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Sediment and Organisms as Marker for Metal Pollution

Ong Meng Chuan and Kamaruzzaman Yunus

Abstract

Pollution caused by metal elements has drawn increasing attention worldwide due to the increase of anthropogenic contaminants to the marine ecosystems. Pollution of the natural environment by metals is a serious problem because these elements are indestructible and most of them have toxic effects on living organisms, when they exceed a certain concentration. Sediments are widely used as geo-marker for monitoring and identifying the possible sources since sediment can act as sink for the pollutants. Most metals are bound in fine-grain fraction because of its high surface area-to-grain size ratio where they have a greater biological availability compared to those in larger fraction. Lying in the second trophic level in the aquatic ecosystem, shellfish species have long been known to accumulate both essential and non-essential metals. Many researchers have reported the potentiality of using mollusks, especially mussel and oyster species, as bioindicators or biomarkers for monitoring the metal contamination of the aquatic system.

Keywords: metal pollution, sediments, geo-marker, organism, bio-markers

1. Introduction

Recently, marine environment such as coastal and estuarine regions is contaminated by waste created by human activities containing elevated concentrations of nutrients, organic pollutants, trace metals, and radionuclide [1, 2]. Some of these chemicals are highly toxic and persistent, and these elements have a strong tendency to become concentrated in marine food webs once they enter this aquatic environment. 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 [3–6]. The addition of waste products into rivers, estuaries, and wetland environment (**Figure 1**), especially those in industrial and population centers, has led to a significant increase in this pollutant level, especially metal contamination [7]. Accumulation of metals in surface sediments from industrial effluents and urban sewage discharged into the aquatic environment without proper treatment will easily be identified through metal spatial variations in sediments [8, 9].

Rivers can transport metals into the marine environment, and the amount of the chemical element input to the oceans depends on their levels in the river sediments, water, suspended particulate matter, and the exchange processes that occur in the estuaries [10]. With recent industrialization and human activities (**Figure 2**) that happen in the coastal region, these metals are continuing to be discharged to

Figure 1.
Wetland ecosystem in Malaysia. This ecosystem may be polluted by metal pollutants derived from human activities. Photo by Ong Meng Chuan.

Figure 2.
Example of human activities (fishery industry) in the Gulf of Morbihan, France. Photo by Ong Meng Chuan.

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.

Metal concentrations in harbor or estuarine sediments usually are high due to significant anthropogenic contaminant loading carried by the upstream of tributary rivers and settled down at this area [11, 12]. The sediments itself can serve as a metal pool that can release metals to the overlying water via natural or anthropogenic chemical and physical processes, causing potential adverse health effects to organisms that live at the ecosystems [13, 14]. Moreover, marine organisms can uptake these chemical elements, which in turn enhances the potential of some elements entering into the food chain. Therefore, metal contaminations are considered by scientists as an environmental problem today in both developing and developed countries throughout the world [15].

Metals 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 [16, 17]. Several processes had been

identified for controlling the metal concentration in sediment, such as direct adsorption by small particle of clays, adsorption of hydrous ferric and manganic oxides which may also associate with clay fraction, adsorption of natural organic substances associated with inorganic particle, and precipitation as new solid phases [18, 19]. With this unique characteristic, sediments are usually used as geo-marker for monitoring and identifying the potential pollution sources in aquatic environment. These sediment analyses are an important tool for the determination of pollutants as they sink in the bottom through different chemical constituents and can reflect the pollutant proxy in the environment. In addition, the sediments act as a useful indicator of long- and medium-term metal flux in industrialized estuaries and rivers, and they help to improve management strategies as well as to assess the success of recent pollution controls [20].

More than 90% of the metal compound load in marine aquatic systems is bound to suspended particulate matter and sediments [21]. Therefore, sediments serve as a pool of metals that could be released to the overlying water from natural and anthropogenic processes such as bioturbation and dredging, resulting in potential adverse health effects toward surrounding organisms [22, 23]. Besides that, it is necessary to determine the metal contamination in estuarine ecosystem because this area is the most productive ecosystem which serves as feeding area, migration route, and nursery area of many juvenile and adult organisms from freshwater and marine water ecosystem. Due of these important to the ecosystem, effective remedial actions to minimize the pollution by metals need to be distinguished if pollution are expected occurs there [24].

2. Sediment as geo-marker for monitoring study

Marine sediments (**Figure 3**), 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 metal pollution evolution [25, 26]. Because of its unique characteristic, sediment always is considered as mirror of sedimentary environmental changes, which can reflect the biological, geodynamic, and geochemical processes of former conditions [27, 28]. On the other side, environmental changes are not only driven by natural forces but also by anthropogenic effects by human [29]. Some studies had concluded that the anthropogenic impacts on the environment have led to eutrophication process in coastal zone and offshore and the interaction of the natural force and human activities has exerted great effects on the whole environmental system[30].

Figure 3.
Sediment sample usually used by researchers as geo-marker for pollution study. Photo by Ong Meng Chuan.

Sediments can pick up metals due to several chemical process and normally will settle down in marine aquatic environment. Because of this characteristic, sediment can act as an appropriate indicator to monitor the metal pollution. In aquatic environment, these pollutants are originated from natural and anthropogenic sources in the same manner [31]; thus, scientists have difficulty to identify and classify the origin of these pollutants in the environment. Therefore, to overcome these obstacles, several scientists were using sediment fraction and characterized them into several sizes to normalize the metal concentration [31, 32]. The rationale applying this approach is normally metals are associated with fine-grain fraction because this fraction has larger surface area and higher cation exchange capacity that can enhance metal adsorption [33]. These fine sediments such as silt and clay with size less than $63\ \mu\text{m}$ (**Figure 3**) are categorized as the most geochemically active fraction in the sediment. With this characteristic, this fraction is suitable to determine the potential pollution in the sediment (**Figure 4**).

Because of their large adsorption capabilities, fine-grain sediments represent a major repository for metals and a record of the temporal changes in contamination. Thus, they can be used for historical reconstruction. Although metals can occur naturally in marine environment due to their presence in local rocks, it is difficult to differentiate whether the source of the metals comes from anthropogenic or natural sources. Therefore, for better understanding about the metal behavior and distribution, it is important to distinguish between metals released from natural processes and those anthropogenic mainly introduced by human activities.

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. This sediment characteristic can regulate the concentration of these minerals and compounds in the water column [34]. Marine sediment also plays a very important role in the physicochemical and ecological dynamics of metals in marine aquatic ecosystems. The physicochemical nature of sediment-bound metals is important in the bioaccumulation of aquatic organisms such as fishes and shellfish.

Figure 4.
Fine-grain sediments have high surface area-to-grain size ratio which can accumulate more metals in the sediment. Photo by Ong Meng Chuan.

Figure 5.
Sediment core collected from mangrove ecosystem to study the metal proxy and sediment accumulation rate.
Photo by Ong Meng Chuan.

Sediment quality has been recognized as an important and sensitive indicator or geo-marker of environmental pollution by various scientists [35, 36] since sediments can act as an important sink for various pollutants, such as metals that had been discharged into the environment [37, 38]. Besides acting as pollution indicator, sediments are also important in the remobilization process of contaminants in aquatic environment under favorable conditions through the interaction process between waste column and surface sediments. Due to this process, scientists had developed several comprehensive methods to identify and assess the sediment contamination mainly to protect the marine aquatic organisms [39].

Over the last few decades, the study of sediment cores has shown to be an excellent tool for establishing the effect of anthropogenic and natural processes on depositional environments. Meanwhile, sediment cores (**Figure 5**) can provide chronologies of contaminant concentrations and a record of the changes in concentration of chemical indicators in the environment. During the early 1960s, sediment profiles from depositional areas were used to trace human activity, witnessed by anthropogenic contamination like phosphorus [40], and later in the 1970s, it was possible to distinguish radioactive isotope inputs due to nuclear tests. Metal accumulation rates in sediment cores can reflect variations in metal inputs in a given system over long periods of time. Hence, the study of sediments core provides historical record of various influences on the aquatic system by indicating both natural background levels and the man-induced accumulation of metals over an extended period of time. In addition, the dating of sediment cores using radioactive traces like ^{210}Pb [41] permitted the precise quantification of the history of the inputs in a system [42].

3. Assessment of metal pollution level

The absolute concentration of metals in marine sediments never indicates the degree of contamination coming from either natural or anthropogenic sources because of its grain-size distribution and mineralogy characteristic [43, 44]. Normalization of metal concentrations to grain sizes, specific surface area, and reactive surface phases such as Li and Al is a common technique to remove artifacts

in the data due to differences in depositional environments [45–47]. This method allows researchers to compare the contamination level directly even if the samples were collected at different locations. The most common normalization technique used is enrichment factor (EF) where this technique uses common elements such as Al, Li, and Fe as normalizer and index of geoaccumulation (I_{geo}) or compares the normalized concentration to average crustal abundance data [47, 48].

In order to examine to sediment status, the determined element concentrations normally were compared to the published background concentrations. Literature data on average world shale or sediment cores or sediments from pristine such as undisturbed wetlands and non-industrialized regions were analyzed to establish the background values. However, to reduce the metal variability caused by the grain sizes and mineralogy of the sediments and to identify anomalous metal contribution, geochemical normalization has been used with various degrees of success by employing conservative elements [49, 50]. Researchers have proposed various elements as normalizer, and these elements have the potential for the environmental studies. Some of them are lithium, Li [51–53]; aluminum, Al [54, 55]; scandium, Sc [56]; cesium, Cs [57, 58]; cobalt, Co [59]; and thorium, Th [60, 61]. Among all proposed normalizers, conservative elements, Li and Al, have been widely applied in marine and coastal study [62–64].

The concentration of metals in marine sediments cannot indicate the degree of contamination coming from either natural or anthropogenic sources because of grain-size distribution and mineralogy [44, 65]. Normalization of metal concentrations to sediment size, specific surface area, and reactive surface phases such as Li and Al is a common technique to remove artifacts in the data due to differences in depositional environments [46, 66]. This allows for a direct comparison to be made between contaminant levels of samples taken from different locations.

Based on the researches by several geochemists [67, 68], if an EF value is between 0 and 1.5, it is suggested that the 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 metals has arisen from non-crustal sources or anthropogenic pollution [61, 69].

Another common approach to evaluate the metal pollution in sediments is the index of geoaccumulation (I_{geo}) introduced by Müller [70] in order to determine and define metal contamination in sediments by comparing current concentrations with the background levels. Similar to metal enrichment factor, I_{geo} can be used as a reference to estimate the extent of metal pollution in sediments. The I_{geo} value is calculated by using the following equation:

$$I_{geo} = \log_2 (C_n/1.5B_n) \tag{1}$$

where C_n is the measured concentration of the element (n) in the sediment and B_n is the geochemical background concentration of the element (n). Factor 1.5 is the correction of background matrix factor due to the lithogenic effects [70]. The upper continental crust values of the studied metals are the same as those used in the aforementioned enrichment factor calculation [71]. Müller [70] has distinguished seven classes of the I_{geo} from Class 0 to Class 6. The highest class (Class 6) reflects at least 100-fold environment above the background value.

Class	Value	Sediment quality
0	$I_{geo} \leq 0$	Practically uncontaminated
1	$0 < I_{geo} < 1$	Slightly contaminated
2	$1 < I_{geo} < 2$	Moderately contaminated

Class	Value	Sediment quality
3	$2 < I_{geo} < 1$	Moderately to heavily contaminated
4	$3 < I_{geo} < 1$	Heavily contaminated
5	$4 < I_{geo} < 1$	Heavily to extremely contaminated
6	$5 < I_{geo} < 1$	Extremely contaminated

Tomlinson et al. [72] elaborated that the application of pollution load index (PLI) provides a simple way in assessing marine and coastal sediment quality by metal pollution. This assessment is a quick tool in order to compare the pollution status of different places [73]. PLI represents the number of times by which the metal concentrations in the sediment exceed the background concentration and gives a summative indication of the overall level of metal toxicity in a particular sample or location [74, 75]. 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 [76]. In addition, it also provides valuable information to the decision-makers toward a better management on the pollution level in the studied region.

PLI is obtained as contamination factor (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:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times CF_4 \times CF_n)^{1/n} \tag{2}$$

where n is the number of metals studied and the CF is the contamination factor. The CF can be calculated from

$$CF = (\text{Metal concentration in samples} / \text{Background metal concentration}) \tag{3}$$

The PLI value more than 1 can be categorized as polluted, whereas less than 1 indicates no pollution at the study area [77, 78].

4. 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 [79, 80]. 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. [79] on sediment quality guidelines (SQGs) provides a useful tool for screening sediment chemical data to identify pollutants of concern and priorities problem sites (x). In their study, the toxicity range of these chemical pollutants in the sediments was estimated from experimental studies in the laboratory, observation, and measurement of these parameters in the field. The finding of the work can estimate the level of two pollutants that have high chances to give impact in adverse biological effect of 10 and 50% of biota population.

Using this approach, scientists classified the toxicity of metals into effect range low (ERL) and effect range median (ERM) concentrations [79]. The concentration value between ERL and ERM represents the intermediate range in which this concentration can give an impact in 10–50% of the organism populations. ERL indicates the chemical pollutant can be considered to be of minimal or low concern, and the adverse effects toward organisms are infrequently observed (<10%

impact on organisms population) if the concentrations are below the ERL value. On the other hand, ERM indicate that if the concentration is above this level which the significant effect can be observed in 50% or more of the organism population considered to be toxic and of significant concern.

5. GIS application in environmental study

Nowadays, the rapid developments of computer technology and geographical information system (GIS) are receiving increasing interest in environmental geochemistry study [81]. This method is becoming popular nowadays in marine environmental pollution studies to graphically and digitally present the distribution of metals in marine environments by using GIS technique [82, 83]. The spatial interpolation methods of geometrical interpolation, trend surface analysis, and kriging method are commonly used [84]. This base chemometric approach was applied to investigate the spatial distribution patterns of metals in marine sediment and to identify spatial human impacts on global and local scales [85, 86].

GIS is a tool for decision-making, using information stored in a geographical form, in this case, in isopleth map form. Some researchers defined major requirements and function of GIS and mentioned spatial data handling tool for solving complex geographical problems [87, 88]. This GIS approach 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 [89]. On the regional and national scales, the geochemical mapping of metals can be used as a tool for visualization which is enhanced by computer-aided modeling 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 [90], soil [91], and nonpoint source identification [92].

6. Organisms as biomarker for monitoring study

Marine aquatic organisms can accumulate metals from various sources in their surrounding environment. The possible sources of these metals include sediments and soil erosion [93, 94], air depositions of dust and aerosol [93, 95], and discharges of wastewater [93, 94]. The accumulation of metals in marine aquatic organisms can pose a long-term burden on biogeochemical cycling in the ecosphere [96]. Once the metals enter the food chain, they may accumulate to dangerous levels and be harmful to human health.

Shellfish species which are laying at the second trophic level in the aquatic ecosystem have long been known to accumulate both essential and nonessential metals. Many researchers have reported the potentiality of using mollusks, especially mussel and oyster species, as bioindicators or biomarkers for monitoring the metal contamination of the aquatic system [97, 98]. Besides being a biomarker for marine pollution studies, these mollusk species have also been used in ecotoxicology and toxicity studies. Individual biomonitors respond differently to different sources of bioavailable chemical elements, for example, in the solution, in sediments, or in foods. In order to conclude a complete picture of total metal bioavailability in a marine habitat, it is necessary, therefore, to use a correct biomonitor that can reflect the metal bioavailability in all available potential sources [99]. Such comparative use of different biomonitors should allow identification of the particular source of the contaminant elements [100] (**Figure 6**).

Figure 6.
Shellfish (left, green mussel; right, oyster) are commonly used as biomonitor to study the pollution status.

Metal accumulation in marine aquatic organisms depended on several factors, including the environmental concentrations of metals in water and sediments; the species of organisms; and body size and age of the marine organisms. Different concentrations of metal can also be found in different organs (stomach, gill, muscle, tissue) in the same biological sample [101, 102]. However, scientists mainly focused on the general metal burden in shellfish species such as oyster and mussel and the potential major pathways for metal contaminant in the coastal environment.

7. Choice of biomonitors for environmental study

Aquatic 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 during feeding process [103]. When the pollutants enter the organism body, some contaminants can quickly pass through several organs; however, some may be absorbed and accumulated in organism tissues, particularly fatty tissues [104]. Certain contaminants such as mercury and PCBs are easily dissolve in organism fats and oils but do not dissolve in water. Due to the organism metabolism process, bioaccumulation process can be clearly seen in carnivorous animals in higher tropic of food chain, ranging from big organism such as fishes and to human [105].

The choice of a suitable biomonitor needs to consider the potential sources of metals to the organism. For example, sea grass not in contact with sediments, therefore, will take up metals from dissolved sources only [99]. Suspension feeders take up metals both directly from seawater and from the suspended particles collected during feeding. Thus, mussels, oysters, and barnacles are all candidates as suspension feeding biomonitors, and a careful choice will differentiate between suspended particles of different size ranges. As a generalization, sessile barnacles, but not stalked barnacles, have evolved micro-feeding, 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 [106].

Deposit feeding bivalves will reflect the bioavailability of metals in the surrounding water via respiratory currents but also metal bioavailability in newly deposited particles, for they suck up such particles via the inhalant siphon during feeding [107]. 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 [108].

As concluded by monitoring scientists [109, 110], species to be chosen as bio-monitors should fulfill several criteria such as:

- i. Sedentary organism or those fixed in one spot
- ii. Easy to identify the species
- iii. Abundant
- iv. Long-lived
- v. Available for all the time
- vi. Large enough to provide sufficient sample
- vii. Resistant to handle the organisms' stress during test preparation
- viii. Adapt to environmental variations in physicochemical parameters such as salinity and temperature

8. Organisms as laboratory testing organisms

Besides using the organisms as a biomarker for metal pollution studies in the field, mollusk species also have been used in ecotoxicology and toxicity studies in the laboratory. Several criteria had been set in order to choose suitable organisms as testing organisms. Despite that, in order to achieve the objectives, these testing organisms should fulfill several criteria as follows:

- i. Organisms should be commercially important and sensitive to the environment.
- ii. Organism must be easy to obtain and maintain in the laboratory.
- iii. Biology, feeding behavior, and their characteristic of the organism must be known.
- iv. Organism must be healthy and free from disease.
- v. Organisms should be acclimatized for at least 2 weeks before use.
- vi. Mortality of organism in control tank must be less than 10%. If more than 10% mortality, the testing should be repeated.

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Conflict of interest

The authors certify that they have no conflict of interest during preparation of this chapter.

Notes/thanks/other declarations

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