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Environmental Fate and Transportation of Cadmium, Lead and Manganese in a River Environment using the EPISUITE Program

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ABSTRACT

The Mekong River is an essential source of water and protein for the inhabitants of Thailand and the Lao Peoples' Democratic Republic. It is hypothesized that pollution may be adversely affecting the water and sediment quality, which directly affects the health and population of aquatic life and ultimately human health. The quality of the river can be assessed using various chemical and physical parameters, one of which is the metal content of both the water and the sediment. The introduction of environmental quality standards allows comparison of the values obtained with the guidelines. Furthermore, the modeling program EPISUITE was used to determine the environmental partitioning of pollutants within different environmental compartments. Using the data produced for metals, the experimental model was compared to the default model. This involved experimentally measuring the log K_{oc} (the organic carbon partition coefficient) and from this determining the log K_{ow} (octanol-water partition coefficient). High availability of metals in sediment may lead to greater biomagnification in fish, finally accumulating in humans. The potential for this was shown by accumulative values exceeding both the chronic value (ChrV) and lethal concentration 50 (LC_{50}) for fish in comparison with the guidelines, as the amount of cadmium and lead in sediment was above the lowest effect level but below the severe effect level.

Key words: EPISUITE program, sediment-water partition coefficient, organic carbon partition coefficient, octanol-water partition coefficient, metals ion

INTRODUCTION

The Mekong River (known in Tibet as *Dza-chu*, China as *Lancang Jiang* and Thailand as *Mae Nam Khong*), is a major river in southeastern Asia. It is the longest river in the region. From its source in China's Qinghai province near the border with Tibet, the Mekong flows generally southeast to the South China Sea, a distance of 4,200 km. The Mekong crosses Yunnan province, China, and forms the border between Myanmar (Burma) and the Lao Peoples' Democratic Republic (Laos) and most of the border between Laos and Thailand. It then flows across Cambodia and southern Vietnam into a rich delta before emptying into the South China Sea.

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In the upper courses are steep descents and swift rapids, but the river is navigable south of Luang Prabang in Laos.

The natural resource management issues and priorities vary significantly depending on the level of development and population in each country. In northeast Thailand, with over 20 million people, the water resources are virtually fully developed. In Laos, with five million people and a much poorer country from a GDP perspective, the water resources are largely underdeveloped. Cambodia, with 10 million people, is recovering from decades of war, and in the Mekong delta, some 20 million Vietnamese live on some of the most highly productive agricultural land in the world. Utilization of water and soil by the population in these regions of the Mekong River can cause serious environmental problems.

Pollution of both the water and sediments may adversely affect wildlife and human health. Heavy metals are of great ecological importance as pollutants to the river system. Water and sediments act as reservoirs for heavy metals that may lead to greater bioavailability, bioaccumulation and biomagnification through the food chain. In particular, the solubility and the soil/ sediment-water distribution coefficient of heavy metals (K_d) are of supreme importance in predicting the behavior and mobility of pollutants within the environment (Carlon *et al.*, 2004; ASTM International, 2001). K_d is determined by Equation 1:

$$K_d = \frac{\mu\text{gs chemical / g solids}}{\mu\text{gw chemical / g } H_2O} \qquad (1)$$

The partitioning of heavy metals between sediment-water is dependent on both the physical and chemical properties of each metal. K_{oc}, the organic carbon partition coefficient, is calculated from Equation (2), using the K_d value. The proportion of organic carbon in the sediment is relevant to this study for two reasons. Firstly, the organic content of the sediment may form chelates or ligands with the metals and thus show greater partitioning to the organic (sediment) phase than would be expected. Secondly, EPISUITE uses the organic carbon content to calculate the percentage in each environmental media (Equation 2).

$$K_{oc} = \frac{Kd}{\%OC} \times 100 \qquad (2)$$

High concentrations of metals in the environment directly affect the potential for bioaccumulation. To predict the amount of metals that contaminate organisms, the dimensionless octanol-water partition coefficient (K_{ow}) is used. K_{ow} is one of the most important descriptors of chemical behavior in the environment, whereby octanol is selected to be representative of lipids because of the similar carbon to oxygen ratio (Mackay, 2001). Therefore, in an organism, hydrophobic contaminated substances can be assessed.

$$K_{oc} = 0.41K_{ow} \qquad (3)$$

Cadmium, manganese and lead were used, as they are representative of the three classes of heavy metals. Cadmium and manganese are d-block metals, Mn^{2+} is regarded as a hard acid, while Cd^{2+} is regarded as a soft acid. Lead is a p-block metal and as such is regarded as a borderline acid.

Samples were taken from 10 stations and analyzed for total organic carbon (TOC) and metals Cd, Pb and Mn (Chartsakulthong, 2004). The objective of this study was not just to analyze the metals, but also to model partitioning in various media (sediment, water and organisms in term of K_{ow}) from the sediment measured values.

The values obtained were used in EPISUITE to compare the experimental values with the default. Moreover, the experimental data were compared to the standard limits set for environmental quality and impact assessment. Using an estimation program interface (EPI) suite, several parameters for each of the heavy metals were obtained (USEPA, 2004). These included the percentage of the compound expected in each environmental compartment, which was calculated from the chemical and physical properties of the compound, and the bioconcentration factor (BCF). Using ECOSAR, the fish chronic value (ChrV) and the predicted 14 days lethal concentration 50 (LC_{50}) for fish were also obtained (USEPA, 2000). Finally, the amounts of metals were assessed in terms of sediment quality guidelines and severe effect level as pollution indicators using the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC, 2000a).

MATERIALS AND METHODS

Chemical

All reagents used were of analytical reagent grade. Potassium dichromate was purchased from APS Finechem (Seven Hill, Australia). Ferrous (II) sulfate and lead nitrate were purchased from Merck (Darmstadt, Germany). Sulfuric acid and manganese chloride were purchased from Carlo Erba (Milan, Italy). Cadmium nitrate was purchased from APS Ajax Finechem (Auburn, Australia).

Sample collection

Sediment and water samples were collected from 10 sampling sites along the Mekong River as shown in Figure 1. All sediment samples were collected from the surface layer within the top six inches of the solid profile using a dredge sampler and passed through a two mm sieve before storage in polyethylene bags. Surface water samples were collected and stored in polypropylene bottles. The samples were kept refrigerated and analyzed within three days.

Determination of partition coefficient (K_d) in sediment

The standard test method for determining a sorption constant for an organic chemical in soil and sediments (E1195-01) was used for the determination of K_d in sediment (ASTM International, 2001).

Determination of organic carbon in sediment

Soil survey standard test methods (C6A/2) were used for the determination of organic carbon in sediments (Rayment and Higginson, 1992).

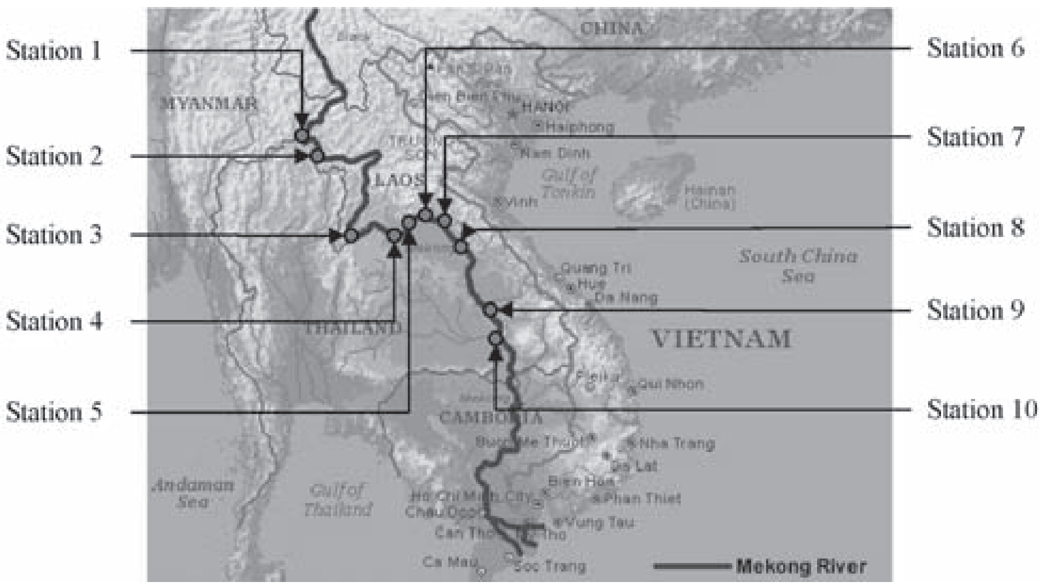

Figure 1 Sampling station locations on the Mekong River (ASTDR, 1993).

Determination of cadmium, manganese and lead in sediment

The MARS-X (CEM Corporation, USA), pressurized microwave-assisted digester was used to digest sediment samples. The AAnalyst 800 (Perkin Elmer, USA) atomic absorption spectrophotometer was used to analyze each metal in the samples.

Calculation by using EPISUITE

The estimation program interface (EPI) suite is a calculation model that was considered in this work to describe the behavior of heavy metals in the environment. The EPI was used to estimate the bio-concentration factor (BCF) and the percentage of the compound expected in each environmental compartment. ECOSAR (USEPA, 2000) was used to calculate chronic values (ChrV) and lethal concentration 50 (LC_{50}).

RESULTS AND DISCUSSION

The soil-water distribution coefficient of heavy metals (K_d) is related to various environmental indexes. The higher the K_d value is, the greater the percentage of partitioning to solids. This also affects the aquatic concentration for the ChrV and LC_{50} values. From Table 2, it

Table 1 Sampling stations along the Thai-Laos Mekong.

Station No.	Rational for sampling at specific locations
1	Golden Triangle - Mekong River enters Thailand
2	Wat Jam Pong - Mekong leaves Thailand into Laos
3	Chiang Karn - Mekong re-enters Thailand
4	Nong Khai - Thai-Laos friendship bridge
5	Phonpisai – Large residential areas
6	Wat ArHong - the deepest point of Mekong
7	Sri Song Kram - Sri Song Kram River meets Mekong
8	Dhat Panom - busy port between Thai-Laos
9	Wat Khongchiampurawat - River from Laos meets Mekong River
10	Khong Chaim - the last point before Mekong leaves Thailand into Laos and Cambodia

Table 2 Amount of organic carbon and partition coefficient (K_d) of metals in sediments from 10 stations of the Mekong River.

Station No.	% organic carbon	K_d		
		Cd	Mn	Pb
1	0.69	22.39	72.11	31.62
2	0.67	81.28	34.04	85.11
3	0.80	56.23	70.15	30.20
4	0.69	26.92	26.73	56.23
5	1.00	38.90	33.11	38.02
6	1.10	22.39	35.81	52.48
7	1.78	13.18	30.06	21.38
8	1.29	16.60	26.73	26.30
9	0.81	13.18	30.55	43.65
10	1.10	41.69	37.07	52.48
	0.99 ± 0.33	33.28 ± 21.85	39.64 ± 16.96	43.75 ± 18.82

was found that the percent organic carbon in sediments of all stations was quite low (less than 2%). The K_d values of sediments for Cd, Pb and Mn from stations 1-3 were relatively higher than other stations, which may have been due to the presence of high montmorironite content in the sediment (Chartsakulthong, 2004). Montmorironite is the mineral sediment that tends to adsorb metal more readily than other minerals. Moreover, K_d was related to the percentage of organic carbon which may be important, as absorbed metals form organometallic compounds (Fukue *et al.*, 2006). From Table 2, the relative K_{oc}, K_{ow} and aqueous concentration (C_{aq}) were calculated as shown in Table 3 and Table 6.

Table 4 shows the considerable difference between experimental values obtained and the values given from the computational model. The program calculation used only the inherent chemical and physical properties of each metal and did not account for local environmental conditions. The different coefficients lead to dissimilar predictions of environmental fate, BCF and toxicity. The fugacity model shows most of Cd, Pb and Mn partitioning into the sediment (Table 5), with each metal showing greater percent

Table 3 $logK_{oc}$ and $logK_{ow}$ were calculated from experimental data.

Metal	K_d	$logK_{oc}$	$logK_{ow}$
Cd	33.28 ± 21.85	3.47 ± 0.36	3.86 ± 0.36
Mn	39.64 ± 16.96	3.59 ± 0.25	3.98 ± 0.25
Pb	43.75 ± 18.82	3.63 ± 0.28	4.02 ± 0.28

Table 4 Comparison of $logK_{oc}$ and $logK_{ow}$ values between default and experimental data of metals from Mekong River sediment.

Metal		$logK_{oc}$	$logK_{ow}$
Cd	*Default	1.16	-0.07
	Experimental ($\bar{x}$)	3.47 ± 0.36	3.86 ± 0.36
Mn	*Default	1.16	0.23
	Experimental ($\bar{x}$)	3.59 ± 0.25	3.98 ± 0.25
Pb	*Default	1.16	0.73
	Experimental ($\bar{x}$)	3.63 ± 0.28	4.02 ± 0.28

*Default from EPSUITE

Table 5 Bio-Concentration factors, percentage of metals in each environmental compartment, ChrV and LC_{50} values (from EPI suite) compared between default and experimental data.

Metals		BCF	Partitioning			ChrV	LC_{50} fish
			%solid	%air	%water	(mg/L)	(mg/L)
Cd	*Default	3.16	6.23	38.10	55.70	678.75	2567.69
	Experimental ($\bar{x}$)	187.20	83.78	4.19	12.00	-	-
Mn	*Default	3.16	6.32	38.10	55.60	9,589.12	251.94
	Experimental ($\bar{x}$)	231.50	84.53	3.87	11.60	-	-
Pb	*Default	3.16	6.00	34.10	59.90	181.88	3,552.71
	Experimental ($\bar{x}$)	248.50	89.00	2.90	8.11	-	-

*Default= BCF and partitioning from EPISUITE, ChrVand LC_{50} from ECOSAR.
Experimental= BCF from $logK_{ow}$ value calculated from experimental K_d, modeled in EPISUITE.

partitioning to solids. Therefore, bioaccumulation is greater in mud-dwelling, bottom- feeding fish. Higher bioaccumulation may also occur for all fish, as suspended solids would also be heavily contaminated.

The ChrV and LC_{50} values indicated toxic concentrations in water, which can be used comparatively with the potentially accumulated concentrations. Toxicity tests for the accumulation of heavy metals are difficult to assess due to variation in BCFs for each heavy metal and each species of fish. Phanwichien *et al*. (2005) demonstrated the correlation between Cd, Cu and Zn accumulations in liver, kidney and muscle of the Mekong Catfish and concomitant adverse physiological effects. In this investigation, the potential accumulative values for cadmium, lead and manganese were under the ChrV and LC_{50} values except for the experimental manganese and lead that exceeded the ChrV. However, this does not account for biomagnifications through the food chain. The presence of aquatic metals, particularly cadmium and mercury, adversely affects fish health, especially those mechanisms that protect against diseases (Rand, 1995). This results in depletion of fish stocks, which would be devastating for the 60 million inhabitants of the Mekong as fish is their major source of protein. Biomagnifications that occurs through the food chain may attain dangerous levels for the consumer, although animals exposed may not exhibit any visible, adverse physiological effects. The most documented evidence of this effect comes from two episodes of mercury poisoning in Japan that resulted in many human fatalities. Levels such as those found in the Mekong may result in similar scenarios (Keenan *et al*., 2006).

C_{sed} of Cd, Mn and Pb in sediments of the Mekong River were in the range 3.24-10.50 ppm, 123.02-244.36 ppm and 54.22-89.72 ppm, respectively. Therefore, the C_{bio} value of Mn was quite high compared with Cd and Pb. Comparing the C_{bio} values with ChrV and LC_{50}, Mn and Pb exceeded the threshold for water.

Table 8 shows the comparison between the mean value of C_{sed} of Cd, Mn and Pb with the LEL (lowest effect level) and SEL (severe effect level) of the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC, 2000b). Only the C_{sed} values of Cd and Pb were higher than the LEL values for all stations but only cadmium at one station exceeded the SEL value.

Although the sources are difficult to assess, there is little industry along the Thai-Laos section of the Mekong River. Previous studies showed that the ratio of Cd to Zn is approximately 10:1 (Keenan *et al*., 2006).This was greater than naturally occurring volcanic rock sources predicted at a ratio of greater than 50:1 (Degens

Table 6 Relationship between C_{aq} and C_{bio} compared with the ChrV and LC_{50} values for all 10 sampling stations of metals.

Metals		C_{aq} (mg/L)	C_{bio} (mg/L)	ChrV (mg/L)	LC_{50} fish (mg/L)
Cd	*Default	-	0.70	↓	↓
	Experimental ($\bar{x}$)	0.22	41.51	↓	↓
Mn	*Default	-	13.16	↓	↓
	Experimental ($\bar{x}$)	4.16	963.14	↓	↑
Pb	*Default	-	4.96	↓	↓
	Experimental ($\bar{x}$)	1.57	390.05	↑	↓

*Default C_{bio} was calculated from BCF: $C_{aq} = C_{sed}/K_d$, $C_{bio} = C_{aq}$ x BCF

↑ = C_{bio} values above threshold for water, ↓ = C_{bio} values below threshold for water.

Table 7 Sediment quality standards of metals (Australian and New Zealand Guidelines for Fresh and Marine Water Quality) (ANZECC, 2000b).

Metals	Standards (mg/kg dry wt)	
	LEL	SEL
Cd	0.6	10
Mn	460	1110
Pb	31	250

LEL = lowest effect level (A lowest effect level is a level of sediment contamination that can be tolerated by the majority of benthic organisms).
SEL: severe effect level (severe effect level indicates a level at which pronounced disturbance of the sediment-dwelling community can be expected).

et al., 1991). This indicated anthropogenic sources. Therefore, this was most probably inherited from heavy industrial activity upstream.

CONCLUSION

This study demonstrated the prediction phases of Cd, Pb and Mn in the Mekong River. The comparison between the results and the guidelines used indicated that the Mekong River may be considered polluted by Cd and Pb from upriver sources especially in the first part of the river entering Thailand and where river joins the Mekong at station 7. However, the prediction results indicated Pb was also another polluting metal because of the higher value of C_{bio} over ChrV, and the C_{bio} level of Mn was greater than LC_{50} as shown in Table 6. However, the C_{sed} value of Mn was still within the limit of the lower level guideline.

Furthermore, the Australian and New Zealand Guidelines for Fresh and Marine Water Quality should be used with caution because the guidelines have been developed specifically for those countries and the climatic conditions and species used in deriving the guidelines may be different to those in the Mekong River.

Table 8 Comparison of quality standards for 10 sampling stations of metals.

Station	C_{sed} (mg/kg)		
	Cd	Mn	Pb
1	9.34	179.12	54.22
2	7.43	139.65	56.62
3	5.78	147.40	61.04
4	6.76	123.02	62.26
5	8.42	136.35	74.93
6	9.38	137.69	67.72
7	10.50	207.73	70.67
8	5.92	205.65	72.54
9	3.24	128.27	76.96
10	7.06	244.36	89.72

Light shading indicates the metal level is above LEL (lowest effect level).
Dark shading indicates the metal level is above SEL (severe effect level).

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