INTERNATIONAL JOURNAL OF ENVIRONMENTAL SCIENCES Volume 6, No 1, 2015

Research article **ISSN 0976 – 4402**

Chemical speciation of copper and cadmium in Kameng river sediments using sequential extraction procedure

Bidyut Bikash Sharma[1], Hari Prasad Sarma[1], Lukumoni Borah[2]
1- Department of Environmental Science, Gauhati University, Guwahati-781014, India
2- Department of Chemical Engineering, Indian Institute of Technology, Guwahati -781039, India
bidyut.bikash.sarma@gmail.com
doi:10.6088/ijes.6010

ABSTRACT

Kameng River is a major north bank tributary of the Brahmaputra River and it originates in the Himalayas. The Kameng river traverses through West Kameng and East Kameng districts in Arunachal Pradesh and happens to be the lifeline of the scattered human population within the river basin. To understand the behavior of toxic trace elements in the bed sediments, chemical speciation studies are commonly applied. In this study a modified sequential extraction procedure was applied to study the geochemical partitioning of Cu and Cd in the sediments, their bioavailability and also the degree of risk associated with their remobilization from the sediment matrix. Cadmium was found to be highly associated with the labile fraction in all the sampling sites and thus posed a high risk of remobilization in the water system. Risk assessment criteria applied to the experimental data also suggested high risk of toxicity to living beings due to Cd bioavailability. Cu was found to poses low to medium risk owing to its affinity to the residual and non-labile phases.

Keywords: Chemical speciation, Bioavailability, SEP, Risk assessment criteria

1. Introduction:

Sediments are generally described as indicators of heavy metal pollution. Metals originating from both natural and anthropogenic sources can contaminate aquatic ecosystems. The sediment in such environment not only acts as scavenging agent but also as adsorptive sink for heavy metals (Okoro et al., 2012), The threats from sediment contaminants arise when bioaccumulation occurs in aquatic organisms which in turn are consumed by man (Mulligan et al., 2001), Skin lesions, reproductive disorders in fish, physiological and pathological disorders in fish eating birds and mammals, loss of biodiversity in aquatic ecosystem are some of the recorded ecological adversities arising due to sediment contamination (Lasheen and Ammar, 2009), Thus sediments turn into a major source of bioaccumulative toxic elements and compounds. These are all persistent chemicals and are a direct threat to both ecology and human health even if these are no longer released from their source of origin (Lasheen and Ammar, 2009),

Assessment of the environmental risks associated with heavy metals in aquatic environment is commonly done based on the total metal contents in sediments and its comparison to established quality standards. The total metal concentration is often relied upon while studying heavy metal contamination. The total concentration of metal is relevant but bioavailability, reactivity and mobility are further more important owing to the threats to living beings. Further, it is found that only a part of the total metal concentration in sediments is available for biological processes (Morillo et al., 2004; Ramirez et al., 2005), Thus, simply estimating only the total metal concentration cannot fulfill the objective of understanding the concentration and behavior of trace elements in sediments. Zhang et al., (2009) observed that metal contamination needs to be examined by investigating the geochemical speciation and distribution of the metals in sediments. According to Hoque et al., (2011) the trace element mobility and their availability is a function of their chemical speciation and fractionation within or on sediment matrices. Thus to fully understand the environmental effects of the trace metals, it is pertinent to study the individual fractions (Okoro et al., 2012), For the speciation of solid phase associated metals, sequential extraction techniques are applied. Among the various techniques available, the scheme of Tessier et al., (1979) ¬¬¬is widely used directly or in a modified way.

The general characteristics of various metal fractions are tabulated below in Table 1. The relative strength of association of trace metals to different chemical phase alongwith their mobility are shown in Table 1.

Table 1: Relative mobility and availability of trace metals

Metal Association	Mobility
Exchangeable	High; Change in the cationic composition can release metals due to ion exchange
Carbonate Phase	High; sensitive to pH changes
Fe-Mn oxides	Medium; metals released under oxidizing conditions
Organic and Sulfide phase	Medium/High; With time decomposition/oxidation of organic matter occurs. Under aerobic conditions oxidation of sulphide minerals leads to release of metals
Residual/Crystalline Phase	Low; Only available after weathering or decomposition

In this paper a comparative assessment of Copper (Cu) with another toxic metal Cadmium (Cd) is carried out with respect to their distribution across different chemical phases and their bioavailability and also their risk of toxicity to living beings.

2. Materials and method

2.1 Study area

The Kameng river basin covers an area of 11,280 km^2 lying within 91˚55'E - 93˚25'E longitudes and 26˚35'N - 28˚0'N latitudes. Kameng river is an important tributary of the Brahmaputra river. The Kameng river was known as Bhareli river in the past. It now flows as Kameng within the Arunachal Pradesh and takes the name Jia Bharali in the Assam part. The upper region of the entire Kameng (Jia Bharali) catchment falls within the Himalayan range and the lower stretches flows through the alluvial pains of Brahmaputra. The river originates in the upper Himalayan ranges at an approximate elevation of approximately 5400m and traverses a total distance of approximately 242 km through mountain, hills and plains until reaching its confluence with the Brahmaputra. The variations in altitude, location, topography, aspect, density of vegetation, slope, drainage density, soil characteristics, orientation of ridges and valleys govern the climate at micro level and thereby create microclimatic regime (Hussain, 2002), The region displays a character of “montane climate” having 3 distinct vertical belts – tropical belt upto 1500m, temperate belt between 1800-3500m and alpine belt above 3500m. The average annual temperature in the foothill regions is around 24.5˚C and that in the mid-altitude zone of the lesser Himalayas is 13˚C (Hussain, 2002), There occurs snowfall above 2000m and rains below 2000m (Hussain, 2002), The western part of Kameng, generally receives less than 200cm annual rainfall, it being above the 2000m altitude. Again, the eastern region receives rainfall in the region of 200-400cm. As the Kameng river descends down and flows through the plains, the precipitation received in the sub-Himalaya region is in the range of 300-400cm.

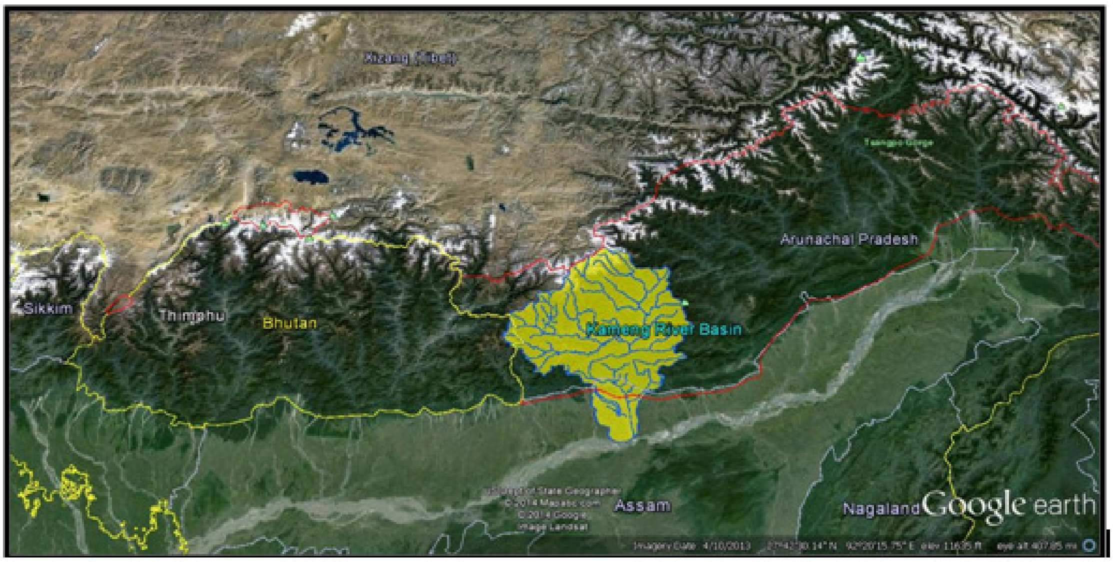

Figure 1: Location map of the Kameng river basin

2.2 Sampling

Freshly deposited bed sediment samples were collected from below the water column at a distance of 1m from the bank of the river at 3 locations – Tenga, Seppa and Bhalukpong using a stainless steel scoop, put in polyethylene zip-lock bags and transported to the lab. The sediment samples were dried in air and then in an air oven at 102oC till constant weight ensuring complete removal of water content. The dried sample was then ground with an agate mortar, sieved through a 2mm sieve and stored in polyethylene pouches for further analysis.

2.3 Sample analysis

Metal Speciation: The sequential extraction procedure (SEP) as proposed by Tessier et al., (1979) and further modified by Elsokkary and Müller (1990) was used for partitioning the heavy metals (Cu and Cd) in the sediments into 5 different fractions. The following five fractions were extracted: exchangeable fraction (F1), fraction bound to carbonates (F2), fraction bound to Fe-Mn oxides (F3), fraction bound to sulfide (F4) and residual fraction (F5), Cu and Cd associated with the various extracted fractions were estimated using an atomic absorption spectrophotometer (Model: Perkin Elmer AAnalyst 200 with FIAS) as per methods of APHA (2005),

3. Results and discussion

3.1 Distribution of Copper (Cu) and Cadmium (Cd) across chemical phases

The concentrations of Cu and Cd across the five chemical phases in the different sampling locations are given in the Table 2. Also the distributions of the metals across the different phases in the different sampling sites are shown graphically in theFigure. 2 andFigure. 3. The distribution patterns of Cu and Cd in different chemical phases in different locations in an ascending order of concentration are shown in Table 3.

Table 2: Concentration of Cu and Cd in the sequentially extracted chemical phases at different sampling locations

Sampling Locations	Sample Fractions	Cu (mg/g)	Cd (mg/g)
Bhalukpong	BhF_1	0.100 (03.34%)	0.089 (10.86 %)
	BhF_2	0.330 (11.03%)	0.157 (19.16 %)
	BhF_3	0.690 (23.00%)	0.129 (15.75 %)
	BhF_4	0.160 (05.35 %)	0.201 (24.45 %)
	BhF_5	1.710 (57.19 %)	0.243 (29.67 %)
Seppa	SF_1	0.250 (09.26 %)	0.850 (24.25 %)
	SF_2	0.320 (11.85 %)	0.760 (21.68 %)
	SF_3	0.320 (11.85 %)	0.910 (25.96 %)
	SF_4	0.100 (03.70 %)	0.760 (21.68 %)
	SF_5	1.710 (63.33 %)	0.225 (06.42 %)
Tenga	TF_1	0.020 (00.35 %)	0.880 (28.89 %)
	TF_2	0.270 (04.80 %)	1.060 (34.81 %)
	TF_3	3.440 (61.69 %)	0.091 (02.98 %)
	TF_4	0.840 (15.06 %)	0.830 (27.25 %)
	TF_5	1.006 (18.04 %)	0.184 (06.04 %)

$F_{1\text{-}5}$ implies the extracted fractions as stated earlier

Table 2: Distribution pattern of Cu and Cd in different chemical phases in ascending order of concentration

Seppa	Copper (Cu)	$F_4 < F_1 < F_3 = F_2 < F_5$
	Cadmium (Cd)	$F_5 < F_2 = F_4 < F_1 < F_3$
Tenga	Copper (Cu)	$F_1 < F_2 < F_4 < F_5 < F_3$
	Cadmium (Cd)	$F_3 < F_5 < F_4 < F_1 < F_2$
Bhalukpong	Copper (Cu)	$F_1 < F_4 < F_2 < F_3 < F_5$
	Cadmium (Cd)	$F_1 < F_3 < F_2 < F_4 < F_5$

From Figure 2 & 3 it can be easily inferred that Cu and Cd showed their affinities to various sediment fractions differently in different sampling sites. Cu showed highest affinity towards residual fraction in the river system with the exception of it being associated with the reducible phase at Tenga. The general trend of Cu to associate with the inert phase is in agreement with the findings of Bhattacharjee (2006), The results indicate that Cu formed stable organic complexes and metal sulfides in the Tenga river sediments. Similar associations of Cu to reducible phases were reported by Hawker *et al.,* (2005), Galan *et al*., (2003) and Sharmin *et al.,* (2010), It is to be noted that Cu was also found to be associated with the carbonates in the Seppa region. This association is probably due to the significant presence of clay and carbonate minerals in the Seppa region which was confirmed from the earlier mineralogical studies. *Since Cu was least associated with the exchangeable fractions, this reduced its potential of bioavailability.*

Unlike copper, it was found that *Cadmium had higher affinity to the exchangeable phase of the sediments*. Also, there was significant association with the carbonate and reducible phase. This finding corroborates with the findings of Schintu *et al*., (1991), According to their research it was established that in fluvial sediments Cadmium is mostly bound to exchangeable site, carbonate phase and the Fe-Mn oxide minerals. *Thus with change in the environmental conditions Cadmium bound to such phases are susceptible to remobilization in the water system.*

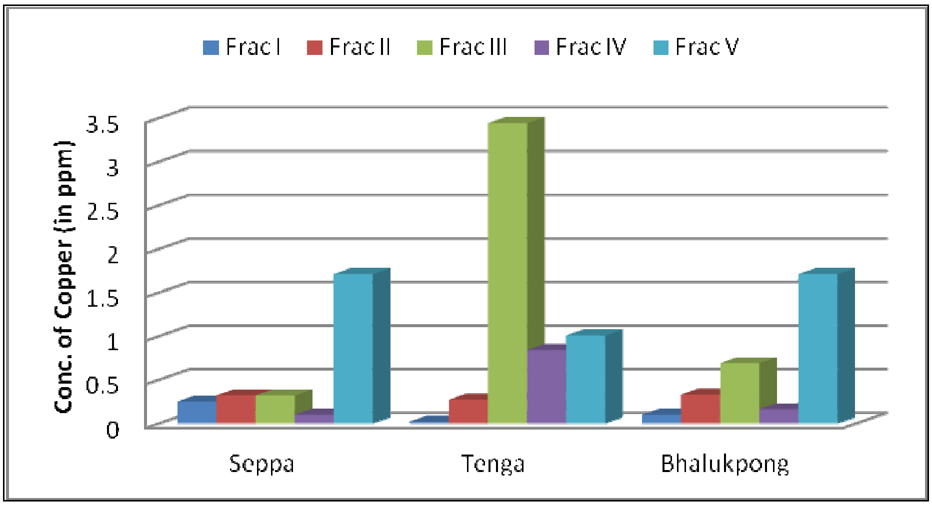

Figure 2: Chemical fractionation of Cu in Kameng River sediments

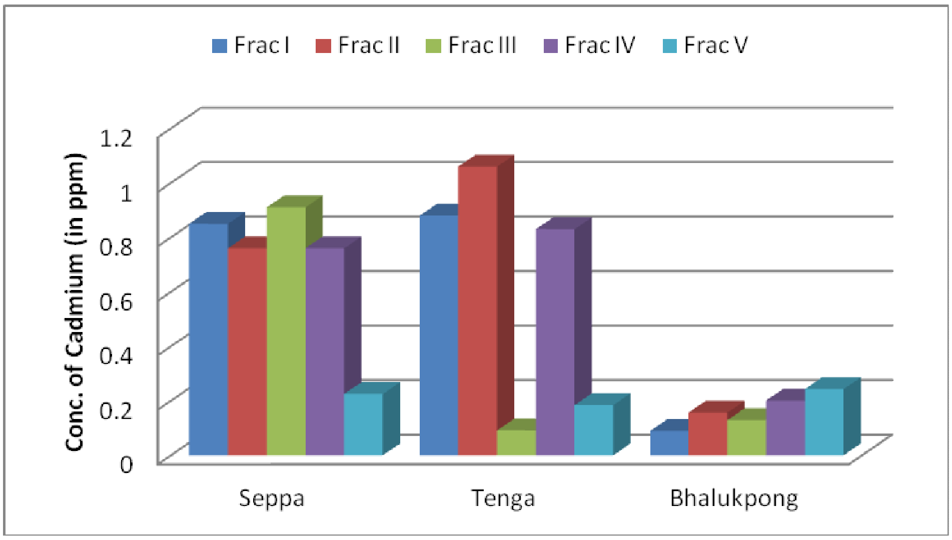

Figure 3: Chemical Fractionation of Cd in Kameng River Sediments

3.2 Bioavailability of Copper and Cadmium

Bioavailability is the amount of substance available or accessible to living organisms, is an important characteristics of contaminant evaluation (Becerra, 2003; Campbell & Recee, 1991), In Tessier's SEP, the bioavailability of an element decreases with the decreasing order of the chemical phases from the exchangeable to the residual. In the SEP, heavy metals associated with the F_1 and F_2 phases of sediments are more labile and readily leachable or bioavailable. The percentage of total labile fractions of both Cu and Cd in each of the sampling locations are calculated and shown in the Table 4 and the corresponding graph is shown Figure 4.

Copper: Although Copper is an essential element to human health, yet at higher concentration it can cause serious disorders by accumulating in blood, liver and other vital organs. There are records of cases of anemia, renal and intestinal disorders, Wilson's disease, all of which are due to Cu toxicity (Gratten *et al.,* 2003; Pais and Jones, 1997), Carbonate minerals and also iron-manganese oxide minerals are very efficient scavengers of Copper.

Table 3: Percentage of total labile fraction (F_1 + F_2) in different sampling sites

	F_1	F_2	F_3	F_4	F_5	$F_1 + F_2$
Seppa						
Copper	0.25	0.32	0.32	0.1	1.71	0.57 (21.11%)
Cadmium	0.85	0.76	0.91	0.76	0.225	1.61 (45.93%)
Tenga						
Copper	0.02	0.27	3.44	0.84	1.006	0.29 (05.20%)
Cadmium	0.88	1.06	0.091	0.83	0.184	1.94 (41.26%)
Bhalukpong						
Copper	0.1	0.33	0.69	0.16	1.71	0.43 (14.38%)
Cadmium	0.089	0.157	0.129	0.201	0.243	0.246 (30.03%)

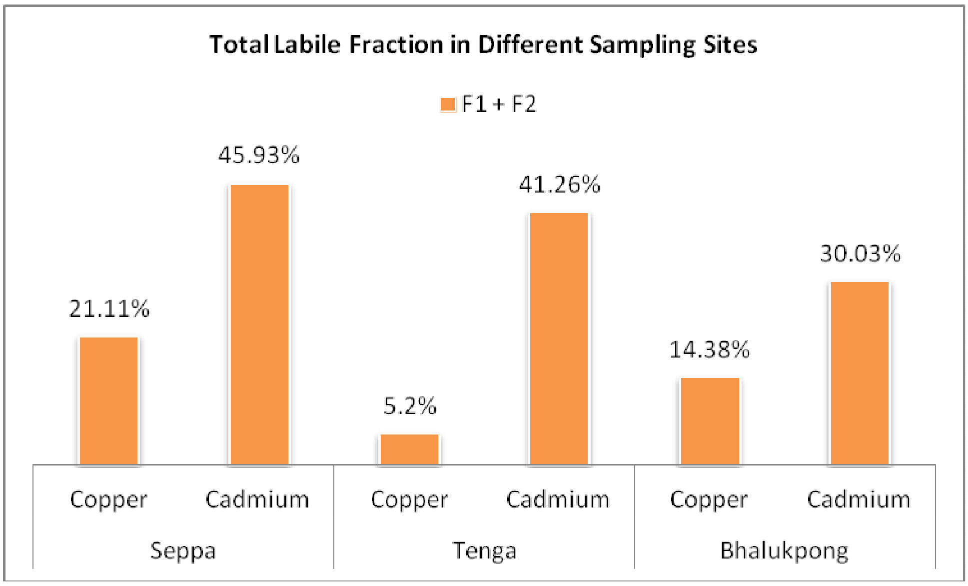

Figure 4: Total labile fraction of Cu and Cd in sampling sites

This is supported by the fact that at Seppa and Bhalukpong the total labile fraction was represented by a good percentage of 21.11% and 14.38% respectively. However, the labile fraction associated Copper was quite low in the Tenga region (5.2 %), Generally, the presence of elevated levels of Chloride results in greater solubility and mobility of copper (Bourg, 1988; Gambrell *et al.,* 1991), When the concentration of chloride is compared with the data on labile fraction, it can be similarly inferred that higher Cl^- content in the water column at Bhalukpong and Seppa resulted in the comparatively higher percentage of Cu associated labile fraction. The bioavailability of Cu was found to be in the following order in the sampling sites: Seppa (21.11%) > Bhalukpong (14.38%) > Tenga (5.2%),

Cadmium: In the Kameng river, Cd was found to be very labile and bioavailable. In the present study, the order of bioavailability order of Cadmium in the sampling sites is as follows: Seppa (45.93%) > Tenga (41.26%) > Bhalukpong (30.03%), According to this we find that the percentage of association of Cadmium with labile fraction was highest in the Seppa region and lowest in the Tenga region. However, *the percentage of Cadmium associated labile fraction was significantly high in all the sampling sites*.

4. Risk assessment criteria

Perin *et al.,* (1985) first proposed the risk assessment criteria for identifying toxic metals in sediments posing as serious concern for living beings. The percentage of exchangeable and carbonate fraction that can be released from the sediment is taken as the basis for this criteria. The sediment is considered environmentally safe when it is estimated that the potential release of exchangeable and carbonate fraction is less than 1% of the total metal in the sediments. The RAC for Kameng river sediments is shown below in Table 5.

Table 4: Risk Assessment criteria for Kameng River sediments

Category	% of Exchangeable and Carbonate phase as per RAC	RAC for Kameng river sediments with respect to Copper and Cadmium
No Risk	<1	Nil
Low Risk	1-10	Cu at Tenga region
Medium Risk	11-30	Cu at Bhalukpong and Seppa
High Risk	31-50	Cadmium at all the sampling sites
Very High Risk	>50	-Nil-

Thus, following the Risk Assessment Criteria it can be inferred that the association of Cadmium with exchangeable and carbonate fraction poses a high risk of causing deleterious effects to the aquatic life in the river system. Due to changes in environmental condition like pH, redox potential, salinity etc., rapid remobilization of the metal can occur. Cu poses a medium risk and it indicates lower availability to the organisms.

5. Conclusion

In this study it was observed that Cu showed highest affinity towards the residual fraction in the river system with the exception of it being associated with the reducible phase at Tenga. Since Cu was very less associated with the exchangeable fractions, its potential of bioavailability was drastically reduced. Unlike Copper, it was found that Cadmium had higher affinity to the exchangeable phase of the sediments. Cadmium was mostly bound to exchangeable site, carbonate phase and the Fe-Mn oxide minerals. Thus with change in the environmental conditions Cadmium bound to such labile phases can easily remobilize in the water system. The percentage of Cadmium associated labile fraction was significantly high in all the sampling sites. Thus in the Kameng river, Cd was found to be very labile and bioavailable. Based on the results of the calculations according to Risk Assessment Criteria it was found that the association of Cadmium with exchangeable and carbonate fraction poses a high risk of causing deleterious effects to the aquatic life in the river system. On the other hand Copper in the present condition poses low risk and that indicates its lower availability to the organisms.

Acknowledgement

The authors acknowledge the Head of the Department of Environmental Science, Gauhati University for providing the facilities for conducting this research work. The first and the second author also acknowledge the financial support received from the Department of Science and Technology, Government of India through a project under the "Bio Geo Database and Ecological Modeling for Himalayas" programme.

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