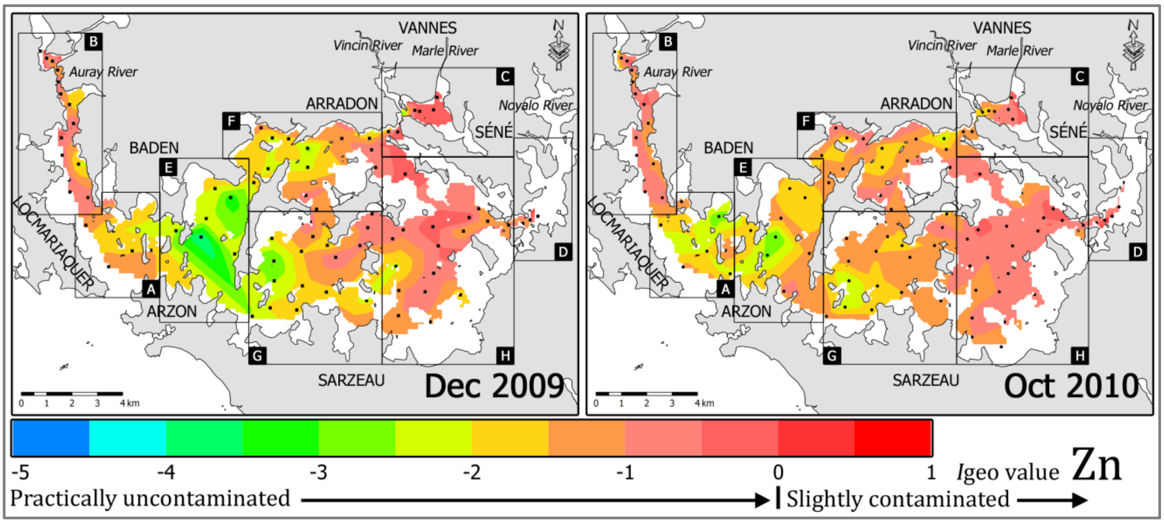

Figure 4–82. *Contamination category based on Igeo values for Zn in gulf of Morbihan surficial sediments for both samplings.*

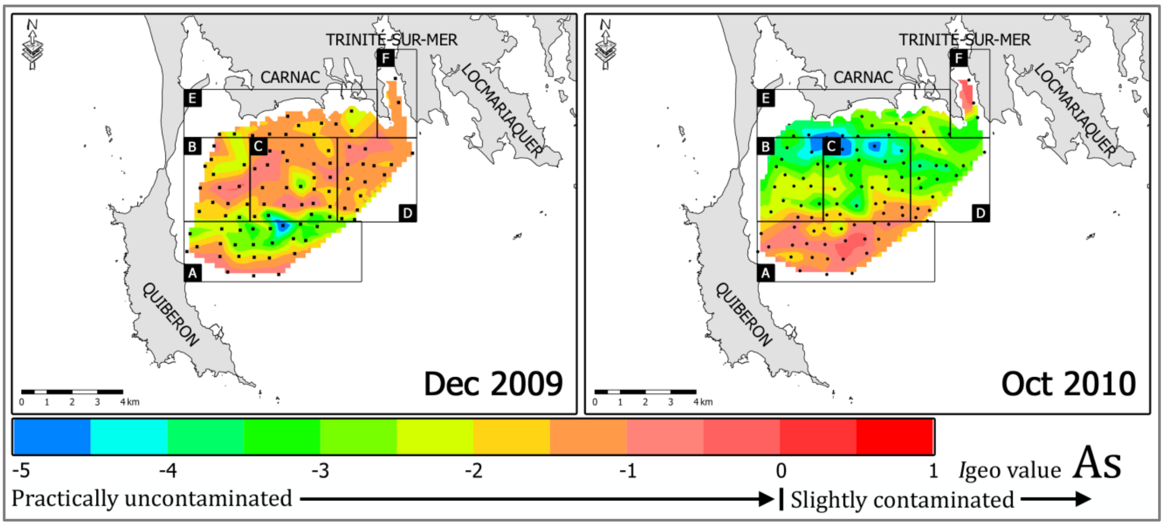

Figure 4–83. *Contamination category based on Igeo values for As in Quiberon bay surficial sediments for both samplings.*

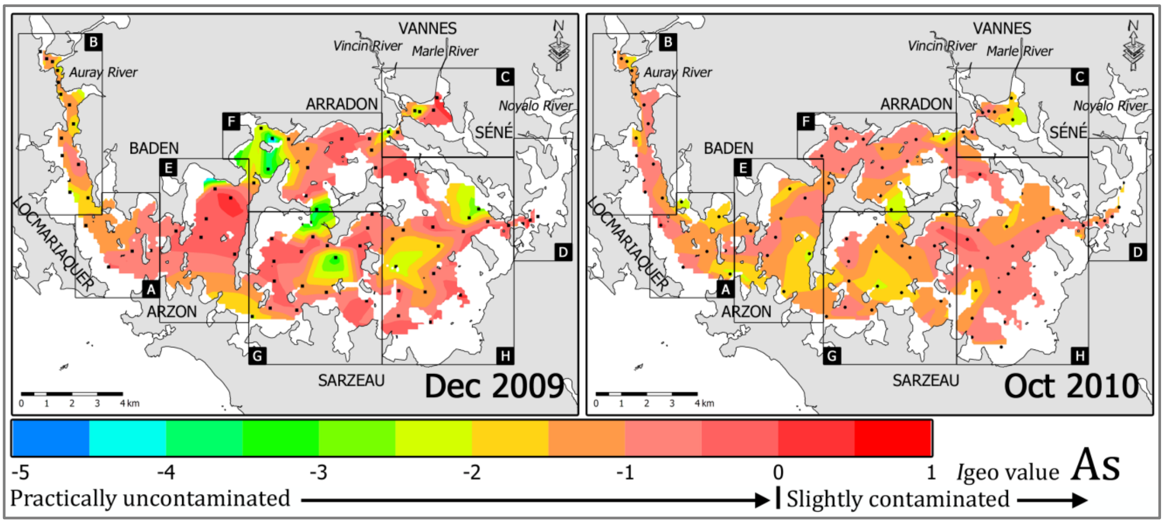

Figure 4–84. *Contamination category based on Igeo values for As in gulf of Morbihan surficial sediments for both samplings.*

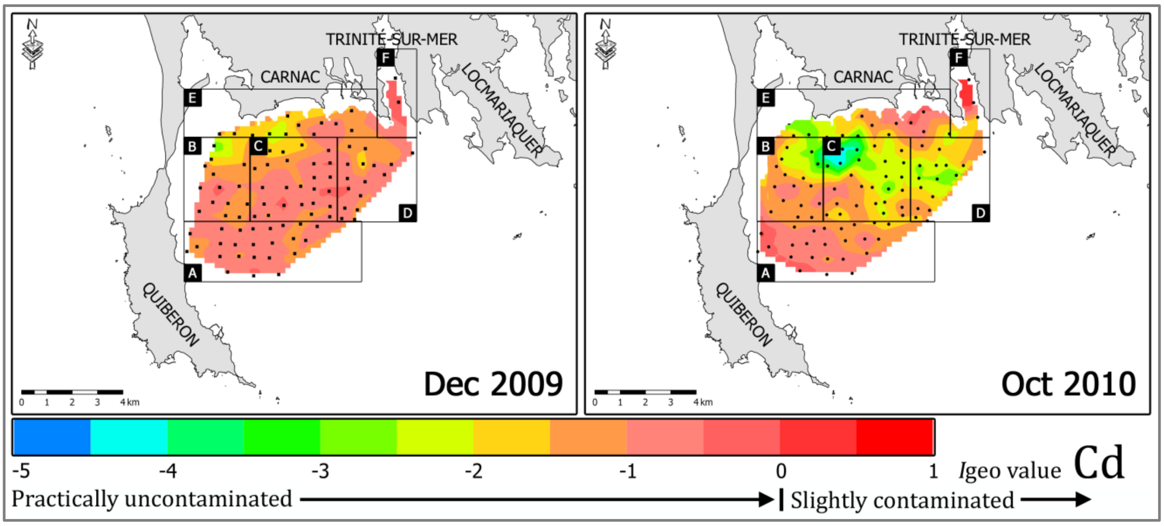

Figure 4–85. *Contamination category based on Igeo values for Cd in Quiberon bay surficial sediments for both samplings.*

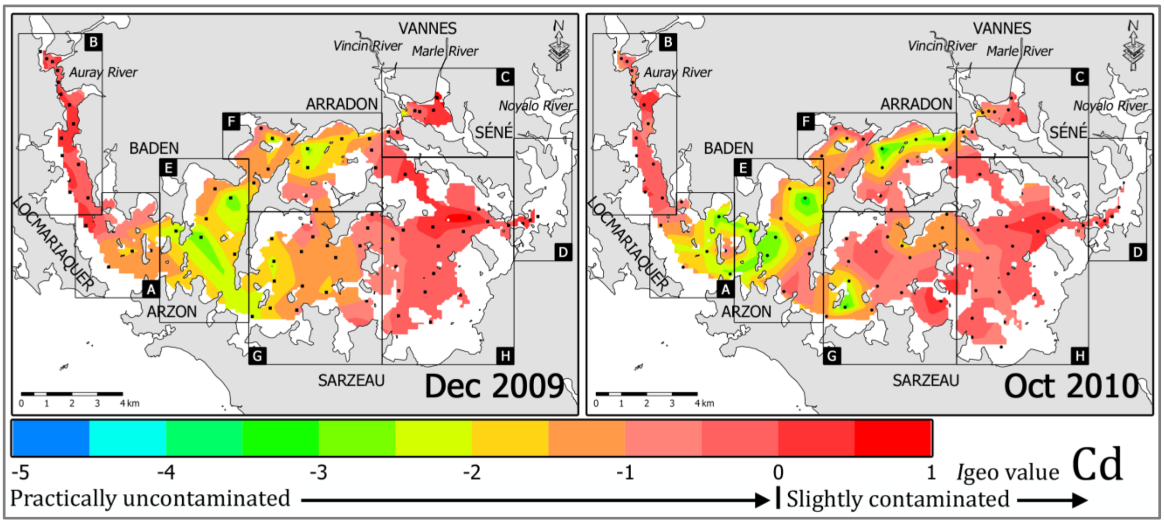

Figure 4–86. *Contamination category based on Igeo values for Cd in gulf of Morbihan surficial sediments for both samplings.*

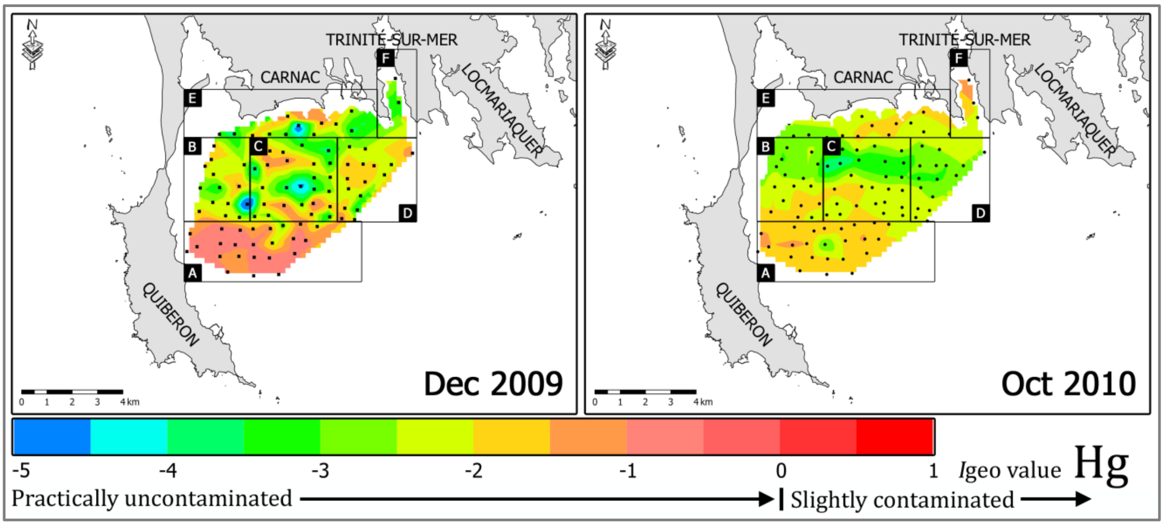

Figure 4–87. *Contamination category based on Igeo values for Hg in Quiberon bay surficial sediments for both samplings.*

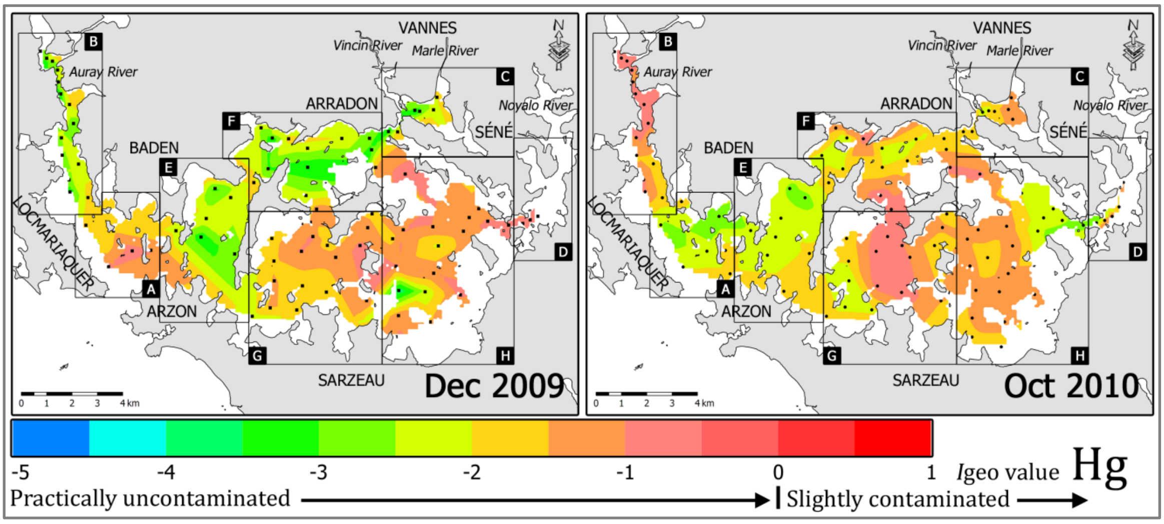

Figure 4–88. *Contamination category based on Igeo values for Hg in gulf of Morbihan surficial sediments for both samplings.*

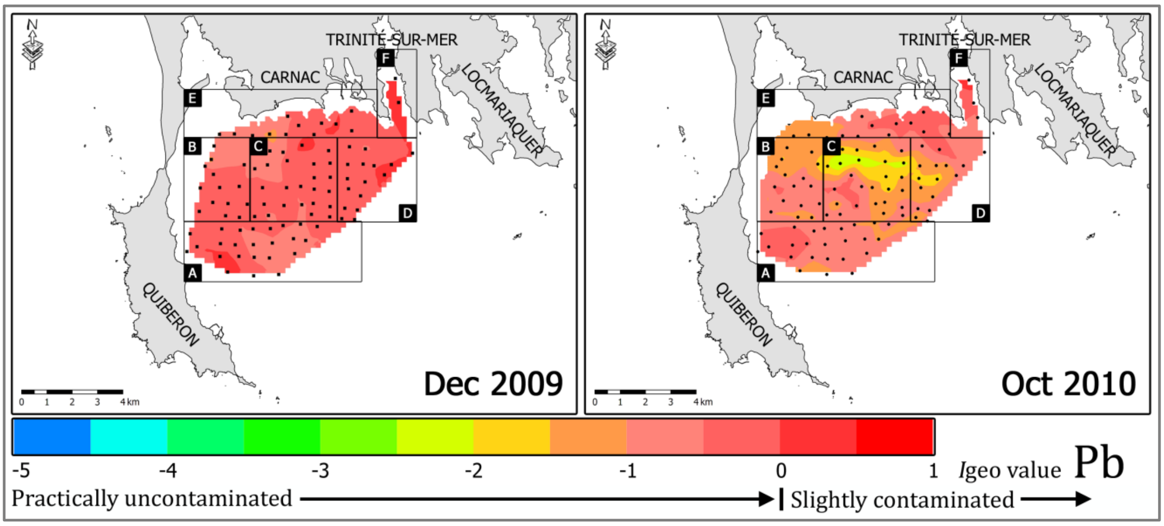

Figure 4–89. *Contamination category based on Igeo values for Pb in Quiberon bay surficial sediments for both samplings.*

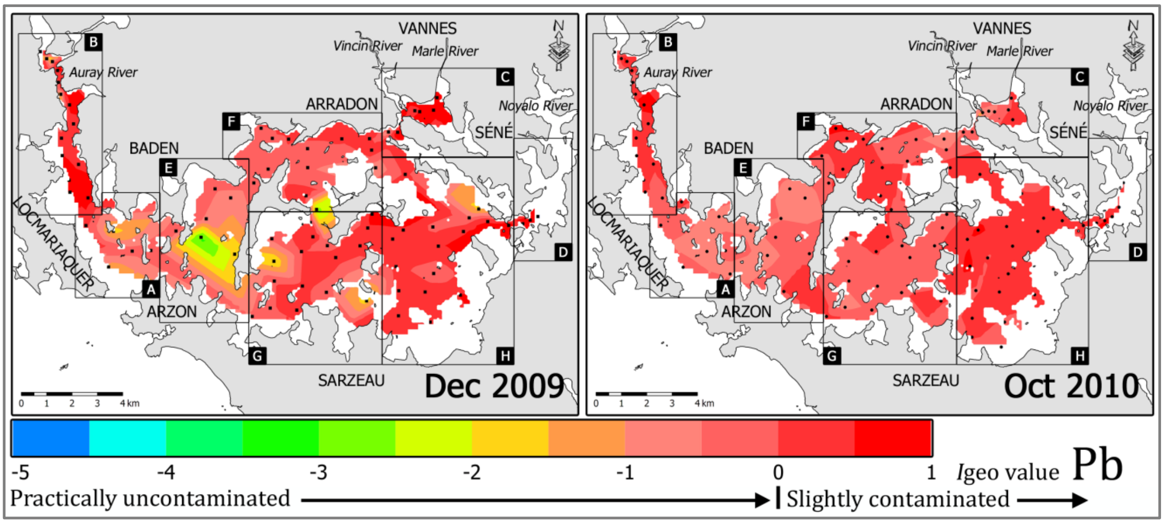

Figure 4–90. *Contamination category based on Igeo values for Pb in gulf of Morbihan surficial sediments for both samplings.*

4.6.3 Assessment 3 – Pollution load index

Tomlison *et al.* (1980) elaborated that the application of pollution load index (PLI) provides a simple way in assessing estuarine and coastal sediment quality. This assessment is a quick tool in order to compare the pollution status of different places (Karbassi *et al*., 2006). PLI represents the number of times by which the MTE concentrations in the sediment exceed the background concentration, and give a summative indication of the overall level of MTE toxicity in a particular sample or location (Priju and Narayana, 2007; Rabee *et al*., 2011). The PLI can provide some understanding to the public of the surrounding area about the quality of a component of their environment, and indicates the trend spatially and temporarily (Harikumar and Jisha, 2010). In addition, it also provides valuable information to the decision makers towards a better management on the pollution level of Quiberon bay and gulf of Morbihan region.

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 from the following relation:

$$Pollution\ load\ index = (CF_1 \times CF_2 \times CF_3 \times CF_4 \times CF_n)^{1/n}$$

where, n is the number of metals (10 in the present study) and CF is the contamination factor. The CF can be calculated from:

$$Contamination\ factor = \frac{Element\ concentration\ in\ the\ sediment}{Background\ value\ of\ the\ element}$$

The PLI value > 1 is categorized as polluted whereas <1 indicates no pollution at the sampling point (Nasr *et al*., 2006; Chakravarty and Patgiri, 2009; Seshan *et al*., 2010) (*Table 4–33*).

Table 4–33. *Sediment contamination categories based on PLI value*

Value	**Sediment quality**
PLI < 1	Low contamination factor
1 < PLI < 3	Moderate contamination factor
3 < PLI < 6	Considerable contamination factor
PLI > 6	High contamination factor

The strong correlation of PLI with TOC content (r = 0.766) indicates the MTEs accumulation ability of organic matter (*Figure 4–91*). Shokkovitz and Copeland (1981) and Saha *et al*. (2001) reviewed that the increased organic matters in the fine particles catalyze the MTEs scavenging ability of the sediment.

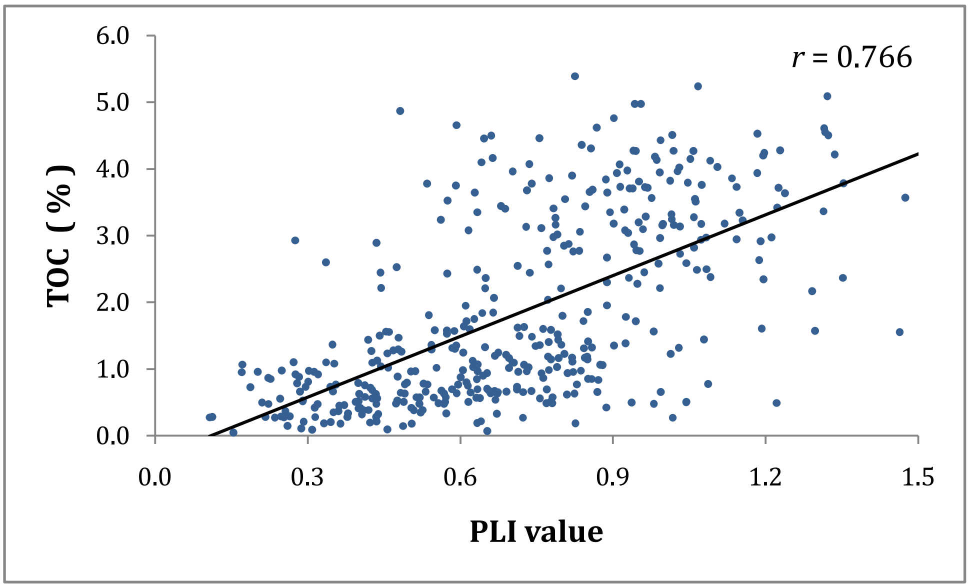

Figure 4–91. *Relationship between PLI and TOC contents in surficial sediments from Quiberon bay and gulf of Morbihan.*

PLI values of the analyzed surficial sediments were visualized by ArcGIS software and shown in *Figure 4–90* for Quiberon bay and *Figure 4–91* for gulf of Morbihan, which confirmed either Quiberon bay, or gulf of Morbihan is not seriously polluted with MTEs studied. PLI were found to be generally low (<1) in all the studied location in the Quiberon bay apart from Trinité–sur–Mer area. Compared with the above–mentioned for EF and *I*geo assessment, the eastern zone and rivers (Auray, Marle and Noyalo) zones also exhibit a PLI value above 0, therefore these areas can be classified as moderate contamination factor according to (Seshan *et al.*, 2010). The sequences of PLI value follow the decreasing order: zone F>A>D>B>C>E in Quiberon bay and zone D>H>B>C>G>F>E>A in gulf of Morbihan.

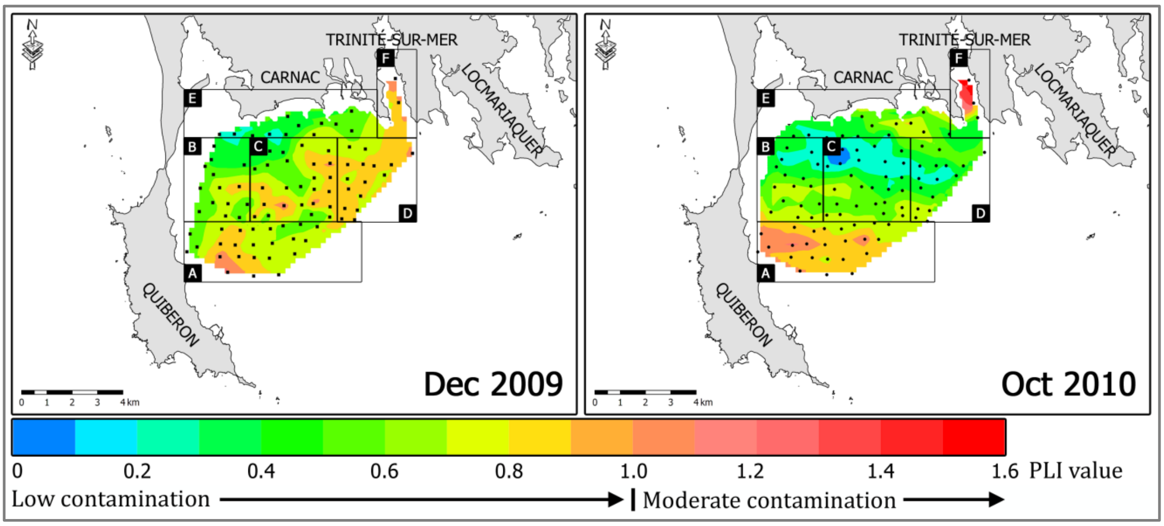

Figure 4–92. *Contamination category based on PLI values in Quiberon bay surficial sediments for both samplings.*

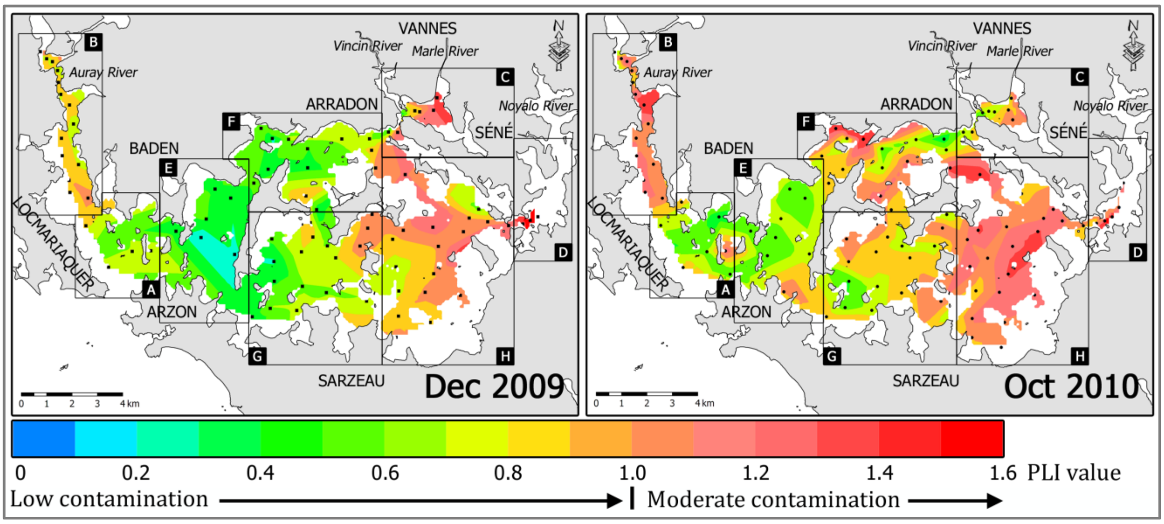

Figure 4–93. *Contamination category based on PLI values in gulf of Morbihan surficial sediments for both samplings.*

4.6.4 *Assessment 4 – Sediment toxicity and ecology risk indices: Sediment quality guidelines approach*

In recent decades different MTEs assessment indices applied to the coastal environments have been developed (Hakanson, 1980, Caeiro *et al.*, 2005; Luo *et al.*, 2010). Each one of these assessment aggregates the concentration of MTE contaminants and can be classified into three types, namely, (i) contamination indices: which compare the contaminants with clean and/or polluted stations measured in the study area or simply aggregate the MTE concentrations; (ii) background enrichment indices: which compare the results for the contaminants with different baseline or background levels, available in literature, that can be used for any study area; and (iii) ecological risk indices: which compare the results for the contaminants with sediment quality guidelines (SQGs).

Sediment contaminant chemistry has been correlated with measured biological effects to develop a several correlative–derived toxicity thresholds to the organisms. For example, organism growth, reproduction or community metrics has been correlated with measured concentrations of specific contaminants in the sediment (typically based on dry weight concentrations), to establish toxicity thresholds for that specific site and substance. SQGs derived using the correlative approach are then applied to sediment chemistry measurements from other sites to indicate possible toxicological risks associated with these sediments (McCauley *et al.*, 1984).

The original SQGs, which were compared with a reference or with background, provided little insight into the potential ecological impact of sediment contaminants; however, they did provide a base from which to evaluate SQGs. This is particularly important with MTEs contaminant, which may occur naturally in high concentrations in some areas of the world. The new generation of empirically based SQGs was developed relying on field sediment chemistry paired with the field or laboratory biological effects data (Burton, 2002). They are often based on frequency distributions and account for the impact of all chemicals present, but they do not establish cause and effect. These approaches have also been shown to be useful and predictive of biological effects in many marine and freshwater systems (Long *et al.*, 1998; Ingersoll *et al.*, 1996; Long *et al.*, 2000; MacDonald *et al.*, 2000)

SQGs are very useful to investigate the sediment contamination by comparing the MTEs concentration with the corresponding published guidelines. These guidelines evaluate the degree to which the sediment–associated chemical status might adversely affect biota organism especially benthic organisms and are designed to assist sediment assessors and managers responsible for the interpretation of sediment quality (Wenning and Ingersoll, 2002). They have been largely developed for marine waters (Long *et al.*, 1995) but a few have been specifically developed for estuarine waters (Chapman and Wang, 2001).

When using these summary indices, normalized to a reference value, substantial loss of information can occur during the conversion of multivariate data into single proportional indices, including spatial information. However, such indices have provided useful information in the past and continue to do so. They also provide a single and highly visual data presentation, which can be explained to and understood by non–scientists (Chapman, 1990).

In order to assess the sediment toxicity and ecological risk to benthic organisms for MTEs studied in Quiberon bay and gulf of Morbihan surficial sediments, two approaches were employed. The first approach was to compare the concentrations of MTE to SQGs promulgated by United State Environmental Protection Agency (USEPA) which reviewed by Giesy and Hoke (1990). This approach was used only to screen the contaminants of concern in aquatic ecosystems. On the other hand, the second approach, was to apply two set of SQGs developed for marine and estuarine ecosystems (Long and McDonald, 1998) to assess the ecotoxicology sense of MTEs concentration in sediments, namely, (a) the effect range low (ERL)/effect range median (ERM) and (b) the threshold effect level (TEL)/probable effect level (PEL) values.

4.6.4.1 Sediment contamination status according to sediment quality guidelines by USEPA

Based on the SQGs proposed by USEPA obtained from Giesy and Hoke (1990), sediment contaminations are defined into three classes, non–polluted, moderately polluted and heavily polluted (*Table 4–34*) and this SQGs classification do not consider the natural background or multiple elements (Luo *et al.*, 2010). So far, no SQGs data were found for Mn, Fe and Co. By comparing the mean concentrations of MTEs in Quiberon bay and gulf of Morbihan surficial sediments with the SQGs, sediments in both areas were classified as non–polluted for Zn, Hg and Pb, to moderately polluted by Cr, Cu, Cd and As where these metals exceed the SQGs. Surficial sediments from Trinité–sur–Mer zone in Quiberon bay, Auray, Marle and Noyalo river zones and eastern zone in gulf of Morbihan catchment were moderately enriched with these metals. However, no surficial sediments from both sampling areas were classified as heavily polluted with the MTEs studied according to SQGs.

Table 4–34. *Classification of Quiberon bay sediment samples based on the proposed SQGs.*

	Cr	**Cu**	**Zn**	**As**	**Cd**	**Hg**	**Pb**
Quiberon bay							
Mean	24.6	14.4	40.7	2.38	0.07	0.022	15.1
Min	2.94	2.56	4.60	0.12	0.01	0.001	3.61
Max	68.9	40.9	98.9	6.80	0.19	0.060	28.0
Gulf of Morbihan							
Mean	37.4	21.9	38.4	3.97	0.11	0.028	23.8
Min	5.43	1.20	4.78	0.19	0.01	0.006	2.43
Max	112	48.5	89.9	9.16	0.30	0.060	42.7
SQG							
Non–polluted	<25	<25	<90	<3	–	≤1.0	<40
Moderately polluted	25–75	25–50	90–200	3–8	–	–	40–60
Heavily polluted	>75	>50	>200	>8	>6	>1.0	>60

* No data on Mn, Fe and Co

4.6.4.2 *Ecotoxicology significance of metallic trace elements concentration by TEL/PEL and ERL/ERM*

Concentration of MTEs was evaluated in a screening–level ecological risk assessment, by comparing to another numerical SQGs, namely threshold effect level (TEL)/probable effect level (PEL) and effect range low (ERL)/effect range medium (ERM) which these SQGs have been reviewed by Long *et al.* (1990) and Long and McDonald (1998). Low range values (i.e. ERL and TEL) are the concentration less than which adverse effects upon sediment dwelling fauna would not be expected. In contrast, the ERM and PEL represent chemical concentrations above which adverse effects are likely to occur in the aquatic ecosystem (Long and MacDonald, 1998).

The incidence of toxicity was determined among samples in which none of the substance equaled or exceeded the ERL concentrations, in which one or increasing number of substances exceeded ERL concentrations, but none exceeded any ERM; and in which one or increasing number of substances exceeded ERM concentrations (Pekey *et al.*, 2004; Zheng *et al.*, 2008). The same approach was used to evaluate the predictive ability of the TELs/PELs (Long *et al.*, 1998). It has been suggested that the ERMs and PELs are better at predicting toxicity than are the ERLs and TELs (Long *et al.*, 1998). The U.S. National Oceanic and Atmospheric Administration (NOAA) guidelines provide two values for each chemical, classifying the sediment either rarely (<ERL), occasionally (≥ERL and <ERM) or frequently (≥ERM) associated with adverse biological effects (Birch and Taylor, 2006; Christophoridis *et al.*, 2009).

The SQG values for MTEs studied in surficial sediments from the Quiberon bay and gulf of Morbihan and the classification of the sediments based on these guidelines are shown in *Table 4–35* and *Table 4–36*. The results of classifying sediments based on the SQGs suggest that all MTEs in the sediments would rarely be expected to cause adverse effects on biota. Iron concentration never exceeded ERM or TEL values, 28 % in the sediment samples from any of the site, thus Fe was considered to be an unlikely candidate for posing a toxic risk to the aquatic organism (Roger *et al.*, 2002).

Table 4–35. *Classification of Quiberon bay sediment samples based on the proposed SQGs.*

	SQGs (µg g^{-1})				**Percentage of the samples exceeding SQGs (%)**			
	ERL	**ERM**	**TEL**	**PEL**	**ERL**	**ERL–ERM**	**TEL**	**TEL–PEL**
Cr	81	370	52.3	160.4	100	0	97	3
Mn	*n.m.*	360	*n.m.*	*n.m.*	62	38		
Fe	*n.m.*	28,000	*n.m.*	*n.m.*	100			
Co	*n.m.*	10	50	*n.m.*	52	48	100	
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
As	8.2	70	7.2	41.6	100	0	100	0
Hg	0.15	0.71	0.17	0.49	100	0	100	0

**n.m. : Not mentioned*

Table 4–36. *Classification of gulf of Morbihan sediment samples based on the proposed SQGs.*

	SQGs (µg g^{-1})				**Percentage of the samples exceeding SQGs (%)**			
	ERL	**ERM**	**TEL**	**PEL**	**ERL**	**ERL–ERM**	**TEL**	**TEL–PEL**
Cr	81	370	52.3	160.4	95.7	4.1	79.3	20.7
Mn	*n.m.*	360	*n.m.*	*n.m.*	57.2	42.8		
Fe	*n.m.*	28,000	*n.m.*	*n.m.*	100	0		
Co	*n.m.*	10	50	*n.m.*	41.5	58.5		
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
As	8.2	70	7.2	41.6	99.1	9	100	0
Hg	0.15	0.71	0.17	0.49	100	0	100	0

**n.m. : Not mentioned*

Majority MTEs studied did not surpass the corresponding ERL and TEL guideline values and therefore does not represent a danger to marine organisms that living in Quiberon bay and gulf of Morbihan. Only a small percentage of surficial sediments would be classified as possibly presenting an occasional threat to organism due to concentrations of Cr, Cu and As. However, Cr, Cu and Pb in a certain location exceeded the TEL value particularly from the gulf of Morbihan surficial sediments. Thus, at concentration greater than the TEL, toxic effect from long–term exposure to these MTEs would be predicted to occur in the station sampled.

In order to estimate the effect of a multiple contamination on metallic trace elements, mean–ERM–quotient (M–ERM–Q) were calculated in each surficial sediment in the Quiberon bay and gulf of Morbihan according to Long *et al*. (1998), Larrose *et al*. (2010) and Tessier *et al*. (2011) as follows:

$$M - ERM - Q = \frac{\sum_{i=1}^{n}(C_i / ERM_i)}{n}$$

where C_i is the surficial sediment concentrations of element (i), $ERM_i$is the ERM for element (i) and n is the number of elements, e.g. ten metallic trace elements in this study. Long *et al*. (1998) 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 to be 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 ten MTEs studied (Cr, Mn, Fe, Co, Cu, Zn, As, Cd, Hg and Pb), value of the m–ERM–Q were calculated and the obtained distribution visualized by ArcGIS software in Quiberon bay and gulf of Morbihan are presented in *Figure 4–94* and *Figure 4–95*.

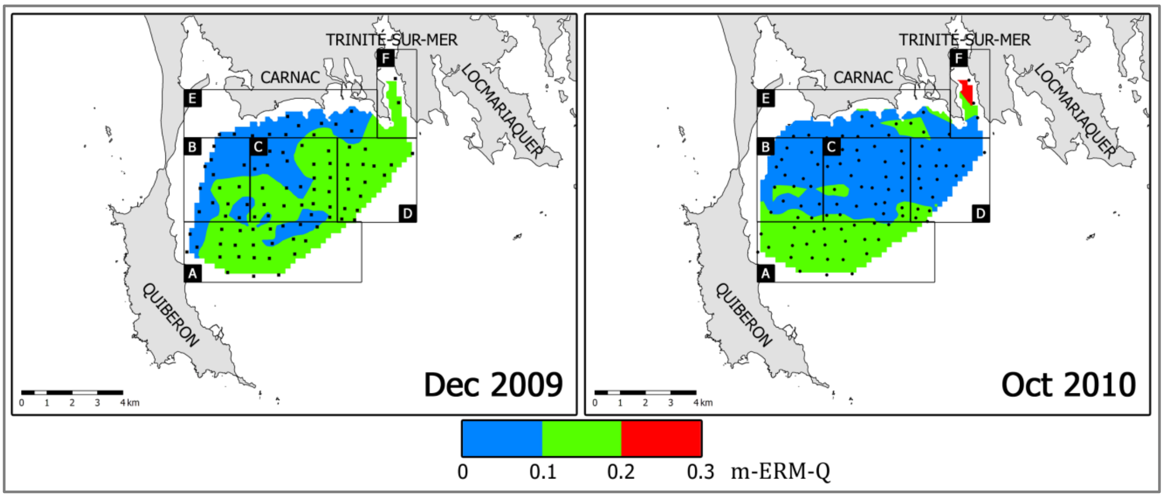

Figure 4–94. *Contamination category based on m–ERM–Q values in gulf of Morbihan surficial sediments for both samplings.*

The m–ERM–Q distribution pattern in Quiberon bay surficial sediments showed that inner the bay zone presented values lower than 0.1, which intended a 9 % probability of being toxic to the benthic organisms in that area for both sampling periods, Dec 2009 and Oct 2010. In outer bay, the m–ERM–Q values slightly exceed 0.1 but not more than 0.2 indicate that this zone is both fall between 9 % and 21 % probability of being toxic to benthic organisms. However, in Trinité–sur–Mer area especially during Oct 2010 sampling, the m–ERM–Q ranged between 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.* (1998) classification.

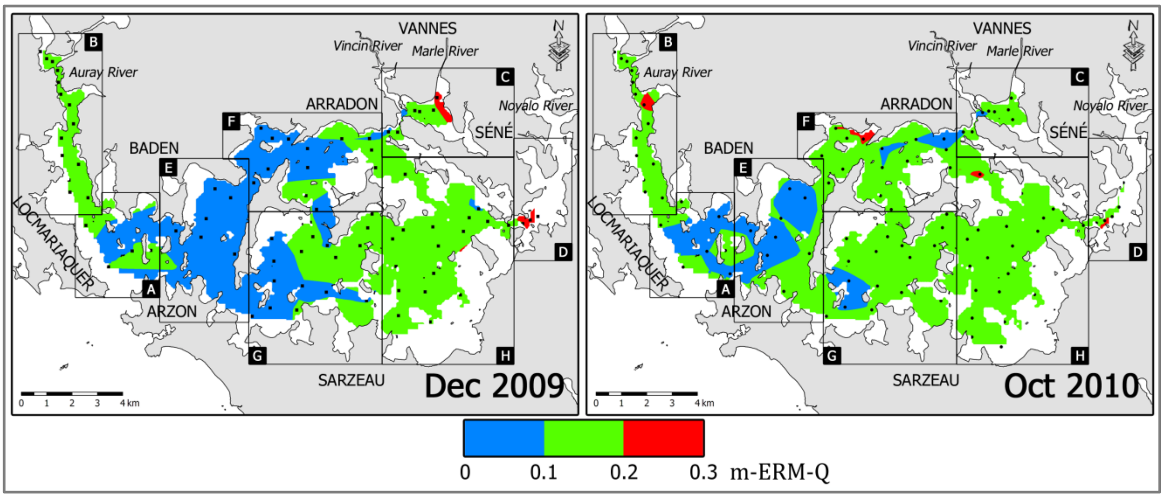

Figure 4–95. *Contamination category based on PLI values in gulf of Morbihan surficial sediments for both samplings.*

Meanwhile, in the gulf of Morbihan sediments, the m–ERM–Q values at the western zone of the gulf were lower than 0.1 and therefore this zone can be categorized as 9 % probability of being toxic to the benthic organisms. Toward the inner gulf of eastern zone, the m–ERM–Q values were increased; however, the values do not exceed the 21 % probability of toxicity to the benthic organisms, 0.2. Generally, some sampling location located at the rivers zone (Auray, Marle and Noyalo) have 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 due to re–suspension and remobilization processes in aquatic ecosystem (Zoumis *et al*., 2001; Tankere–Muller *et al*., 2007; Kalnejais *et al*., 2010)

4.7 Sedimentation rate in core sediments from gulf of Morbihan

Radionuclide such as ^{210}Pb dating is an important tool widely used by researchers to assess the spatial variability in recent accumulation rate on a ~100 years time scale (Chague–Goff *et al.*, 2000; van der Bergh *et al.*, 2003; Boer *et al.*, 2006) in coastal environments such as estuary, mangrove and lagoon ecosystem. ^{210}Pb with a half life of 22.3 years is produced by the decay of atmospheric ^{222}Rn and is removed from the atmosphere as fallout. In the marine environment, ^{210}Pb rapidly adheres to the surface of sediment particles, to become incorporated into accumulating sediments (van der Bergh *et al.*, 2007). As a result, sedimentation rate can be estimated from the decrease in $^{210}Pb_{ex}$ activity with depth in the core sediment due to radionuclide decay. Assuming if there are no sediments mixing activity due to bioturbation by benthic organisms or physical disturbance by overlying water movements such as tides and bottom currents, the data points for the activity of $^{210}Pb_{ex}$ versus the core sediment depth measured in terms of distance or cumulative weight, fit straight lines whose slopes yield the appropriate sedimentation rates (Koide *et al.*, 1972; Koide *et al.*, 1973; Miralles *et al.*, 2005; Huh *et al.*, 2006).

$^{210}Pb_{ex}$ inventory tends to be higher in deep–water sites because the higher standing stock of ^{226}Ra results in higher ^{210}Pb flux to the sea bottom. It has also been shown that resuspension may cause canyon and slope sediments have ^{210}Pb activities that are two to seven times higher than those of shelf sediments (Carpenter *et al.*, 1981). High sedimentation rate is commonly linked to higher ^{210}Pb inventory, though this is not necessarily true where sedimentation outpaces the rate of ^{210}Pb scavenging by particles (DeGeest *et al.*, 2008).

Bulk densities of the core sediments from the gulf of Morbihan were not adequately measured, hence in this study we compared the sedimentation rate on a relative basis, without accounting for possible sediment compaction (White *et al.*, 2002). Most $^{210}Pb_{ex}$ profiles were uniform or depressed in the top layer (<20 cm), which may be the result of sediments bioturbation and sediments mixing activity (Nittrouer *et al.*, 1979), or the result of inadequate sediment sampling due to plant roots and organics (White *et al.*, 2002). Below the root zone, ~20 cm, all core sediments collected in this study appear to be homogeneous and the profiles of $^{210}Pb_{ex}$ activities were found to decrease with the core sediment depth.

On the other hand, $^{210}Pb_{ex}$ inventory is commonly higher in fine grain sediments or muddy sediments. Consequently, previous researchers reviewed that the cores appeared with the silty character of the sediment is to be suitable for ^{210}Pb analysis (Carpenter *et al.*, 1981; Smith *et al.*, 1993; van Santen *et al.*, 2007). The activities of ^{210}Pb were extremely high which aligned with respect to the high organic carbon contents and percentage of clay in core sediments due to the higher scavenging efficiency by clay sediments (Lewis *et al.*, 2002). Smaller grain sediments result in a higher specific surface area and thus in a higher potential to capture ^{210}Pb fallout (Eisma *et al.*, 1989). Organic carbon and clay content may control ^{210}Pb activities since ^{210}Pb is tendency to associate smaller grains due to its higher specific surface area and thus in a higher potential to capture ^{210}Pb fallout (Eisma *et al.*, 1989) compared to coarse sediment and indicating the affinity of ^{210}Pb with organic carbon content for incorporation into the sediment (Mahmood *et al.*, 2011). This also may conclude that organic carbon contents were the main geochemical carrier of this radionuclide to the sample core location.

4.7.1 Factors controlling sedimentation rate

The rates of sedimentation are controlled largely by the hydrological, morphological and sedimentological characteristics that define the differing fluvial settings. Prior to human alterations that markedly decreased sedimentation and increased submergence, the flooding frequency and deposition rate in the gulf environments were controlled by average annual rainfall (White *et al.*, 2002). Strong precipitation during the winter season and high river (Auray, Marle and Noyalo rivers) discharges transport huge amounts of terrigenous matter to the ocean (Munoz *et al.*, 2004).

Thus, when the sediments from Auray, Vincin, Marle and Noyalo rivers enter the gulf, the river flow is opposed by the tide and tidal current. Hence, the heavier suspended sediments have the possibility to settle down at the bottom. Therefore, a large part of the suspended sediment will never make it to the Biscay bay and Atlantic ocean but accumulate in the gulf. Consequently, it may traps for sediment and sedimentation rates in close environment will higher due to the major role in the transport sediment from rivers to open sea. These higher activities could be associated with particle advection from shallower depths where these sediments are easily re–suspended which these articles were enriched in ^{210}Pb during repeated resuspension events (Radakovitch and Heussner, 1999; Smoak *et al.*, 2000; Lewis *et al.*, 2002).

In addition, several factors may influence the $^{210}Pb_{ex}$ such as sediment texture, atmospheric deposition rate of ^{210}Pb, sediment mixing process and sediment resuspension. It is well known that rates of sea–level rise can partly control rates of sediment accretion in coastal environments (McCaffrey and Thomson, 1980). However, other sources of sediment contribute, such as natural erosion hillside, effluent discharge from urban sewage and storm–water drain outfalls, sediment losses from dredging and dumping operation, reclamation works and illegal dumping (Tanner *et al*., 2000; Ip *et al*., 2004). Different sampling location in the gulf may be subjected to specific factors, especially within the mariculture area, typhoon shelters zone and near drainage outfalls zone. The main factors influencing them were the sediment density, the presence of the biotic component, seasonality, frequency of flood events, suspended matter concentration and short–term dynamics (Ciavola *et al.*, 2002; Amos *et al.*, 2004; Andersen *et al.*, 2006).

Fuller *et al.* (1999) and Alvarez–Iglesias *et al*. (2007) discussed that the effect of bioturbation by benthic organisms are minimal in areas where sediment accumulation is fast, i.e. about 5 mm/year. Furthermore, benthic organisms may dilute the $^{210}Pb_{ex}$ activity by mixing the surface sediments with older and deeper sediment (Rutgers van der Loeff and Boudreau, 1997). The core sediments that have low excess ^{210}Pb activities indicate that the sediments from the area are being deeply mixed by burrowing organism (Lewis *et al.*, 2002) such as crabs, worms, crustaceans, bivalves and gastropods. Radakovitch and Heussner (1999), in their study at Biscay bay, suggested that the biological activity in the axis of the canyons could be responsible for the ^{210}Pb redistribution. They attributed the differences within core sediments from the same stations to small scale variability in the mixing process.

Estuarine organisms influence both the settling and resuspension of sediments. Seagrass beds reduce current velocities and dampen wave action near the sediment bed. Filter feeders such as oysters, ingest a considerable amount of fine suspended particulate matter, both organic and mineral, which otherwise remain in suspension (Ahn, 1993). They eject their waste in the form of pellets either in the faeces or pseudofeces process, which will be settled to the bottom sediment (Hayakawa *et al.*, 2001; Pietros and Rice, 2003). This oyster feeding behavior is contrary to our finding where the sedimentation rate between core G (0.14 cm/y), core J (0.14 cm/y) and core E (0.12 cm/y) were higher compared to other sites (0.10 to 0.11 cm/y) due to the location of core sediments sampled located within the mariculture farms.

From the sedimentation rates, 210Pb dating technique was used to determine the sediments age in the core sediments. Sediment age can be determined by dividing the sediment depth with the sedimentation rate values. The lower sedimentation rate indicates the older age of the sediments. Assuming that the sedimentation rate values were accurate, this implies that the sediment in the upper 50 cm at the gulf of Morbihan sediment were deposited during the past ranged from 384 (year 1626) to 509 (year 1501) years. However, if based on the mean sedimentation rates, 0.12 cm/year, sediments in the gulf of Morbihan had been deposited almost 434 year (year 1576) in the upper 50 cm.

4.7.2 Comparison with sedimentation rates in other continental shelves from European and Asian regions

In the last 20 years, there have been numerous studies on sedimentation processes on the continental margins particularly from European and Asian regions. The comparisons were shown in *Table 4–37* and the geographical location in *Figure 4–96*. Estimated average sedimentation rates for gulf of Morbihan is 0.12 cm/year, and this sedimentation is lower with the negligible values, by comparison with other region that have a similar ecosystem in France such as Seine estuary (0.68 cm/y), Gironde estuary (0.1–0.56 cm/y), Rhône estuary (0.15–0.63), and gulf of Lions (0.65 cm/y). However, our sedimentation rate values were comparable with study on gulf of Venice, Italy (0.11 cm/year), Basque region, Spain (0.13 cm/y), Arabian gulf (0.15 cm/y) and Kuala Selangor, Malaysia (0.10–0.20 cm/year). However, our sedimentation rate was slightly higher compared to Gouleau *et al*. (2000) study from Montportail–Brouage intertidal mudflat located at the Marennen Oléron bay, 0.07 cm/y. Generally, the pattern of sedimentation rates can be summarized as: open sea < close environment (lagoon and gulf) < estuary (or tidal mudflat).

Table 4–37. *Comparison of sedimentation rate in core sediment with other studies reported from European and Asian regions.*

Continental shelf	**Sedimentation rate (cm/y)**	**Reference**
Gulf of Morbihan	0.12 (0.10–0.14)	This study
European region		
Marennen Oléron bay	0.07	Goueau *et al*., 2000
La Grande Vasière, Biscay bay, France	0.22	Dubrulle *et al*., 2007
Seine estuary, France	0.68	Frouin *et al*., 2007
Gironde estuary, France	0.1–0.56	Lesueur *et al*., 2001
Gulf of Lion, France	0.65	Miralles *et al*., 2005
Rhône estuary, France	0.15–0.63	Zuo *et al*., 1991
Basque, Spain	0.13	Jouanneau *et al*., 2008
Palmones estuary, Spain	0.7	Rubio *et al*., 2003
Ria de Vigo, Spain	0.6	Alvarez–Iglesias *et al*;, 2007
Ebro, Spain	0.25	Diaz *et al*., 1996
North Portugal	0.16–0.55	Carvalho and Ramos, 1990
Gulf of Venice, Italy	0.11	Serandrei–Barbero *et al*., 2006
Humber estuary, UK	0.4	Lee and Cundy, 2001
Asian region		
Arabian gulf	0.15	Al–Ghadban and Abdali, 1998
Thane Creek, India	0.17–0.92	Jha *et al*., 1999
East China Sea, China	0.46	Huh and Chen, 1998
Okinawa Trough, China	0.023	Xiong *et al*., 2005
Jinhae bay, South Korea	0.4	Park *et al*., 1995
Sagami bay, Japan	0.06–0.14	Kato *et al*., 2003
West Malaysia coast	0.24–0.48	Wan Mahmood *et al*., 2011
Kuala Selangor, Malaysia	0.10–0.20	Choong *et al*., 2007

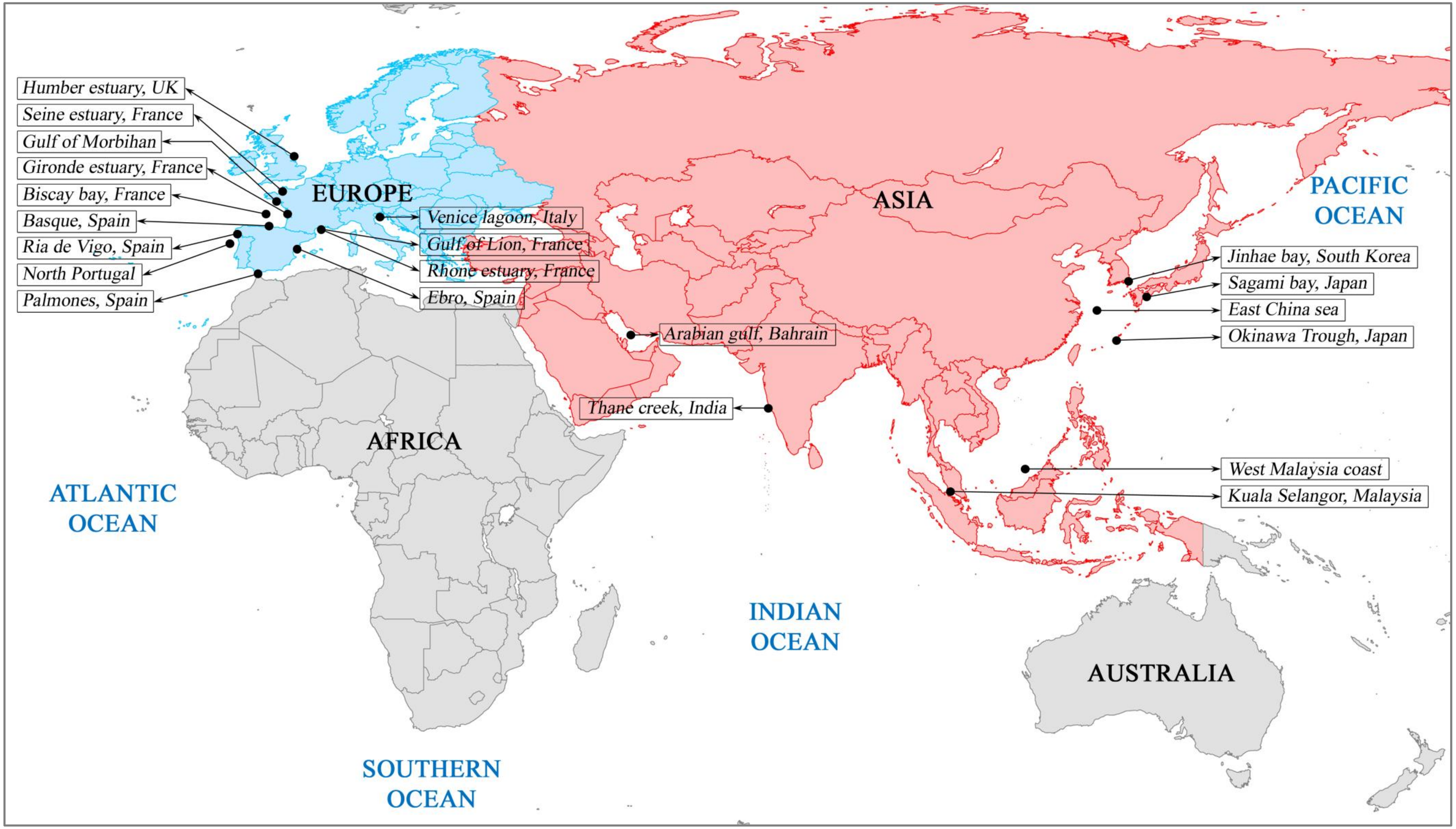

Figure 4–96. *Comparison of sedimentation rate in core sediments with other studies reported from European and Asian regions.*

4.8 Concentration of metallic trace elements in oysters and its risk assessment

4.8.1 Evaluation of oysters quality by pollution load index evaluation

The Tomlinson is claimed to be easily and quickly understood by unskilled personal in order to compare the pollution status of different places. The pollution load index (PLI) of Tomlinson (Tomlinson *et al*., 1980) is obtained as concentration factors (CF) of the contents for each metallic trace element (MTE) in the oyster. This CF is the quotient obtained by dividing the concentration of each MTE between the minimal concentrations detected or that element according to published baseline concentration data (Angulo, 1996). *Table 4–34* shows the baseline concentration of copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb), arsenic (As) and mercury (Hg) for the European region in PLI calculation. Once calculated the CF for each MTE in each location, the PLI of the location are calculated by obtaining the n–root from the n–CFs that were obtained for all the MTEs.

Table 4–38. *Baseline concentration of metallic trace elements in mollusk species from European region.*

MTEs	Concentration (mg kg^{-1} *dw.*)
Cu	0.06
Zn	13.9
Cd	0.10
Pb	0.13
As	0.10
Hg	0.02

The PLI value of oyster samples from the Quiberon bay and gulf of Morbihan are shown in *Table 4–39*. According to Chapman (1995) and Angulo (1996), a PLI < 50 indicates that drastic rectification measures are not needed and no immediate action is required. A PLI ≥ 50 indicates a more monitoring program is required to study the area. The key PLI value that indicates extreme pollution is ≥ 100 and an immediate intervention to ameliorate the pollution. Oyster samples from all sampling areas have a relatively low PLI values, therefore no action is necessary to be taken to monitor the quality of the oyster in Quiberon bay and gulf of Morbihan.

Table 4–39. *PLI values for oyster samples in Quiberon bay and gulf of Morbihan.*

Sample ID	Species	Min – Max	PLI value
Q1	*C. gigas*	1.18 – 5.28	2.85
Q2	*C. gigas*	1.46 – 4.04	2.90
Q3	*C. gigas*	1.34 – 6.86	5.48
Q4	*C. gigas*	1.27 – 4.97	3.45
Q5	*O. edulis*	2.24 – 4.09	3.00
M1	*C. gigas*	2.34 – 5.01	3.59
M2	*C. gigas*	2.50 – 10.1	5.21
M3	*C. gigas*	1.39 – 8.16	5.08
M4	*C. gigas*	3.16 – 11.3	6.37
M5	*C. gigas*	3.61 – 13.5	7.22

4.8.2 Factors controlling metallic trace elements concentration in oysters

Aside from species, body size of oyster is one of the most important factors that affect the metallic trace elements (MTE) accumulation rates in their tissue (Meyer *et al.*, 1998). The existence of size–dependent MTEs accumulation by aquatic biota such as bivalves and mollusks have been documented by several investigators (Swaileh and Adelung, 1994; Hamed and Emara, 2006; Sidoumou *et al.*, 2006), although the information reported for *C. gigas* and *O. edulis* is limited in South Brittany waters especially from the Quiberon bay and gulf of Morbihan. *Figure 4–97* shows the relationship between MTE contents and oyster size (in this case, length of oyster shell was used). Generally, the content of all studied MTEs were found to significantly increase with the shell length.

The correlation coefficients and slopes between MTEs and shell length were Cu (r = 0.329), Zn (r = 0.421), Cd (r = 0.193), Pb (r = 0.113), As (r = 0.408) and Hg (r = 0.321), respectively. From the good correlation slope, it may be explained that all the MTEs accumulate in large–sized oysters. Generally, when r is a positive value, the MTEs accumulation rates in small organisms are slower than those in large size ones. On the other hand, when r is a negative value, small organisms will accumulate more MTEs compared to the large organisms. Some researchers observed an inverse correlation between heavy metals concentration and body size

(Amiard *et al*., 1986; Julshamn *et al*., 2001). According to Bordin *et al*. (1992), inverse correlation can occur if the elements uptake by smaller individuals is more rapid than the uptake by large individuals.

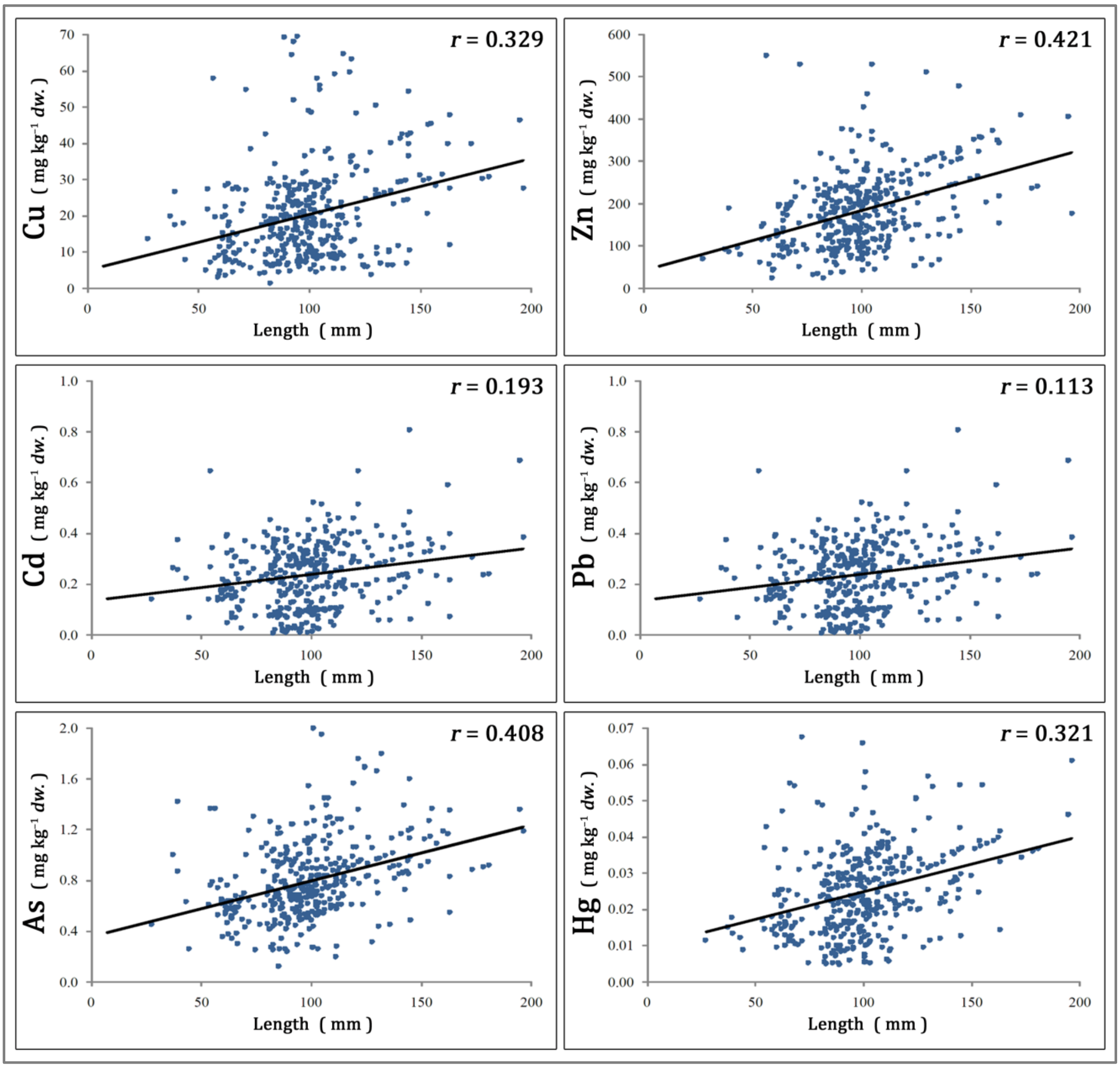

Figure 4–97. *Correlation between metallic trace elements concentration (mg kg^{-1} dw.) and oyster size in length.*

A positive relationship between MTEs concentration and oyster size can be attributed to growth dilution. This situation occurs when tissue is added faster than which is often the case for small individuals and a net–uptake (accumulation) of trace elements throughout the lifetime of the oyster (Brix and Lingby, 1985). Williamson (1980) suggests that the variation in trace element contents between smaller and larger oysters may be due to the difference in their metabolic activity, which may affect the metabolism of trace elements. In summary, younger or small oyster individuals had lower concentrations of Cu, Zn, Cd, Pb, As and Hg than older or larger oyster individuals. This pattern and its variation are attributed to the metabolic activity for specific elements of the oyster species (Han *et al.*, 2000).

Another factor contributing to the difference in oyster MTE concentrations is the salinity gradient. Oysters take up MTEs from solution more rapidly at lower salinities (Wright and Zamuda, 1987; Abbe and Sanders, 1990, Amiard–Triquet *et al.*, 1991). To some extent this simply reflects a decrease in the thermodynamic activity of the free ion due to the increase of ionic strength and complexion by seawater ions. This factor can explain why the MTEs content is higher in the gulf of Morbihan compared to the Quiberon bay area, where the gulf receives freshwater from Noyalo, Marle, Vincin and Auray rivers.

Another potential source of variation in the MTE concentrations of oyster is from the oyster individual diet and feeding habit. Differences in elemental concentration in oysters may be related to organism mobility and feeding habits (Chavez–Villalba *et al.*, 2005) and not to site–specific variations in trace elements loading. Under normal condition, as much as 387 L water is pumped through the gills in a single day (Ingle and Whitfield, 1968) and therefore oysters accumulate a large amount of heavy metals by the ingestion of phytoplankton and organic particles as well as direct uptake from solution. Through the bio–concentration process, particulate matter and phytoplankton are the main sources of MTEs in oysters (Ochoa–Valenzuela *et al.*, 2009). However, MTEs concentration in the soft tissues in the digestive gland might substantially be influenced by the trace elements content in their food (Bustamante and Miramand, 2004). Indeed, oysters are filter feeders using different types of food such as phytoplankton, detritus and re–suspended matter which are major components of the variation in food quality intake through variation in their carbon and nitrogen contents (Grant and Cranford, 1991; Alber and Valiela, 1996).

According to several researchers, seasonal fluctuations also will affect the intake of heavy metals in oyster (Frias–Espericueta *et al.*, 1999; Bendell and Feng, 2009). The variation in the concentrations of MTEs may be linked to mean annual temperature patterns since it has been reported that the amount of MTEs in oyster is positively correlated with seasonal variation (Cherkasov *et al*., 2006). This oyster species was observed to accumulate MTEs actively toward the summer season, particularly from June to September (Al–Sayed *et al*., 1994; Soto–Jimenez *et al*., 2001). Such pattern of increased MTE concentrations in oyster flesh could be attributed to the rise of water temperatures leading to increased filtration and feeding rate of the filter feeding oysters. With temperature rising and oysters starting to feed, this is an optimal situation for the accumulation of the MTEs by oysters (Riedel *et al*., 1996; Rebelo *et al*., 2003).

Depending on the season and availability of food particles, sediment might constitute a significant portion of dietary uptake in *C. gigas* and *O. edulis* (Thomson, 1981; Gray, 1981). Therefore, any MTEs associated with sediment particles will also be ingested by the oysters. The finest particle fraction of sediment (<63 μm) is known to retain the highest proportion of MTEs and is preferentially ingested by many suspension feeding organism such as oyster (Selim and Amacher, 1997; Tarradellas *et al*., 1997). Both species actively feeds on these fine–sediment particles as their daily diet, causing an increased potential exposure to sediment–bound MTEs (Mudroch and MacKnight, 1991; Siegel, 2002).

4.8.3 Geographical comparison of metallic trace elements in oysters in–toto

Table 4–40 shows the comparison between copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb), arsenic (As) and mercury (Hg) concentrations in oysters and mollusks species from different sites around the European and Asian regions (*Figure 4–98*) and the values found in this study. Such variations are due to inter–specific diversity but also to geographic conditions. Differential accumulation abilities of individual oysters in the same or different geographical location or environment has not been ruled out (Ramelow *et al*., 1989).

Table 4–40 *Comparison metallic trace element concentrations (mg kg^{-1} dw.) in oyster flesh obtained in this study with literature data from European and Asian regions.*

Region	Cu	Zn	Cd	Pb	As	Hg	Reference
O. edulis							
Quiberon bay	13.0 (3.5–28.8)	122 (43.1–204)	0.19 (0.03–0.39)	0.98 (0.43–1.61)	0.57 (0.29–0.83)	0.021 (0.009–0.055)	Present study
Brittany, France	32	500	0.25	1.0			Amiard *et al.*, 2008
Cornwall, England	78	800	0.95	7			
C. gigas							
Quiberon bay	19.4 (1.36–59.7)	197 (23.7–459)	0.18 (0.01–0.46)	0.91 (0.08–2.06)	0.73 (0.12–1.36)	0.025 (0.006–0.054)	Present study
Gulf of Morbihan	22.9 (3.07–69.4)	182 (24.7–549)	0.29 (0.07–1.15)	2.08 (0.29–6.46)	0.91 (0.24–1.99)	0.025 (0.005–0.070)	Present study
Noirmoutier, France	13	92	0.2	1.40	–	–	Amiard *et al.*, 2008
Atlantic Coast, France	58	217	0.68	2.25	–	–	
France region	–	–	–	–	2.2	–	Sirot *et al.*, 2009
Southwest coast, Spain	–	–	–	–	1.67–3.58	–	Suner *et al.*, 1999
Qualidia lagoon, Morocco	3.64–42.1	28.3–672	0.67–9.7	1.2–7.4	0.08–0.84	–	Maanan, 2008
Xinghua bay, China	18.2	35.7	0.97	0.6	1.35	0.0011	Yatawara *et al.*, 2010
Taiwan coast	2.29	7.83	1.76	–	10.8	–	Han *et al.*, 2000
Sien–San coast, Taiwan	1265	1849	–	–	–	–	Lin and Hsieh, 1999
Deep bay, Hong Kong	468	913	3.8	10	–	–	Wong *et al.*, 1981
Hansan–Koje bay, South Korea	30.8	543	2.7	–	–	–	Hwang *et al.*, 1986
Ussuriyskiy bay, Russia	250–6576	1683–7262	4.7–27.2	4.1–36	–	–	Shulkin *et al.*, 2003
Others oyster species							
Basque coast, Spain	72.2	470	0.2	0.63	0.38	0.084	Franco *et al.*, 2002
Gulf of Aden, Yemen	4.0–111	3.4–15	0.6–3.1	2.6–15.4	–	–	Mostafa *et al.*, 2009
Saikung, Hong Kong	141	618	0.71	0.7	–	–	Amiard *et al.*, 2008

Table 4–40. *Continued.*

Region	Cu	Zn	Cd	Pb	As	Hg	Reference
Other mollusc species							
Biscay bay, France	15	437	5.7	–	–	–	Bustamante and Miramand, 2004
Mediterranean sea	8.83	14.1	0.34	0.9	–	–	Al–Sikaily *et al.*, 2004
North coast, Spain	5.33–7.2	176–316	0.46–1.4	0.9–3.0	–	0.11–0.61	Besada *et al.*, 2002
Goro bay, Italy	9.4–21.2	62.9–155	3.7–4.3	15.8–29	–	0.167–0.231	Locatelli, 2003
Gulf of Gdansk, Greece	7.24	138	2.13	2.0	–	0.131	Szefer *et al.*, 2002
Gulf of Patras, Greece	7.1	10	0.9	2.4	–	0.01	Kalpaxis *et al.*, 2004
El Jadida Coast, Morocco	4.35–142	113–612	1.33–25.3	0.50–34.2	–	0.02–2.3	Maanan, 2008
Arabian gulf, Bahrain	1.63	8.7	–	5.9	–	–	Al–Sayed *et al.*, 1994
Gulf of Suez, Egypt	3.69–10.1	69.5–164	0.69–2.37	6.92–37.8	–	–	Hamed and Emara, 2006
Southeast coast, India	33.6–49.2	60.4–94.1	1.59–4.40	2.48–6.92	–	–	Senthilnathan *et al.*, 1998
Bohai sea, China	0.98–147	5.1–550	0.14–52	0.02–1.33	0.53–19	0.01–0.31	Wang *et al.*, 2005
Juru river, Malaysia	9.5	110	4.6	0.55	13.4	0.1	Alkarkhi *et al.*, 2008
Hong Kong coast	37.2	116	0.66	7.65	14.8	–	Liu and Kueh, 2005
Korean waters, South Korea	3.93–13.6	70.3–157	0.06–2.36	3.62–52.7	–	0.02–0.07	Szefer *et al.*, 2004
Singapore coast	28	280	<0.2	5.6	21	–	Bayen *et al.*, 2004
West coast, Malaysia	7.76–20.1	75.1–129	0.68–1.25	2.51–8.76	–	–	Yap *et al.*, 2004
Gulf of Thailand	2.94–15.0	24.9–213	0.17–3.25	0.19–3.75	–	–	Ruangwises and Ruangwises, 1998

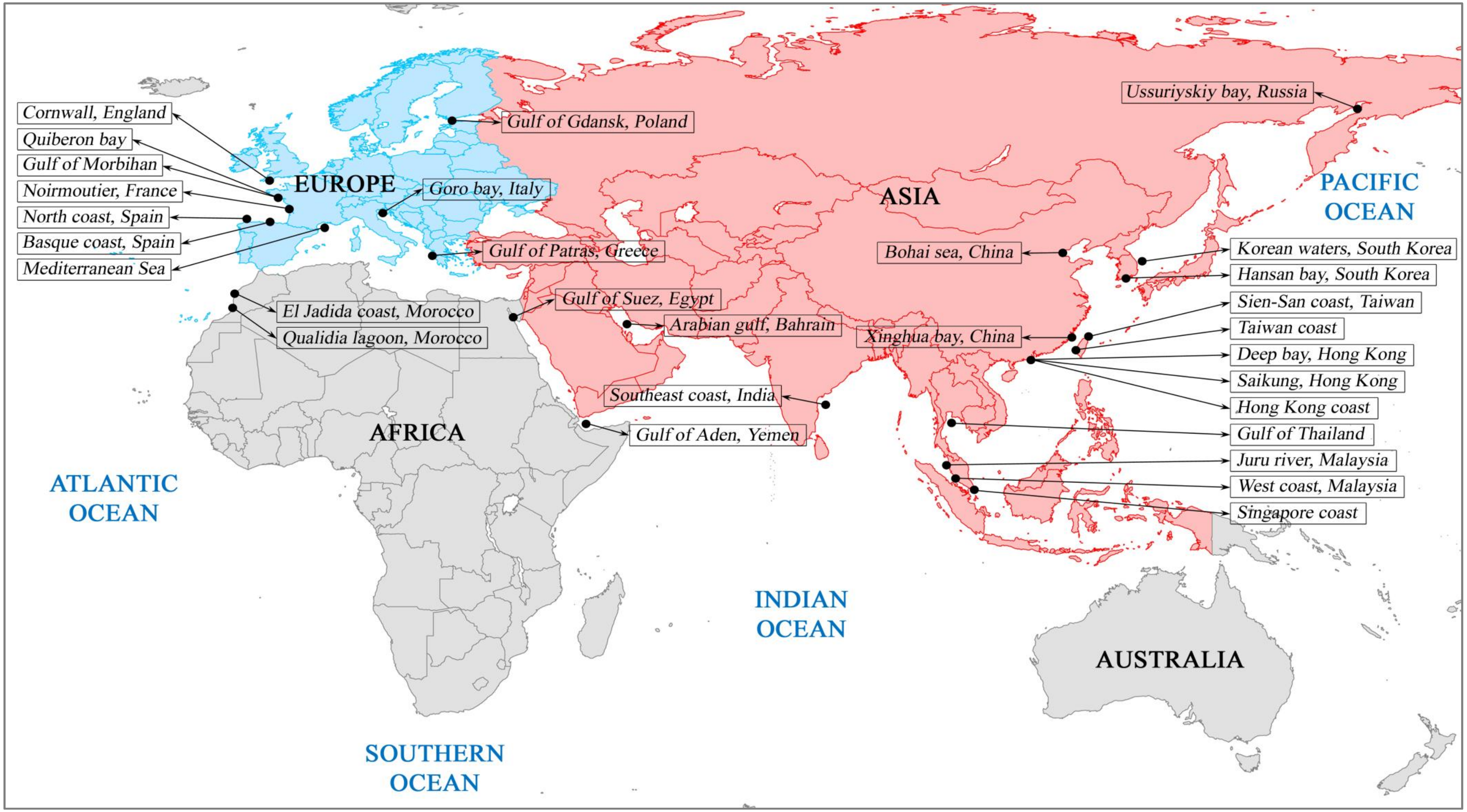

Figure 4–98. *Comparison of results in metallic trace elements in oysters and other mollusk with other studies reported from European and Asian regions.*

Copper, Zn, Cd and Pb concentrations in oyster, *O. edulis* from south coast of Brittany has been reviewed by Amiard *et al*. (2008). In the study, south coast of Brittany is considered as a clean area and the data were used as a background data in the study. Our studied MTEs, Cu, Cd and Pb are comparable to the study by Amiard *et al.* (2008), however our Zn concentration is about four times lower compared to their study. Based on the table, MTEs in oysters from the Quiberon bay and the gulf of Morbihan are lower and comparable than those found by other researchers from European and Asian regions.

4.8.4 Tolerable intake for human consumption

Beside fishes, shellfish such as oysters and mussels are an important source of dietary protein in south Brittany and provide a livelihood for many coastal communities around the Quiberon bay and gulf of Morbihan. Depending on consumer, those oysters can be "swallowed" or masticated normally, increasing the surface of contact between food and digestive fluids. The consumer will consume whole soft part of the oyster, therefore in this study, the MTEs content is examined in–toto or oyster flesh.

High Cu accumulated in oyster can be toxic to human (O'Shaghnessy, 1966; Pringle *et al*., 1968) and Cu does not present a long–term bioaccumulation hazard in the same way as Cd. High levels of Cu in oyster tissue can cause a characteristic green coloration, and an unpleasant taste (Han and Hung, 1990). Thus, is unlikely that Cu accumulation in oysters represents a significant human health threat. However, Cu accumulation presents a significant threat to an oyster fishery because it can make the oyster undesirable.

The last objective of this study was to learn, based on their MTEs level, if the species chosen, *C. gigas* and *O. edulis* were suitable for human consumption in the area studied. Many area residents surrounding south Brittany consume local shellfish, and it is possible that some could exceed the tolerable average daily intake. So far, there are no reports relating MTE concentrations in the cultivated *C. gigas* and *O. edulis* in Quiberon bay and gulf of Morbihan to human and environmental health standard.

To safeguard public health, maximum acceptable concentrations of toxic contaminants have been established in various countries. As a result, there is a specific legislation for shellfish in the European region (EC, 2006), which establishes the maximum allowed concentration for MTEs (*Table 4–41*). When these MTEs compared to the levels set by several countries regulations, we found that all our MTEs concentration were lower when all the data was converted into wet weight basis and expressed in mg kg^{-1} *ww*. These concentrations were converted to wet weight basis equivalents using a conversion wet muscle and dry muscle weight ratio (Phillips *et al*., 1982; Cheung and Wong, 1992; Kumari *et al*., 1992).

Table 4–41. *Maximum permissible levels (expressed in mg kg^{-1} ww.) of MTEs in shellfish from different countries or regions.*

	Cu	**Zn**	**Cd**	**Pb**	**As**	**Hg**	**Reference**
This study	4.9	46	0.05	0.30	0.19	0.06	
Shellfish							
European Community	*n.m.*	*n.m.*	1	1.5	*n.m.*	0.5–1.0	EC (2006)
Spain	20	*n.m.*	1	5	*n.m.*	0.5	BOE (1991)
USA	*n.m.*	*n.m.*	3–4	1.5–1.7	*n.m.*	0.5	USFDA (1990)
Australia	30	150	2	2	1	0.5	AG (2006)
China	*n.m.*	*n.m.*	0.1	0.5	1.0	0.3	CFR (2004)
Hong Kong	*n.m.*	*n.m.*	2	6	1.4	0.5	HKEPD (1997)
Singapore	*n.m.*	*n.m.*	1	2	1	0.5	SFR (1990)
Food category not specific							
Malaysia	30	50	1	2	*n.m.*	0.5	MFR (1985)
Thailand	20	133		1.0	2	0.5	MPHT (1986)
Brazil	30	50	1	2	*n.m.*	0.5	ABIA (1991)

n.m. : not mentioned

International scientific committees such as the Joint FAO/WHO Expert Committee on Food Additives (JECFA), regional scientific committees such as the European Union and national regulatory agencies generally use the safety factor approach for the establishing acceptable of tolerable intakes of substances that exhibit thresholds of the toxicity of contaminants. JECFA derives tolerable intakes, expressed on either a daily or a weekly basis, for contaminants (WHO, 1987) as shown in *Table 4–42*. Pb, Cd, As and Hg is not removed rapidly from human body and for this group of contaminants, provisional tolerable weekly intakes (PTWIs) are allocated. The term tolerable is used because it signifies permissibility rather than acceptability for the intake of contaminants unavoidably associated with the consumption of otherwise wholesome and nutritious foods. Tolerable intakes are expressed on a weekly basis because the contaminants given in this designation may accumulate within the human body over a period of time (Lee *et al*., 2006). On any particular day, consumption of food containing above–average levels of the contaminant may exceed the proportionate share of its weekly tolerable intake.

For contaminants such as Cu and Zn that are not known to accumulate in the body, JECFA establishes provisional maximum tolerable daily intakes (PMTDIs). The term of maximum is used because this designation is often applied to trace elements that are both essential nutrients. In such situations, a range is designated, with the lower value representing the level of essentially and the upper value the PMTDI (WHO, 1987).

Table 4–42. *Maximum consumption of seafood products and provisional tolerable weekly intake (PTWI) or provisional maximum tolerable daily intake (PMTDI) as assess by the World Health Organization.*

	PTWI mg kg^{-1} body weight	**PMTDI mg kg^{-1} body weight**	**Reference**
Cu		0.5	JECFA (1982a)
Zn		1.0	JECFA (1982b)
Cd	0.007		JECFA (2005)
Pb	0.025		JECFA (1999)
As	0.015		JECFA (2010)
Hg	0.0016		JECFA (2003)

JECFA has established regulatory guidelines regarding the dietary intake of heavy metals from shellfish. To assess the risk due to the consumption of these oyster products, the number of individuals of each species from Quiberon bay and gulf of Morbihan mariculture areas as well as natural environment (wild oysters) which has to be eaten before reach the maximum tolerable intake recommended by the

World Health Organization has been calculated (*Table 4–43*). The contribution of seafood to the diet is highly variable, but may be very high in certain group. An inquiry into seafood consumption in France has been reviewed by Leblanc *et al*. (2006) and from their study, the average consumption of shellfish in south Brittany was 276 g/week for an adult.

Table 4–43. *Maximum consumption of oysters and provisional tolerable weekly intake (PTWI) based on standard weight of a man of 65 kg.*

	PTWI / individual mg kg^{-1} body weight	Species	Max consumption kg per week	Max number of shellfish
Cu	228	*O. edulis*	31.5	3618
		[a] *C. gigas*	15.6	720
		[b] *C. gigas*	23.8	873
		[c] *C. gigas*	17.0	1117
		[d] *C. gigas*	23.5	598
Zn	455	*O. edulis*	8.91	1023
		[a] *C. gigas*	5.43	250
		[b] *C. gigas*	5.54	203
		[c] *C. gigas*	5.02	329
		[d] *C. gigas*	4.97	126
Cd	0.45	*O. edulis*	5.17	594
		[a] *C. gigas*	4.33	199
		[b] *C. gigas*	5.70	209
		[c] *C. gigas*	4.13	271
		[d] *C. gigas*	2.38	60
Pb	1.62	*O. edulis*	4.78	549
		[a] *C. gigas*	4.33	199
		[b] *C. gigas*	3.95	145
		[c] *C. gigas*	1.83	120
		[d] *C. gigas*	1.51	38
As	0.97	*O. edulis*	5.88	675
		[a] *C. gigas*	3.70	170
		[b] *C. gigas*	3.57	131
		[c] *C. gigas*	2.31	151
		[d] *C. gigas*	3.52	89
Hg	0.10	*O. edulis*	7.70	884
		[a] *C. gigas*	8.38	386
		[b] *C. gigas*	9.56	351
		[c] *C. gigas*	8.51	558
		[d] *C. gigas*	8.90	226

[a] Farmed oyster from Quiberon mariculture area;
[b] Farmed oyster from gulf of Morbihan mariculture area;
[c] Wild oyster from Quiberon natural environment (Trinité–sur–Mer);
[d] Wild oyster from Auray river natural environment

For cultivated *O. edulis*, the Joint FAO/WHO Expert Committee on Food Additives established a PTWI for Pb of 0.025 mg kg^{-1} body weight/week which was equivalent to 1.63 mg/week for a 65 kg adult. By considering the means of weekly shellfish consumption in south Brittany of 276 g per person (Leblance, *et al.*, 2006), and the minimum and maximum Pb levels in examined samples, weekly Pb intake calculated ranged from 0.03 mg (276 g x 0.10 mg/1000 g) to 0.09 mg (276 g x 0.34 mg/1000 g) per person for Pb in cultivated *O. edulis*. The estimated PTWI of Pb for *O. edulis* is far below the established PTWI. In order to exceed the PTWI level, a 65 kg adult should consume 4.78 kg (1.63 mg x 1 kg/0.34 mg) of *O. edulis* in–toto or 549 individuals (in–toto weight, 8.7 g).

The lowest and highest As level in cultivated *C. gigas* from Quiberon bay mariculture areas were observed at 0.02 and 0.26 mg kg^{-1} wet *wt.*, respectively. Thus, minimum intake of As was 0.01 mg (276 g x 0.02 mg/1000 g) per person for one week period while the maximum weekly As intake was 0.07 mg (276 g x 0.26 mg/1000 g) per person by a 65 kg adult. However, the calculated PTWI value is far below the established by JECFA, 0.015 mg kg^{-1} body weight/week, equivalent to 0.97 mg/week for a 65 kg adult. Assuming that if a 65 kg adult consume 170 individuals or equivalent to 3.70 kg (0.97mg x 1kg/0.26mg) of *C. gigas* flesh (in–toto weight, 21.7 g) where consumption will reach the PTWI level.

PTWI for Hg was established 0.0016 mg kg^{-1} body weight/week and 0.10 mg/week for a 65 kg adult. By using the average of weekly shellfish consumption in south Brittany of 276 g and minimum and maximum Hg levels in the oyster, the consumer will intake from 0.001 mg (276 g x 0.002 mg/1000 g) to 0.003 mg (276 g x 0.012 mg/1000 g) per person weekly. As can be seen, the estimated PTWI of Hg in oyster is below the established PTWI. To exceed the PTWI level for the oyster *C. gigas* from the gulf of Morbihan, this amount would be about 9.56 kg (0.104mg x 1kg/0.012mg) of oyster flesh or 351 individuals (in–toto weight, 27.2 g).

Similar estimation also applied for the sample collected from nature environment or wild oysters. The JECFA established PTWI for Cd of 0.007 mg kg^{-1} body weight/week and equivalent to 0.45 mg/week for a 65 kg person. From the estimation, a 65 kg adult should eat 2.38 kg (0.455 mg x 1 kg/0.19 mg) or 60 of *C. gigas* (in–toto weight, 39.4 g) to reach the PTWI in Cd. Yet, by consider the same average weekly shellfish consumption in south Brittany for cultivated oyster, 276 g per person, the maximum intake of Cd in their body is 0.053 mg (276 g x 0.19 mg/1000 g) and this value is still below the PTWI set by JECFA.

It can be concluded that, from the PTWI estimation for a 65 kg adult, the maximum number of *O. edulis* and *C. gigas* from Quiberon mariculture area that can be consumed before reach the PTWI value was 4.78 kg of *O. edulis* flesh (549 individuals) weekly and 3.70 kg of *C. gigas* flesh (170 individuals) weekly, respectively. For the cultivated *C. gigas* from gulf of Morbihan, this amount would be 131 oysters or 3.57 kg of oyster flesh. On the other hand, for wild oyster *C. gigas*, only 1.51 kg of oyster flesh or equivalent to 38 individuals can be consumed before reach the PTWI estimation.

CONCLUSION AND RECOMMENDATION

As a conclusion, for the first time, the geochemistry studies in the surficial sediments (0–5 cm) of Quiberon bay and gulf of Morbihan were investigated. The results obtained in this study provide an overview of selected metallic trace elements (MTEs), Cr, Mn, Fe, Co, Zn, Cu, As, Cd, Hg and Pb and total organic carbon concentrations in the surficial sediments. Further, the first high resolution GIS–based maps of these chemical elements in the surficial sediments were visualized to show the hotspot of the concentrations. This work represents a significant database on the quality of surficial sediments. It will be useful for managers of the marine environment by allowing them to better apprehend the future maintenance required for the correct functioning of the harbor and mariculture activities.

Generally, the MTEs concentrations were higher during the second sampling, Oct 2010 compared to the first campaign in Dec 2009. In this study, we found that MTE concentrations in surficial sediments sampled in the Quiberon bay and gulf of Morbihan varied :

MTE	**Concentration (µg g^{-1} *dw.*)**	
	Dec 2009	**Oct 2010**
Chromium	5–112	2.94–71.1
Manganese	16.6–732	25.7–781
Iron (%)	0.05–5.47	0.09–5.10
Cobalt	2.12–31.4	1.11–23.0
Copper	1.20–48.4	2.56–47.0
Zinc	4.78–87.1	4.60–98.9
Arsenic	0.16–6.16	0.12–6.80
Cadmium	0.02–0.30	0.01–0.23
Mercury	0.001–0.06	0.005–0.06
Lead	2.43–42.7	3.61–52.4

From the findings, Quiberon bay can be categorized into three regions based on the contamination assessment (*Figure C–1*). The Trinité–sur–Mer area shows the highest concentrations of all studied MTEs, where a huge port for recreation and fishing activities is located in this area. The second region, northern area, which located inner of the bay, shows better environmental conditions. Lower concentrations of MTEs are found in this area. The final region, outer or southern bay also shows a higher concentration of MTEs, however the concentrations were lower compared to the Trinité–sur–Mer area.

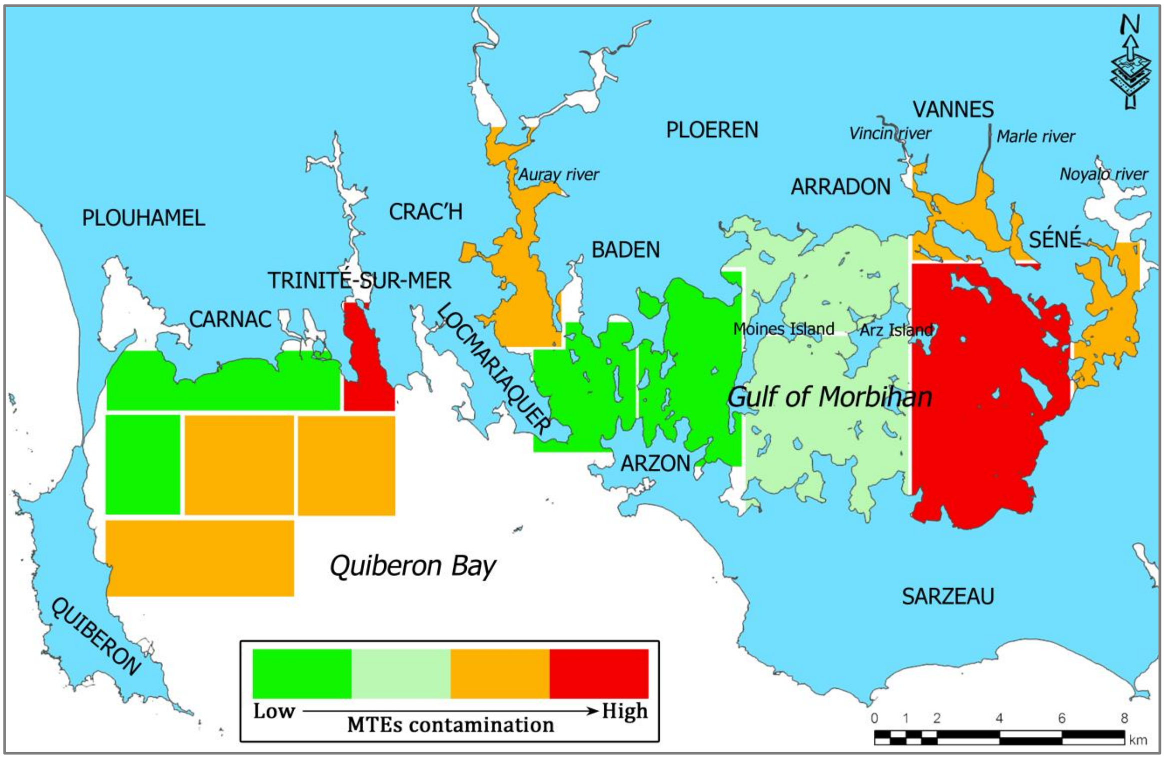

Figure C–1. *Division of region based on the MTEs contamination category.*

On the other hand, gulf of Morbihan can be divided into four regions with different degrees of environmental contamination (*Figure C–1*). The eastern area, which located at the innermost of the gulf show the highest concentrations of MTEs and followed by the river areas (Auray, Marle and Noyalo) which recorded the second higher concentration of MTEs. MTEs in both areas are associated with naval activities and domestic run–off. The third area is the entrance of gulf of Morbihan, which is affected by strong water exchange processes, with sandy sediments and lower concentration of total organic carbon contents. This is due to the sediment characteristics and environmental conditions. Concentrations of MTEs in this area are very low. The fourth and final area is the transitional zone between the entrance of the gulf and eastern areas and shows a range of value from lowest to highest.

Meanwhile, the observed values agree well and occasionally low with levels reported from the highly urbanized coastal area and greatly utilized by human such as for shipping and mariculture accomplishments around the world. From the surveillance, a general assumption can be established, where the pattern of MTEs enrichment are associated with sewage sludge for municipal run–off and from the spillage process during dock undertakings. Direct correlations between all MTEs, fine sediment percentages and total organic carbon contents also agree with observation from similar polluted and clean environments in other regions.

Although the MTEs studied in the surficial sediments meets the upper continental crust values, thus the combination of normalization techniques, enrichment factors, index of geoaccumulation and pollution load index suggest a non–anthropogenic contribution to the chemistry of the seafloor sediments, with the exception of Pb, where the contamination exist in the entire study area particularly in the gulf of Morbihan area. Conversely, contaminations of other MTEs are also present in some locations depending on the contamination sources in the area. These elements are directly associated with point discharge from domestic run–off and dock activities in this area.

This study shows that using the aforementioned normalization techniques only to assess the Quiberon bay and gulf of Morbihan sediment quality cannot properly reflect the sediments toxicity associate with adverse effects to the marine aquatic organisms, especially oysters and mussels. Hence, for the first time, the multiple approaches for potential toxicity were applied for the sediment quality assessment, namely direct screening with the sediment quality guidelines (ERL/ERM and TEL/PEL) for each element. Whereas, mean–ERM–quotient was calculated in surficial sediment to estimate the effect of a multiple elements to the marine organisms, each was calculated in surficial sediment.

Mollusks have been successfully used as bio–indicators in the environmental monitoring experiment. The levels of the selected MTEs studied (Cu, Zn, Cd, Pb, As and Hg) were comparable with previous investigators in South Brittany coastal waste where this area are classified as a clean area or used as a background for their study. From the public health point of view, the levels of the selected MTEs in oysters, *C. gigas* and *O. edulis* were lower than the permitted for human consumption recommended by the World Health Organization; therefore, consumer surrounding this region can ingest both oysters without risk to their health.

Further studies are necessary in order to evaluate the ecological significance of this contamination as well as monitoring programs for assessment and management purpose. Therefore, it is suggested that a continuous monitoring of this coastal waters should be implemented considering that the Quiberon bay and gulf of Morbihan is a site of important recreation area, fishing and mariculture activities and of future increased loading of urban and domestic wastes surrounding the region. Further, to evaluate possible impacts of organic contaminants, particularly metallic trace elements of the coastal environment, the distribution pattern of these contaminants in water, adjacent sea and various benthic organisms should be considered for future studies.

In order to gain more information about the pollution status and management of the contaminants in Quiberon bay and gulf of Morbihan environments, numerous investigators from the chemical and biological expertise should be involved in the aforesaid future studies. Exploration of environmental quality such as hydrocarbons (PAHs/TAHs), water nutrients (phosphorus, nitrate, organic matter), mineralogy analysis (silica and $CaCO_3$) and study of the biological condition (microorganism, bacteria) are recommended for the purpose. Since anthropogenic sedimentation poses a significant threat to benthic ecosystems, pollutant monitoring of sediments should be continued. Moreover, it is well known that the sinking particulate materials are also an important factor for checking chemicals pollution in the marine environment. For this reason, it is important to determine the contaminants level in sediment trap materials such as particulate sediments.

After these initial results were obtained, several approaches can be made in the future to explain the origin of MTEs in Quiberon bay and gulf of Morbihan regions. First, long core sediment should be sampled at Quiberon bay to obtain the background values of these MTEs. With the data, all the MTEs concentration can normalize with the regional background data. Meanwhile, rare earth elements (Y, La to Lu) can also be used to serve as an indicator of sediment quality. Since, the concentration of Pb is relatively higher compared with other MTEs, a study on Pb isotope (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb) can be suggested to determine the source of Pb in both marine environments.

Despite all the analyses of sediment and oysters have been conducted in this study, a specific conclusion of the concentration and movement of heavy metals distribution cannot be done. Therefore, in order to solve this problem, a sampling for each season (winter, spring, summer and fall seasons) should be conducted in sediment, suspended materials and oysters in order to describe the effect of each season towards the concentration of MTEs. Meanwhile, to investigate the linkage between MTEs in Quiberon bay and gulf of Morbihan sediments, the sampling area in the Quiberon bay should be extended. With this adjacent sea, it can be estimated whether the three main harbors, Haliguen, Navalo and Crouesty are the main contributor to the distribution of MTEs in the region.

With all the data obtained during both sampling periods in Dec 2009 and Oct 2010, several general conclusions can be made:

1. In Quiberon bay, muddy sediment occurred in the sheltered zone at Trinité–sur–Mer; and in the gulf of Morbihan, muddy sediment occurred in the inner gulf and rivers zone (Auray, Marle and Noyalo rivers) where slow hydrodynamic process were observed in these area. Meanwhile, the outer Quiberon bay also recorded the muddy type sediment even the high hydrodynamic process occurred in this zone. Therefore, it can be suggested that the hydrodynamic process controlled the types of sediment in gulf of Morbihan, while the bathymetry controlled the types of sediment in Quiberon bay.
2. MTEs concentrations in the closed marine environment, gulf of Morbihan were higher compared to open marine environment, Quiberon bay. This situation was observed during the both sampling periods, Dec 2009 and Oct 2010.
3. MTEs and TOC levels in Quiberon bay and gulf of Morbihan depend on the types of sediment. Higher concentration of MTEs studied occurred in fine–grained or muddy sediments; in contrast, lower concentrations were usually found in the sandy sediments.
4. Li was found to be a suitable as a reference metal compared to Al for the estimation of the degree of pollution by the enrichment factors assessment due to its good correlation with all the MTEs studied and sediment mean size.
5. Multivariate assessment of the surficial sediment contamination, enrichment factors and index of geoaccumulation from Quiberon bay and gulf of Morbihan verified that all the source MTEs studied were dominant by natural and non–anthropogenic processes except Pb which were influenced by both, natural and anthropogenic process.
6. The co–association of all the MTEs studied in Quiberon bay and gulf of Morbihan sediments indicate that their existence and similarity among the MTEs. Some strong correlation between the MTEs showed that the same geochemical process played role in controlling the distribution or the MTEs origin from a same source.

7. Sedimentation in the vicinity of the mariculture activities (ranged from 0.12–0.14 cm/y; average 0.14 cm/y) was higher than areas with no mariculture activities (ranged from 0.10–0.11 cm/y; 0.11 cm/y). This may be explained by the shellfish such as oysters and mussels behavior through feeding and pseudofeces process which were settled to the bottom sediment.
8. In comparison with the sediment quality guidelines for the ecological risk assessment, generally all MTEs studied were not exceeding the effect range low and probable effect level classification. Hence, these MTEs studied were considered to not toxic to the marine organisms. However, the multiple contamination evaluation of MTEs by mean–ERM–quotient shows that in sediment in Quiberon bay and gulf of Morbihan environments, the sediments has not more than 21 % probability to be toxic to the aquatic organism.
9. MTEs in the both oyster species, *O. edulis* and *C. gigas* were controlled by the physiology status, size and age of the oysters. The positive correlation between the each MTEs and the length of the oyster were proved this assumption.
10. The tolerable intake studies for human consumption shows that all the MTEs studied were lower than the legislation for shellfish in the European community and other countries. In the PTWI and PMTDI consideration based on the acceptability of tolerable intake by JECFA, regardless of all the cultivated and wild oysters are safe for human consumption.

To end this dissertation, several conceptual models were created to provide a better under understanding of this study and shown in *Figure C–1*, *Figure C–2* and *Figure C–3*.

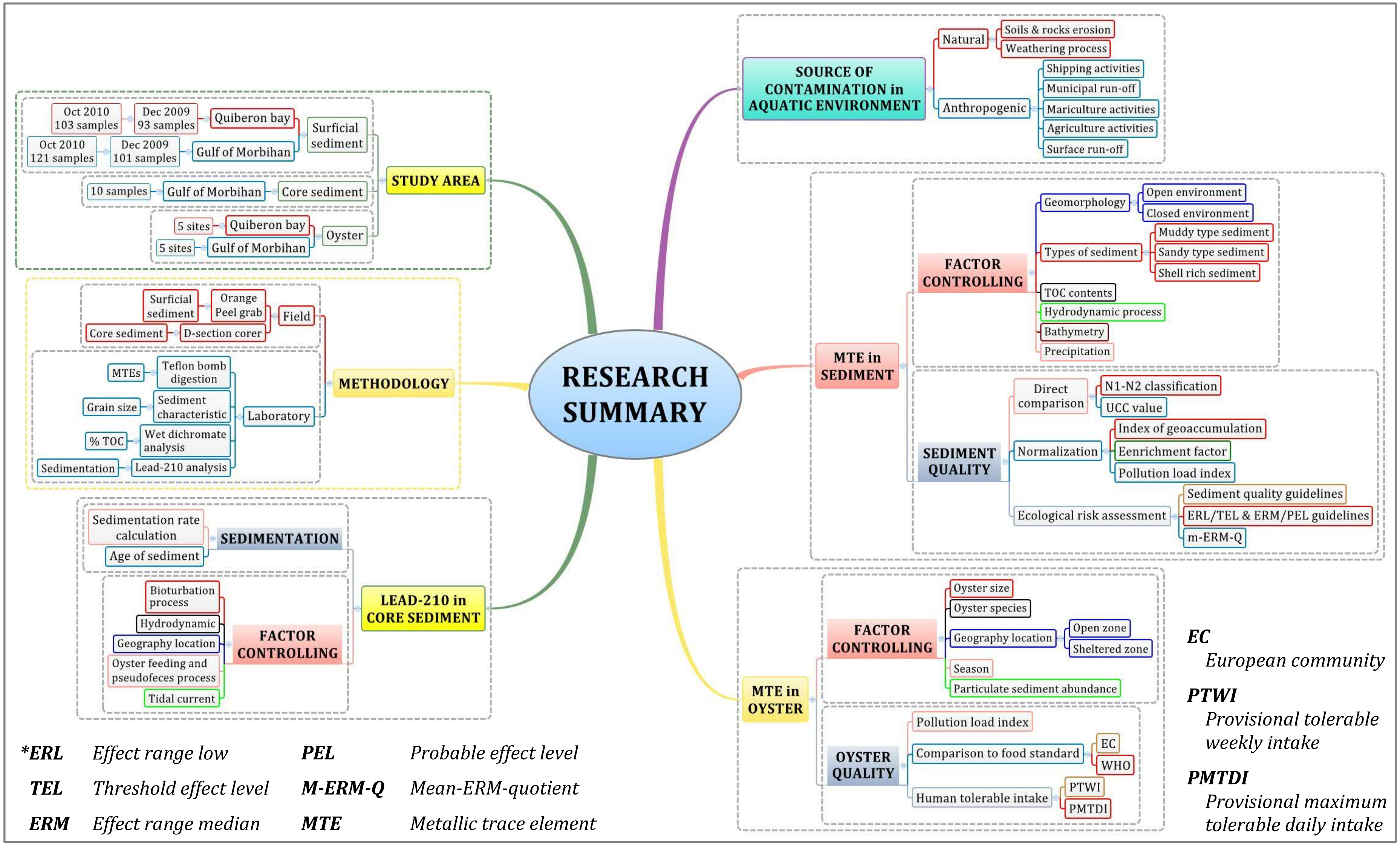

Figure C–2. *Conceptual model shows the overview of this study.*

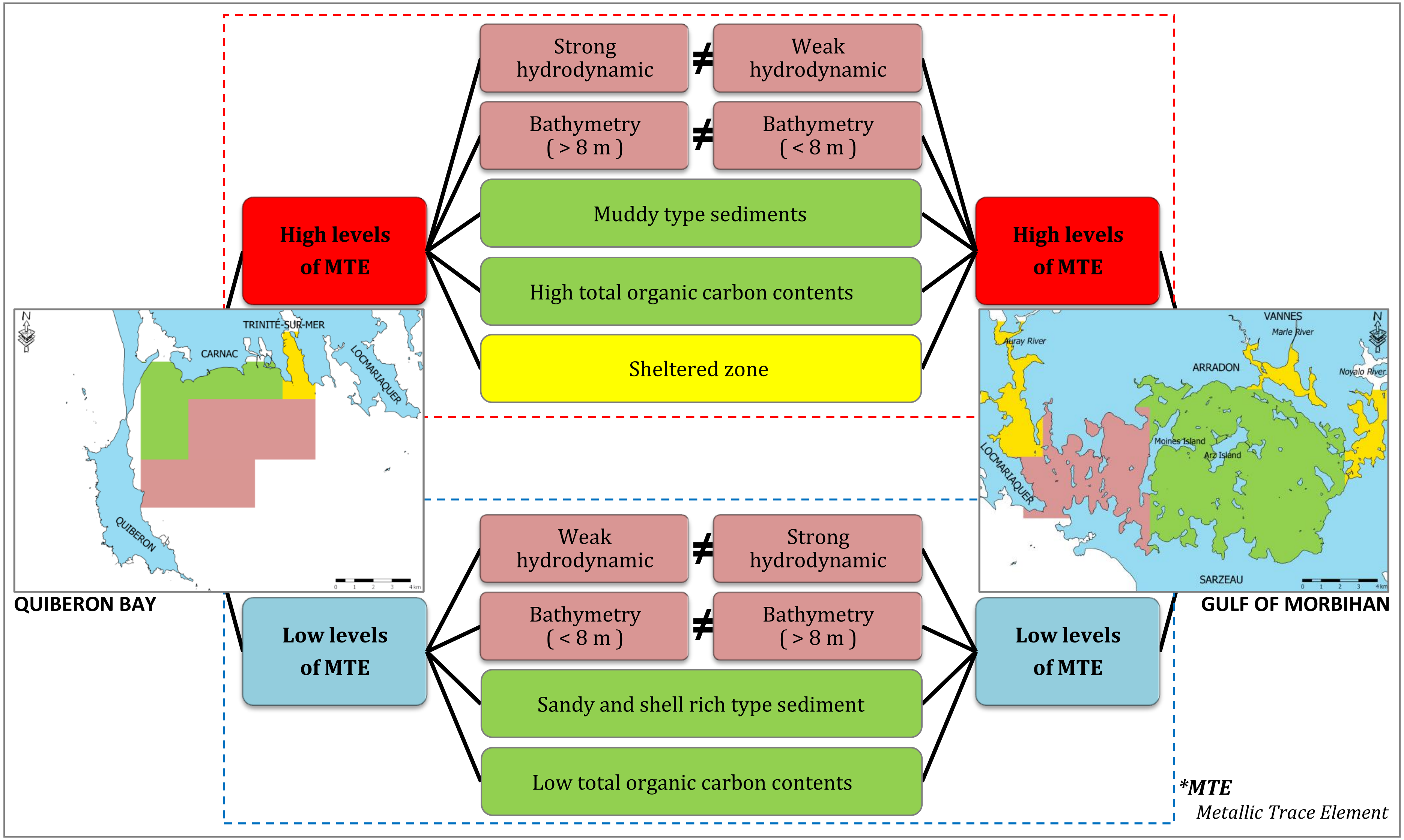

Figure C–3. *Factor controlling metallic trace elements distribution in surficial sediments from Quiberon bay and gulf of Morbihan.*

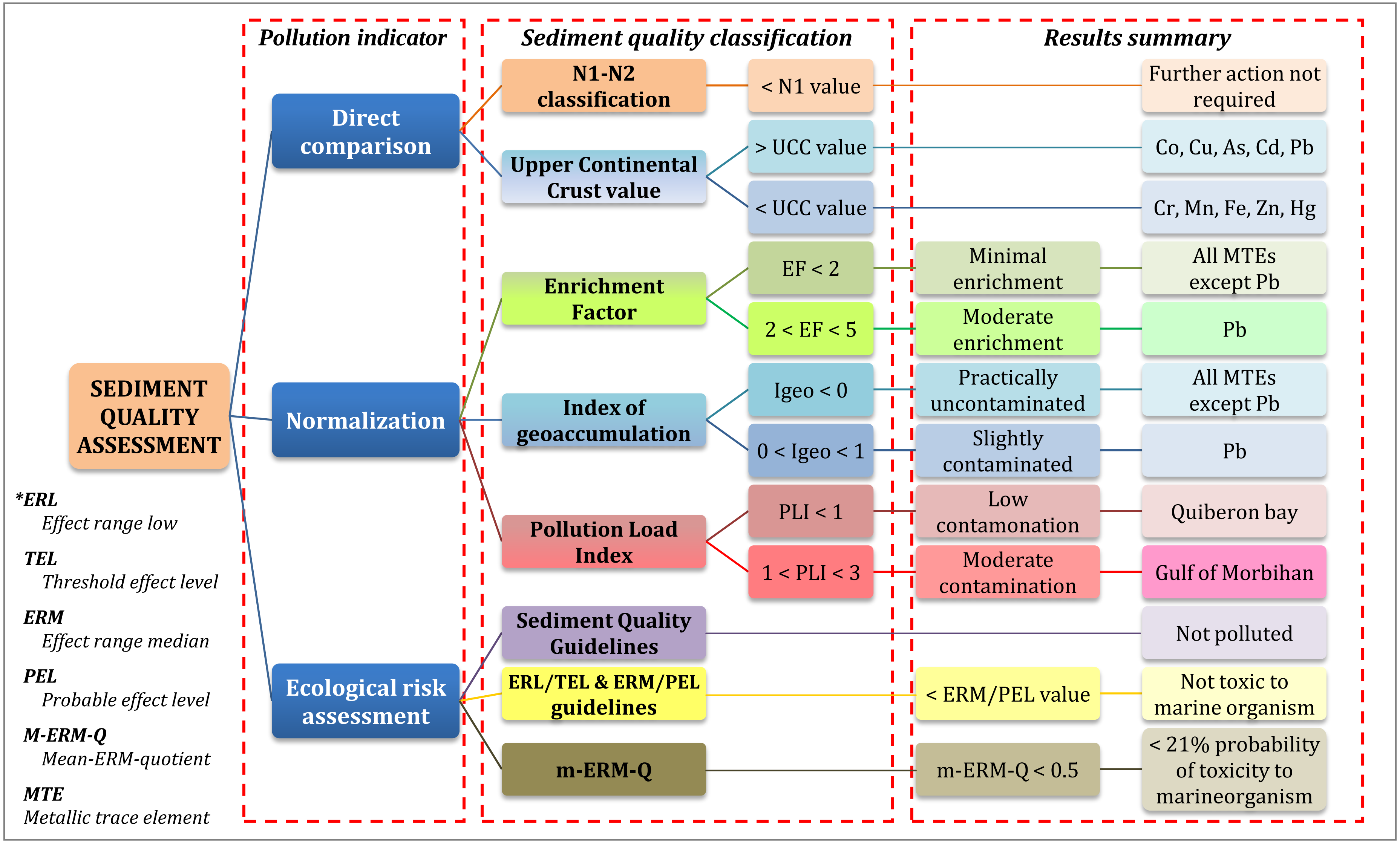

Figure C–4. *Multivariate assessment of surficial sediments contamination.*

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