Environmental fate and transportation of Cadmium, Lead and Manganese in river environment using EPISUITE program

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ABSTRACT

The Mekong River is an essential source of water and protein for the denizens of Thai-Laos countries. It is hypothesized that pollution may be adversely affecting the water and sediment quality, which directly impacts on the health and population of the aquatic life and ultimately to human health. The quality of the river can be assessed from 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 the 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} and from this determining the log K_{ow}. High availability in sediment of metals may lead to greater biomagnification in fish, and accumulates in human finally. The potential for this is shown by accumulative values exceeding both the Chronic value (ChrV) and Lethal concentration 50 (LC_{50}) for fish comparison to the guidelines, 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

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

The natural resource management issues and priorities vary significantly depending on the level of development and populations in each country. In north-east Thailand, with over 20 million peoples, the water resources are virtually fully developed. In Laos, with 5 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 in these regions of the Mekong River by those populations can cause serious environmental problems.

Pollution of both the water and sediments may adversely impact on 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 paramount importance in order to predict the behavior and mobility of pollutants within the environment (Carlon et al., 2004; ASTM Internationa,, 2001). Kd is determined as:

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

The partitioning of heavy metals between sediment-water is dependent on both the physical and chemical properties of each metal. The proportion of organic carbon in the sediment is relevant to this study for 2 reasons.

1. 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.
2. EPISUITE uses the organic carbon content in calculating the percentage in each environmental media.

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

High concentrations of metals in environment directly affect the potential for bioaccumulation. To predict the amount of metals that contaminates organisms, the dimensionless octanol-water partition coefficient (K_{ow}) is used. Kow 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 analysed for total organic carbon (TOC) and metals Cd, Pb and Mn (Chartsakulthong, 2004). The objective of this study was not just to analyse the metals but also to model partitioning in various medium (sediment, water and organisms in term of K_{ow}) from the sediment measured values.

Figure 1 Map shows the areas of sampling stations from Mekong River (ASTDR, 1993).

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

The values obtained were used in EPISUITE to compare the experimental values with the default. Moreover, the experimental data was 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 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 with Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC, 2000).

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).

Determination of partition coefficient (K_d) in sedimen.

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) was used for the determination of organic carbon in sediments (Raymond and Higginson, 1992).

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

Estimation Program Interface (EPI) suite is the calculation model that was considered in this work to describe the behavior of heavy metals in the environment. The EPI was used to estimate 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 K_d value, the greater percentage of partitioning to solids. This is also affects the aquatic concentration for the Chronic Value (ChrV) and LC_{50} values. From Table 2, it was found that the percent organic carbon in sediments of all stations were quite low (less than 2 percent). The K_d of sediments for Cd, Pb and Mn from stations 1-3 were relatively higher than other stations, which may be 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.

Although default models are useful, experimental values differ greatly from those predicted as seen in Table 4. The fugacity model shows that most of Cd, Pb and Mn partitioning into the sediment (Table 5), with each metal showing greater percent 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.

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	Kd		
		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
$\bar{x}$	0.99 ± 0.33	33.28 ± 21.85	39.64 ± 16.96	43.75 ± 18.82

Table 3 $\log K_{oc}$ and $\log K_{ow}$ were calculated from experimental data.

Metal	Kd	logKoc	logKow
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 $\log K_{oc}$ and $\log K_{ow}$ values between default and experimental data of metals from Mekong River sediment.

Metal		logKoc	logKow
	*Default	1.16	-0.07
Cd	Experimental ($\bar{x}$)	3.47 ± 0.36	3.86 ± 0.36
	*Default	1.16	0.23
Mn	Experimental ($\bar{x}$)	3.59 ± 0.25	3.98 ± 0.25
	*Default	1.16	0.73
Pb	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) compare 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 $\log K_{ow}$ value, calculated from experimental K_d, modeled in EPISUITE.

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		Caq (mg/L)	Cbio (mg/L)	ChrV (mg/L)	LC50 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.

The ChrV and LC_{50} values indicate toxic concentrations in water which can be used comparatively with the potentially accumulated concentrations. Toxicity tests for 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 are under the ChrV and LC_{50} values except the experimental manganese and lead that exceed the ChrV. But this does not account for biomagnifications through the food chain. The presence of aquatic metals particularly Cadmium and Mercury adversely affects fish health, particularly those mechanisms that protect against diseases (Rand, 1995). This results in depletion of fish stocks and would be devastating for the 60 million inhabitants of the Mekong as fish is the major source of protein. Biomagnifications that occurs through the food chain may attain dangerous levels for the consumer, although the animal exposed may not exhibit visible adverse physiological effects. The most documented evidence of this comes from two episodes of mercury poisoning in Japan that resulted in many human fatalities. Such levels as found in the Mekong may result in similar scenarios (Keenan et al., 2006).

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

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).

Table 8 Comparison of Quality Standards for 10 sampling stations of metals.

Station	Csed (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 indicate the exceed amount of metal above LEL (Lowest effect level).
Dark shading indicate the exceed amount of metal above SEL (Severe effect level).

C_{sed} of Cd, Mn and Pb in sediments of the Mekong River are in the range of 3.24-10.50 ppm, 123.02-244.36 ppm and 54.22-89.72 ppm, respectively. Therefore the C_{bio} value of Mn is quite high compared with Cd and Pb. Comparing the C_{bio} values with ChrV and LC_{50}, Mn and Pb were 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, 2000). Only C_{sed} values of Cd and Pb are higher than LEL values for all stations but only one station of cadmium exceeds the SEL values.

CONCLUSION

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

Although the sources are difficult to assess, there is little industry along Thai:Laos Mekong River. Previous studies show that the ratio of Cd:Zn is approximately 10:1 (Keenan et al., 2006). This is greater than naturally occurring volcanic rock sources predicted at a ratio of greater > 50:1 (Alper and Zierenberg, 1998; Degens et al., 1991). This indicates anthropogenic sources. Therefore, this is most probably inherited from heavily upstream industry.

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

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Figure captions

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