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Assessing Risk and Sustainable Solutions

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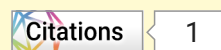
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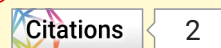


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Ong Meng Chuan and Kamaruzzaman Yunus

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Abstract

Metals pollution has drawn worldwide attention due to increase of anthropogenic contaminants to the coastal area, especially wetlands area. Metals are indestructible and have toxic effects on living organisms. Sediment can act as an indicator of metals pollution due to the ability of the sediment that can trap metals through complex physical and chemical process. Therefore, they are always used as geo-marker for identifying the possible source of metals pollution. Besides that, wetlands such as mangrove have a diverse diversity of organisms that provide proteins to local communities such as clam, oyster, crab, and fishes. Therefore, it is important for us to know the levels of metals in the sediment and those organisms that we consume nowadays that live at the mangrove area. Such findings can provide important information on the seafood safety level and potential impact especially to humans via consumption according to the provisional tolerable weekly intake and daily intake.

Keywords: metals, sediments, geo-marker, organisms, permissible level

1. Introduction

Wetlands ecosystem such as mangrove ecosystem can be defined as the interface between land and sea in tropical and sub-tropical latitude where the mangrove plant can survive in conditions of high salinity, strong winds, extreme high and low tides, high temperature, and anaerobic muddy soils (**Figure 1**). This well-developed morphological and physiological adaptation to these extreme conditions is not present in other groups of plants [1]. Due to these extreme conditions, mangrove ecosystem is rich in biodiversity and constitutes a unique fauna and flora, above the sediment and underneath the sediment.



Figure 1. Tropical wetlands ecosystem in Malaysia. Photo by Ong Meng Chuan.

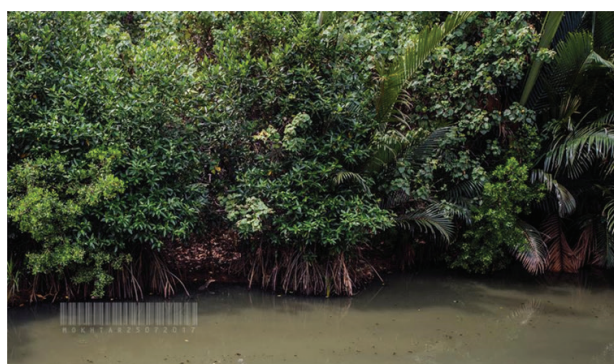


Figure 2. Tropical mangrove ecosystem that can be found in Malaysia coastal. Photo by Mokhtar Ishak.

Mangrove forests such as *Rhizophora* sp. (**Figure 2**) are important ecosystems ecologically and economically toward human beings and organisms that live in the mangrove area. These forests provide breeding and feeding ground for various aquatic organisms such as fishes, shellfishes, reptiles, and some land organisms such as monkeys and snakes. For example, some fishes such as sea bass, the juvenile will stay in this mangrove area before they move to the ocean when they were adult. Besides that, mangrove forest also plays an important role in protecting shorelines from erosion or in some places, minimizing the strong current from tsunami. This protection indirectly can protect the communities that live in coastal area.

2. Metals pollution

Unlike other pollutants, which may be visibly buildup in the environment, trace metals in the environment may accumulate unnoticed to toxic levels. These metals pollutants in the aquatic environment can come from natural or anthropogenic sources. Metals are serious pollutant in our natural environment due to their toxicity, persistence, and bioaccumulation problems

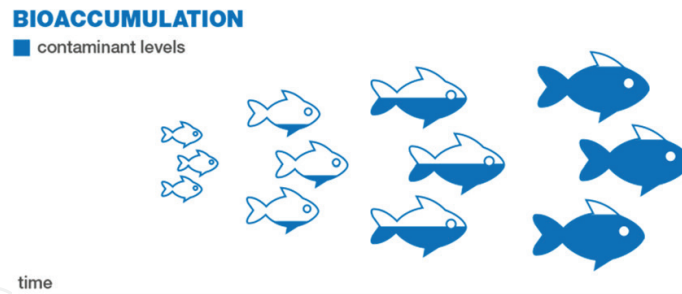


Figure 3. Bioaccumulation process of metals concentration in fish. Picture adapted from <http://www.hydro-industries.co.uk/case-studies.htm?id=10> [2].

(Figure 3). Some are highly toxic and persistent, and have a strong tendency to become concentrated in marine food webs. Excess of these metal levels in aquatic environment may pose a health risk to humans and to the environment.

Organisms require certain trace amounts of some metals, including cobalt, copper, iron, manganese, and zinc in their growth process. Excessive levels of essential metals in the environment, however, can be detrimental to the organism itself. Besides that, nonessential metals of particular concern to surface water systems are cadmium, chromium, mercury, lead, and arsenic, and these metals have no biological function. Metals pollution in aquatic environment can be categorized into four major groups [3] according to their pollution potential:

- i. Very high pollution potential—Ag, As, Cd, Cr, Cu, Hg, Pb, Sb, Sn, Te, and Zn
- ii. High pollution potential—Ba, Bi, Ca, Fe, Mn, Mo, Ti, and U
- iii. Moderate pollution potential—Al, Au, B, Be, Br, Cl, Co, F, Ge, K, Li, Na, and Ni
- iv. Low pollution potential—Ga, I, La, Mg, Nb, Si, Sr, Ta, and Zr

3. Geochemical mapping

Distribution of metals in surficial sediments from industrial effluents and urban sewage discharged into the wetlands ecosystem and aquatic environment without proper cleaning can easily be identified through metals spatial variations in sediments. Geochemical mapping can be used as a tool for visualization, which enhanced by computer-aided modeling using geographical information system (GIS) to make it easier to identify the possible locations of contaminated area. Nowadays, due to the rapid developments of computer technology, GIS applications are receiving increasing interest in environmental geochemistry study [4, 5]. 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 modeling (Figure 4).

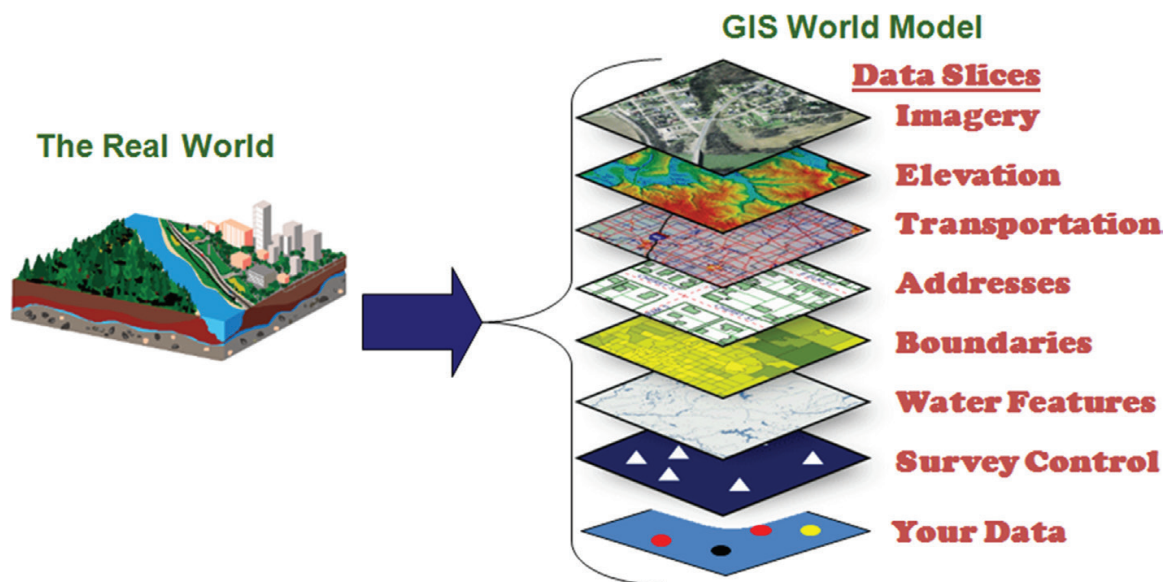


Figure 4. Example of geographical information system (GIS) mapping in environmental studies. Photo adapted from <https://technofaq.org/posts/2017/07/thoughts-on-the-future-of-gis-what-will-change-in-50-years/> [6].

GIS is a tool for decision making, using information stored in a geographical form. Some researchers defined major requirements and functions of GIS and mentioned spatial data handling tool for solving complex geographical problems [7–9]. Besides, GIS is increasingly used in environmental pollution studies because of its ability in spatial analysis and interpolation,

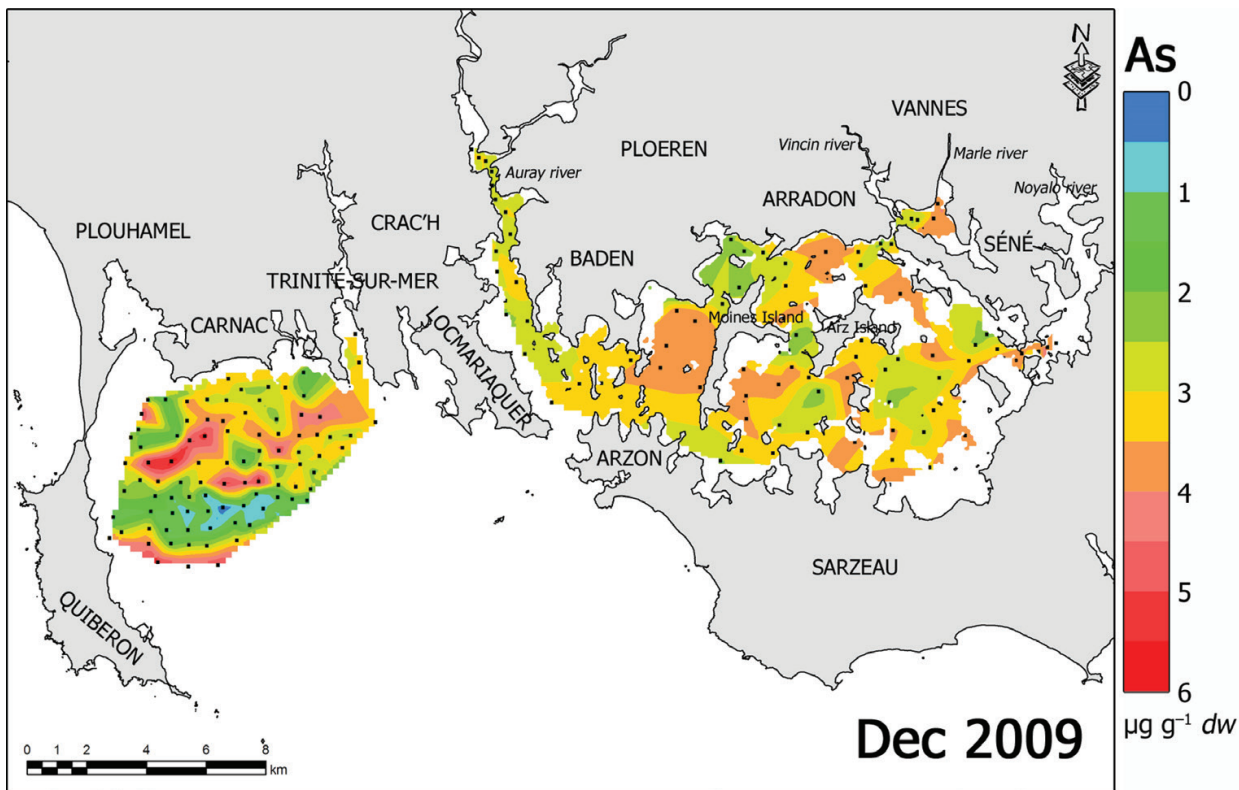


Figure 5. Concentration of Arsenic (As) in sediment of South Brittany waters (Bay of Quiberon and Gulf of Morbihan), France. Figure by Ong Meng Chuan using ArcGIS software 9.3.

and spatial interpolation utilizes measured points with known values to estimate an unknown value and to visualize the spatial patterns [10, 11]. For example, **Figure 5** shows the concentration map of Arsenic in surficial sediment from South Brittany waters analyzed by using ArcGIS software 9.3.

4. Sediment as geo-marker

Sediments are widely used as geo-markers for monitoring and identifying the possible sources of pollution in the coastal environments since sediments are the main sink for various pollutants (**Figure 6**). Sediments can 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. Most metals are bound in the fine-grained fraction ($<63\ \mu\text{m}$), mostly because of its high surface area-to-grain size ratio and humic substance content, where they have a potentially greater biological availability than those in the larger ($2\ \text{mm}$ – $63\ \mu\text{m}$) sediment fraction.

Meanwhile, sediment cores (**Figure 7**) can provide chronologies of contaminant concentrations and a record of the changes in concentration of chemical indicators in the environment. 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.

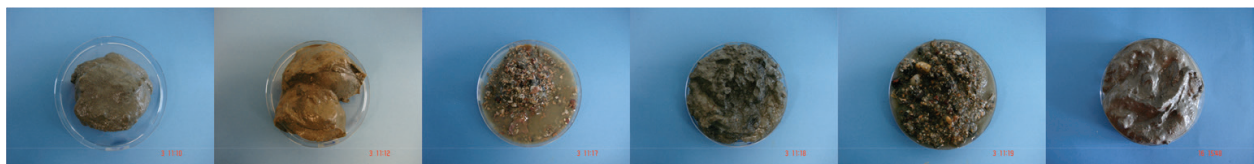


Figure 6. Different types of sediment can be collected from wetlands ecosystem. Photo by Ong Meng Chuan.



Figure 7. Core sample collected from mangrove environment used for metals proxy study. Photo by Ong Meng Chuan.

5. Assessment of sediment pollution status

To evaluate the metals contamination in sediment, determined element concentrations were compared with background concentrations. Literature data on average world shale or sediment cores or sediments from pristine such as undisturbed wetlands, non-industrialized regions were analyzed to establish the background values. However, to reduce the metals variability caused by the grain sizes and mineralogy of the sediments, and to identify anomalous metals contribution, geochemical normalization has been used with various degrees of success by employing conservative elements [12, 13]. 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 [14–16]; aluminum, Al [17, 18]; scandium, Sc [19]; cesium, Cs [20, 21]; cobalt, Co [22]; and thorium, Th [23, 24]. Among above conservative elements, Li and Al have been widely applied in wetlands and mangroves study [25–27]. Li also has been proposed by Loring [14] 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 metals pollution [14] because of several factors, namely, it is a lattice component of fine-grained major trace-metal-bearing minerals such as the phyllosilicates and clay minerals; it reflects the granular variability of its host mineral component, and it is a conservative element.

The absolute concentration of metals in marine sediments never indicates the degree of contamination coming from either natural or anthropogenic sources because of grain-sizes distribution and mineralogy [26, 28, 29]. Normalization of metals 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 [30–34]. 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) [35–37]. The EF value can be calculated according to the following formula:

$$\text{Enrichment Factor (EF)} = \frac{(\text{Metal concentration/Normalizer})_{\text{sample}}}{(\text{Metal concentration/Normalizer})_{\text{background}}}$$

Based on the researches by several geochemists [38–41], 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 have arisen from noncrustal sources or anthropogenic pollution [24, 42].

Another commonly used criterion to evaluate the heavy metals pollution in sediments is the index of geoaccumulation (I_{geo}) originally introduced by Muller [43] in order to determine and define heavy metals 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} is defined by the following equation:

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

where C_n is the measured concentration of the examined element (n) in the 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 [43]. The upper continental crust values of the metals of interest are the same as those used in the aforementioned enrichment factor calculation [44]. Muller [43] 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 (**Table 1**).

Tomlison et al. [45] elaborated that the application of pollution load index (PLI) provides a simple way in assessing mangrove, estuarine, and coastal sediment quality. This assessment is a quick tool in order to compare the pollution status of different places [46]. PLI represents the number of times by which the metal concentrations in the sediment exceed the background concentration, and give a summative indication of the overall level of metals toxicity in a particular sample or location [47, 48]. 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 [49]. 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 factors (CFs). 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:

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

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

$$CF = (\text{Metals concentration in samples} / \text{Background metals concentration})$$

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
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	$5 < I_{geo} < 6$	Extremely contaminated

Table 1. Classification of sediment quality based on I_{geo} value.

The PLI value more than 1 can be categorized as polluted whereas less than 1 indicates no pollution at the study area [50, 51].

6. Aquatic organisms as biomarker

Lying in the second trophic level in the aquatic ecosystem, shellfish species 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 bio-indicators or bio-markers for monitoring the metals contamination of the aquatic system (**Figure 8**). Besides as a bio-marker for marine pollution studies, mollusks species also been used in ecotoxicology and toxicity studies. 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 metals 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 [52]. Such comparative use of different bio-monitors should allow the identification of the particular source of the contaminant elements [53].

Living organisms in aquatic environment 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 feed [54]. Once in the body, some contaminants pass quickly while others can be retained for long periods and accumulate in body tissues, particularly fatty tissues [55]. 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 [56].



Figure 8. Some examples of organism commonly used for environmental biomonitoring study. Photo by Ong Meng Chuan.

7. Tolerable intake

Beside fishes, shellfish such as oysters and mussels are an important source of dietary protein in coastal communities. Depending on consumer, those shellfish can be “swallowed” or masticated normally, increasing the surface contact between food and digestive fluids. The consumer will consume whole soft part of the shellfish (**Figure 9**); therefore, in the pollution study which relates to human health, the metals content is examined in toto or shellfish flesh.

To safeguard public health, who consumes these organisms, maximum acceptable concentrations of toxic contaminants have been established in various countries. As a result, there is a specific legislation for shellfish, which establishes the maximum allowed concentration for metals (**Table 2**).



Figure 9. Oyster in toto tissue use for metals study in relation to human health. Photo by Ong Meng Chuan.

	Cu	Zn	Cd	Pb	As	Hg	References
Shellfish							
European community	n.m.	n.m.	1	1.5	n.m.	0.5–1.0	[57]
Spain	20	n.m.	1	5	n.m.	0.5	[58]
Australia	30	150	2	2	1	0.5	[59]
China	n.m.	n.m.	0.1	0.5	1.0	0.3	[60]
Hong Kong	n.m.	n.m.	2	6	1.4	0.5	[61]
Singapore	n.m.	n.m.	1	2	1	0.5	[62]
Food category not specific							
Malaysia	30	50	1	2	n.m.	0.5	[63]
Thailand	20	133	n.m.	1.0	2	0.5	[64]
Brazil	30	50	1	2	n.m.	0.5	[65]

n.m.: not mentioned.

Table 2. Maximum permissible levels (expressed in mg/kg wet weight) of metals in shellfish from different countries or regions.

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 establishing acceptable of tolerable intakes of substances that exhibit thresholds of the toxicity of contaminants. JECFA derives tolerable intakes, expressed on either daily or weekly basis, for contaminants [66]. Lead, Cd, As, and Hg are not removed rapidly from human body and for this category of pollutants, provisional tolerable weekly intakes (PTWIs) are calculated and expressed on a weekly basis because the pollutant may accumulate within the human body over a period of time [67]. The term tolerable is used because it signifies permissibility rather than acceptability for the pollutants intake unavoidably associated with the consumption.

8. Conclusion

Wetlands are well known to researcher as an ecosystem that are highly sensitive to pollution effects and can change the ecosystem's biogeochemistry process. Sediment and organisms from wetlands ecosystem are important to describe the environmental quality that act as geo-marker and biomarker, respectively. The assessment of metals pollution in the ecosystem has been carried out in different parts of the world and represents the impact of human activities toward the ecosystem. Although some of the metals are present in low concentration, their impacts on wetland ecosystems are significant because of their toxicity especially toward organisms and human. Due to the importance of wetlands to us, it is important to evaluate and monitor the ecosystem health and understand their contamination status to maintain the stability of the environment.

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Conflict of interest

The authors whose names are listed immediately below certify that they have no affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or nonfinancial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

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Author details

Ong Meng Chuan^{1*} and Kamaruzzaman Yunus²

*Address all correspondence to: ong@umt.edu.my

1 School of Marine and Environmental Sciences, Universiti Malaysia Terengganu, Kuala Nerus, Terengganu, Malaysia

2 Kuliyah of Science, International Islamic University Malaysia, Kuantan, Pahang, Malaysia

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