Eco. Env. & Cons. 27 (February Suppl. Issue) : 2021; pp. (S376-S380)
Copyright@ EM International
ISSN 0971–765X

Sediment 'easily, freely, leachable or exchangeable' as a potential geochemical fraction of copper bioavailability and contamination in the aquatic environment: Potentials and some notes

Chee Kong Yap[1]*, Rosimah Nulit[1], Wan Hee Cheng[2], Shih Hao Tony Peng[3] and Chee Wah Yap[4], Moslem Sharifinia[5] and Hideo Okamura[6]

[1]Department of Biology, Faculty of Science, Universiti Putra Malaysia 43400 UPM, Serdang, Selangor, Malaysia
[2]Inti International University, Persiaran Perdana BBN, Nilai, Negeri Sembilan, Malaysia
[3]All Cosmos Bio-Tech Holding Corporation, PLO650, Jalan Keluli, Pasir Gudang Industrial Estate, 81700 Pasir Gudang, Johor, Malaysia
[4]MES SOLUTIONS, 22C-1, Jalan BK 5A/2A, Bandar Kinrara, 47100 Puchong, Selangor, Malaysia
[5]Shrimp Research Center, Iranian Fisheries Science Research Institute, Agricultural Research, Education and Extension Organization (AREEO), Bushehr, Iran
[6]Faculty of Maritime Sciences, Graduate School of Maritime Sciences, Kobe University, Kobe, Japan

(Received 24 September, 2020; accepted 30 November, 2020)

ABSTRACT

The present study aimed to assess the potential of 'easily, freely, leachable or exchangeable' (EFLE) geochemical fraction in the surface sediments as a potential Cu bioavailability in the aquatic environment in relation to its total Cu concentration. Although the basis of this suggestion is merely based on the relationship between Cu EFLE and total concentrations of Cu in the surface sediments, it is still a potential indicator because the relationships are based on different aquatic ecosystems including offshore, intertidal, polluted urban lake, a polluted river and rivers and drainages. In addition, the use of a biomonitor (Snail *Pomacea insularum*) as an indicator of Cu bioavailability of the polluted site, agreeing with the higher EFLE geochemical fraction of Cu of the polluted sediment. Hence, Cu EFLE geochemical fraction in the surface can be suggested as a potential indicator of Cu bioavailability and contamination in the aquatic ecosystem, even though further studies are required.

Key words: *Bioavailability, Copper, Sediment, Biomonitor.*

Introduction

For a better environmental management, simple and cheap methodology is preferred. In this study, the potential of Easily, Freely, Leachable or Exchangeable (EFLE) Cu as a direct indicator of Cu contamination and bioavailability that could pose immediate effect on living organisms was investigated. The EFLE fraction of metals in the sediments accounts for the metals adsorbed to the negatively charged surfaces or clay minerals or organic matter and those easily soluble (Badri and Aston, 1981).

This geochemical fraction is therefore of ecotoxicological significance and any metal concentrations found in this fraction should be of the most readily posing the immediate effects on the biota living above them.

The use of biomonitor (single species) to indicate the bioavailability of heavy metals have been wide established since 1990s. Several papers on the similar topic have been published from Southeast Gulf of California (Ruelas-Inzunza and Páez-Osuna, 2000); Malaysia (Yap *et al.*, 2006, 2009; Yap, 2018), Isle of Man (Gibb *et al.*, 1996), UK (Rainbow *et al.*, 2002), Gulf of Suez (Hamed and Emara, 2006), and Black Sea (Romania) (Romeo *et al.*, 2005).

Even though total metal concentration in sediments had been widely reported in the literature (Yap *et al.*, 2002), total metal concentrations in sediment receive argument that they cannot provide the phase which is bioavailable to living organisms. One of the ways to assess the speciation of metals bound to sediments, especially EFLE geochemical fraction of the metals, has been proposed by Badri and Aston (1983).

It is only a biomonitor (any living organism) can represent an integrated measure of the metal bioavailability (Rainbow, 1995; Rainbow *et al.*, 2002). The heavy metals are present in different chemical forms in sediments such as easily exchangeable ions. This would regulate the capacity of their mobilization and metal bioavailability (Lopez-Sanchez *et al.*, 1996; Weisz *et al.*, 2000; Yu *et al.*, 2001; Morillo *et al.*, 2002). In this study, samples were geochemically fractionated for EFLE fraction, which is known to be bioavailable to living organisms (Badri and Aston, 1983).

Theobjective of the present study is to assess the potential of EFLE to be used as a Cu bioavailability in the aquatic environment in relation to total Cu concentration.

Materials and Methods

The Cu data in the different tissues of *Pomacea insularum* between a polluted site at Kuala Juru and unpolluted sites at Universiti Putra Malaysia (UPM) were cited from Yap *et al.* (2009), in which the samples were collected between July-October 2007. Table 1 shows the sources of Cu data cited from different citations that are used in the present study.

Sepang River collected from 2003 were cited from Yap *et al.* (2007a), Kelana Jaya urban lakes collected in 2003 from Ismail *et al.* (2004) while rivers and drainages from Peninsular Malaysia from Yap *et al.* (2007b). Offshore of the west coast of Peninsular Malaysia (The Straits of Malacca) collected from 1998-1999, and intertidal area of the west coast of Peninsular Malaysia collected from 1999-2001 were cited from Yap *et al.* (2002). Briefly, the Cu analysis followed that by Yap *et al.* (2002) while Cu EFLE geochemical fractionfollowed that by Badri and Aston (1983). These total Cu concentrations in the surface sediments were plotted against Cu EFLE geochemical fractions, by using KaleidahGraph (Version 3.08 by Synergy Software).

Results and Discussion

Relationships between Cu total concentrations and EFLE geochemical fractions of Cu, based on Urban lakes, Sepang River, intertidal area, offshore area,

Table 1. Cu data cited from different citations that are used in the present study.

No.	Site	Specific area covered	Year of sampling	Anthropogenic sources	Reference
1.	Offshore	Shipping lines of the Straits of Malacca from Langkawi to Kukup Island	1998-1999	Shipping and offshore dumping	Yap *et al.* (2002)
2	Intertidal 1999-2001	West coast of Peninsular Malaysia	1999-2001	Industries, mining and domestic wastes.	Yap *et al.* (2002)
3.	Sepang River	Sepang River and its tributaries Rambai River and Pelanduk River	2003	Farming and agriculture	Yap *et al.* (2007a)
4.	Urban Lakes	Kelana Jaya urban lakes	2003	Domestics and highway runoff	Ismail *et al.* (2004)
5.	Rivers and drainages	Major cities in Peninsular Malaysia including Alor Setar and Shah Alam	2005	Highway runoff, urban and industries.	Yap *et al.* (2007b)

and rivers and drainages are presented in Figure 1. In Figure 1, the highest relationships of Cu between EFLE and total Cu concentrations were found in 1999-2001 intertidal sediments (R= 0.97), Sepang River sediments (R= 0.85), urban lakes (R= 0.80) river and drainage sediments (R= 0.75) and offshore sediments (R= 0.68). These high R values strongly support the use of EFLE geochemical fraction as a potential indicator of Cu bioavailability of the sampling site.

Mean Cu concentrations of Cu in the different tissues of *Pomacea insularum* between a polluted site at Kuala Juru and an unpolluted site at UPM are given in Figure 2. It is clearly shown that the Cu levels in shell, remainder, cephalic tentacle, foot, mantle, operculum, lung sac, pineal sac and digestive tract

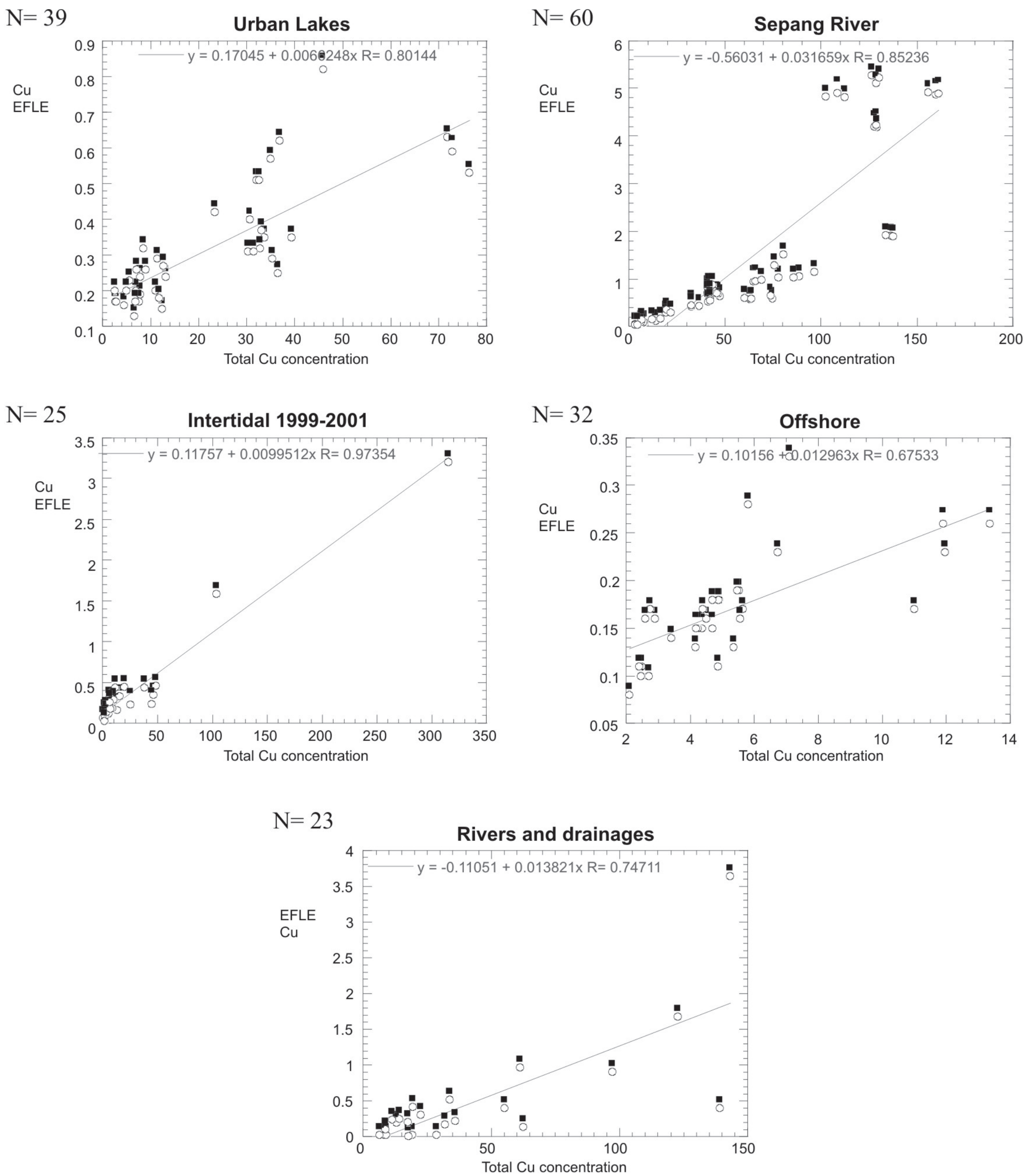

Fig. 1. Relationships between Cu total concentrations and 'easily, freely, leachable or exchangeable' (EFLE) geochemical fractions of Cu, based on Urban lakes, Sepang River, intertidal area, offshore area, and rivers and drainages.

of snail *P. insularum* are higher in the polluted site at Kuala Juru than those in UPM. This indicated the higher bioavailability of Cu in Kuala Juru to *P. insularum* than that in UPM. Biomonitor*P. insularum* is useful due to facts that they can be used to measure bioavailable metals that are taken up from their habitat (Yap *et al*., 2009). They provide integrated measure of the bioavailable metals which are of ecotoxicological significance in a habitat (Rainbow *et al*., 2002). There is a simple correlation between metal concentration in body tissues and average ambient bioavailable metal concentration over a recent period in the biomonitor (Rainbow, 1995; Rainbow *et al.*, 2002).

Table 2. Mean concentrations (mg/kg dry weight) of Cu in the different tissues of *Pomacea insularum* between a polluted site at Kuala Juru and an unpolluted site at UPM.

Parts	Juru River	UPM
Shell	8.0	7.4
Remainder	118	43.8
Cephalic tentacle	95.6	55.4
Foot	128	44.6
Mantle	129	65.6
Operculum	11.8	10.8
Lung sac	144	54.6
Pineal sac	35	33.1
Digestive tract	168	73
Sediment total Cu	82.9	24.6
Sediment Cu EFLE	0.43	0.21

Note: *= all data were cited from Yap *et al.* (2009), in which the samples were collected between July-October 2007. Sediment data are unpublished data.

This is the first point to support the use of EFLE Cu as an indicator of Cu pollution since it is highly correlated between the total Cu levels and EFLE Cu levels. The advantages of using EFLE fraction as an indicator of Cu pollution include wet acid digestion is not needed, there is significant correlation ($P< 0.001$) between EFLE and total concentrations of Cu, elevated concentrations of EFLE Cu is more related to anthropogenic sources than total concentrations or even the non-resistant (anthropogenic) fractions and in the surrounding activities of the sampling sites.

Future studies are needed to better recognise the sources, transport processes (such as atmospheric pathways and sediment resuspension) and biological or chemical reactivity of Cu in the intertidal area of Peninsular Malaysia.

Conclusion

In conclusion, the Cu EFLE geochemical fraction in the surface sediment is a potential indicator of Cu bioavailability in the aquatic ecosystem. Although the basis of this suggestion is merely based on the relationship between Cu EFLE and total concentrations of Cu in the surface sediments, it is a potential indicator because the relationships are based on different aquatic ecosystems including offshore, intertidal, polluted urban lake, a polluted river and rivers and drainages. In addition, the use of a biomonitor (*P. insularum*) as an indicator of Cu bioavailability of the polluted site, agreeing with the higher EFLE geochemical fraction of Cu of the polluted sediment. Hence, Cu EFLE geochemical fraction in the surface can be suggested as a potential indicator of Cu bioavailability and contamination in the aquatic ecosystem.

References

Badri, M. A. and Aston, S. R. 1983. Observation on heavy metal geochemical associations in polluted and non-polluted estuarine sediments. *Environ. Pollut. Ser.B.* 6 : 181-193.

Gibb, J., Allen, J.R. and Hawkins, S.J. 1996. The application of biomonitors for the assessment of mine-derived pollution on the west coast of the Isle of Man. *Mar. Pollut. Bull.* 32 : 513-519.

Hamed, M.A. and Emara, A.M. 2006. Marine molluscs as biomonitors for heavy metal levels in the Gulf of Suez, Red Sea. *Mar. Sys.* 60 : 220-234.

Ismail, A., Yap, C.K. and Chan, F.F. 2004. Concentrations of Cd, Cu and Zn in sediments collected from urban lakes at Kelana Jaya, Peninsular Malaysia. *Wetland Sci.* 2(4): 248-258.

Lopez-Sanchez, J. F., Rubio, R. Samitier, C. and Rauret, G. 1996. Trace metal partitioning in marine sediments and sludges deposited off the coast of Barcelona (Spain). *Wat. Res.* 30: 153-159.

Morillo, J., Usero, J. and Gracia, I. 2002. Partitioning of metals in sediments from the Odiel River (Spain). *Environ. Int.* 28 : 263-271.

Rainbow, P. S. 1995. Biomonitoring of heavy metal availability in the marine environment. *Mar. Pollut. Bull.* 31 : 183-192.

Rainbow, P.S., Smith, B.D. and Lau, S.S.S. 2002. Biomonitoring of trace metal availabilities in the Thames estuary using a suite of littoral biomonitors. *Mar. Biol. Assoc. UK.* 82 : 793-799.

Romeo, M., Frasila, C., Gnassia-Barelli, M., Damiens, G., Micu, D. and Mustata, G. 2005. Biomonitoring of trace metals in the Black Sea (Romania) using mussel *Mytilus galloprovincialis*. *Wat. Res.* 39 : 596-604.

Ruelas-Inzunza, J.R. and Páez-Osuna, F. 2000. Comparative bioavailability of trace metals using three filter-feeder organisms in a subtropical coastal environment (Southeast Gulf of California). *Environ. Pollut.* 107 : 437-444.

Weisz, M., Polyak, K. and Hlavay, J. 2000. Fractionation of elements in sediment samples collected in rivers and harbours at lake Balaton and its catchment area. *Microchem. J.* 67 : 207-217.

Yap, C.K., Ismail, A., Tan, S.G. and Omar, H. 2002. Concentrations of Cu and Pb in the offshore and intertidal sediments of the west coast of Peninsular Malaysia. *Environ. Int.* 28 : 467-497.

Yap, C.K. 2018. Selected organs of marine mussels as accurate biomonitors of metal bioavailability and contamination in the coastal waters: Challenges. *EC Pharmacol. Toxicol.* 6 (7) : 528-534.

Yap, C.K., Edward, F.B., Pang, B.H., Ismail, A., Tan, S.G. and Jambari, H.A. 2009. Distribution of heavy metal concentrations (Cu, Cd, Zn, Pb, Ni and Fe) in the different soft tissues of *Pomacea insularum* and sediments collected from a polluted site at Juru River, Penang. *Toxicol. Environ. Chem.* 91 (1): 17–27.

Yap, C.K., Ismail, A., Edward, F.B., Tan, S.G. and Siraj, S.S. 2006. Use of different soft tissues of *Perna viridis* as biomonitors of bioavailability and contamination by heavy metal (Cd, Cu, Fe, Pb, Ni, and Zn) in a semi-enclosed intertidal water, the Johore Straits. *Toxicol. Environ. Chem.* 88 (1-4) : 683-695.

Yap, C.K., Noorhaidah, A., Azlan, A., NorAzwady, A.A., Ismail, A., Ismail, A.R., Siraj, S.S. and Tan, S.G. 2009. *Telescopium telescopium* as potential biomonitors of Cu, Zn, and Pb for the tropical intertidal area. *Ecotox. Environ. Saf.* 72 : 496-506.

Yap, C.K., Ismail, A., Low, C.H. and Tan, S.G. 2007a. Interpretation of Cu and Zn contamination in the aquatic environment of Peninsular Malaysia with special reference to a polluted river, Sepang River. *Wetland Sci.* 5(4) : 311-321.

Yap, C.K., Pang, B.H., Fairuz, M.S., Hoo, Y.I. and Tan, S.G. 2007b. Heavy metal (Cd, Cu, Ni, Pb and Zn) pollution in surface sediments collected from drainages receiving different anthropogenic sources from Peninsular Malaysia. *Wetland Sci.* 5 (2) : 97-104.

Yu, K. C., Tsai, L. J., Chen, S. H. and Ho, S. T. 2001. Correlation analysis on binding behaviour of heavy metals with sediment matrices. *Wat. Res.* 35 : 2417-2428.