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Spatial and Temporal Variations of Physical-Chemical Water Quality and some Heavy Metals in Water, Sediments and Fish of the Mae Kuang River, Northern Thailand

CHANAGUN CHITMANAT[1]†‡ AND SIRIPEN TRAICHAIYAPORN¶
International Postgraduate Program in Environmental Management, Graduate School, Chulalongkorn University, Bangkok, Thailand
†*National Center of Excellence for Environmental and Hazardous Waste Management (NCE-EHWM), Chulalongkorn University, Bangkok, Thailand*
‡*Faculty of Fisheries Technology and Aquatic Resources, Maejo University, Chiang Mai, Thailand*
¶*Biology Department, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand*
[1]Corresponding author's e-mail: chanagun@hotmail.com

ABSTRACT

The present study was conducted to investigate heavy metal (Cd, Pb & Zn) contaminants in water, sediments and fish of the Mae Kuang River, Northern Thailand during July, 2008-June, 2009. It was found that the worst water qualities in dry seasons were caused by low water flow, municipal effluents and industrial discharges. The surface water in the river was classified into class 3-4 referring to medium-fairly clean water used for consumption after special water treatment. Pb and Cd in water were below detection limits, while Zn concentrations in water ranged 0.01-0.11 mg L^{-1}. The Pb, Cd and Zn concentrations in sediment were 3.13-27.56, <0.02-0.43 and 3.42-10.32 mg kg^{-1}, respectively. No Cd and Pb residues were found in *Henicorhynchus siamensis* and *Puntioplites proctozysron* flesh, while the concentrations of Zn in these fish were 4.57-6.58 mg kg^{-1}. On the other hand, Pb and Cd residues in snakehead fish (*Channa striata*) were <0.05-2.13 and <0.02-0.24 mg kg^{-1} wet weight, while the concentrations of Zn in these fish were 3.37-12.19 mg kg^{-1}. This information provides a useful reference in heavy metal contamination in the Mae Kuang River for river management.

Key Words: Heavy metal; Cd; Zn; Pb; Mae Kuang River

INTRODUCTION

Mae Kuang River is located in the northern part of Thailand. This river flows through large catchment areas into the Ping River, merges with others and finally converges to the Chao Phraya River, a major river in Thailand. It also flows past the Lamphun Northern Industrial Park, where is suspected as one of the main potential pollution sources. In addition to industrial wastewater disposal, this river is continually degraded by municipal effluent and surface runoff as well. As a consequence, it turns to be black and stinking river in summer. Some contaminants in aquatic environment could be removed from water compartment by suspended solid interactions and subsequently be sunk as bottom sediments (Cundy & Croudace, 1995). The fate of heavy metal contamination in sediments relies on erosion, local mixing, resuspension, diagenesis and bioturbation (Lee & Cundy, 2001). Since heavy metals are not readily biodegraded over time, a great concern has currently grown over the possible harmful effects of the water discharges especially from industrial park into the Mae Kuang River. Although metal contamination in water does not reach a toxic level to aquatic organisms, a metal polluted river possibly generates a hazard to local residents, who consume contaminated water, aquatic plants and fishes because of bioaccumulation. The toxic metal pollution of this river has been appealing to public attention; however, no study was conducted for the assessment of heavy metals in sediment and fish from the Mae Kuang River.

The present study aimed to investigate physical-chemical parameters in the Mae Kuang River and the heavy metal contamination in water, sediments and some freshwater fish (*Henicorhynchus siamensis*, *Puntioplites proctozysron* & *Channa striatus*).

MATERIALS AND METHODS

Study area: This research was conducted in the Mae Kuang River, Thailand. Six sites were chosen for physico-chemical investigation and monitoring of Cd, Pb and Zn pollution (Fig. 1). Site 1 is located upstream far from Chiangmai and

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Lamphun Municipalities and was used as reference site. Some sites (2 & 3) are affected from industrial and municipal effluents. Site 4 is close to Lamphun Downtown. Site 5 is below from Lamphun Municipality. Site 6 is the station that Mae Kuang River merges to Ping River. Surface water, sediment and fish were randomly collected from different sites during June, 2008 to July, 2009.

Sampling Protocol

Water: Water samples were collected once a month and placed in clean acid-washed polyethylene bottles. Samples were immediately added with 10% HNO_3 and placed in an ice container.

Some physico-chemical parameters including dissolved oxygen, temperature, pH and conductivity were instantly determined on-site by using the YSI 556 multi-probe meter. Other parameters; for instant, Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), ammonia, nitrate and phosphate were immediately analyzed upon laboratory arrival according to the procedures by APHA, AWWA and WEA (1999).

Sediment: Surface bottom sediment (0-5 cm) samples were collected from each station with the use of an Ekman grab sampler, placed in plastic bags and kept in an ice box. After being collected, sediment samples were then air dried until they reached constant weight. Sampling was performed every month from July, 2008-June, 2009.

Fish: Three indigenous fish species (individually 50-200 g in weight) including Jullien's mud carp (*H. siamensis*), Smith's barb (*P. proctozysron*) and snakehead (*C. striatus*) were caught from selected sampling sites by local fishermen using electro-fishing and netting. Jullien's mud carp is omnivorous, pelagic feeding on phytoplankton and aquatic insects. Smith's barb is omnivorous, feeding on phytoplankton and animal detritus. Snakehead is a voracious carnivore feeding mainly on live animals. The sample size was 5 fishes for each station. Sampling was done every four months to compare seasonal effects.

Metal Preparation and Analysis

Cadmium, lead and zinc analysis in water: The method was followed the AOAC Official Method 974.27. Briefly, transfer aliquot of well mixed water sample to beaker and add 3 mL HNO_3. Cover with watch glass, heat and evaporate to dryness. Filter and dilute with deionized distilled water to 50 mL.

Sediment preparation for metal analysis: A 5 g air-dried sample of sediments was crushed and screened through a 1 mm sieve. Cd, Pb and Zn contents were analyzed using the *aqua regia* method (Hseu *et al*., 2004). The extracts were stored at -4°C in acid washed polyethylene bottle until analyzed by AAS.

Fish preparation for analysis: Fish samples from each site were weighed, enwrapped in aluminum foil and kept at -20 C until digestion. The method of the Association of Official Analytical Chemists (AOAC) was used for preparation of fish tissues. Fish samples were digested using nitric/perchloric (2:1) in a beaker placed on a hot plate. Filter and dilute with deionized distilled water to 50 mL.

Heavy metal analysis: Pb, Cd and Zn were analyzed by Graphite Atomic Absorption Spectrophotometry (Varian Spectra AA-220FS). The wavelengths used for measurements were 213.9 nm for Zn, 217.0 nm for Pb and 228.8 nm for Cd. Data provided were the average of three replicates. The detection limits were 0.005 mg/L Cd, 0.01 mg/L Pb and 0.015 mg/L Zn for this study. Sample blank with double-distilled water were analyzed using the same acid ratio applied in tissue and sediment samples.

RESULTS AND DISCUSSION

Water chemistry: The general water chemistry in the Mae Kuang River in winter, summer and rainy seasons is listed in Table I. Water temperature ranged 22.13-31.86 C; pHs were 6.71-8.97; Dissolved Oxygen (DO) were from 1.07-7.26 mg L^{-1}; ammonia varied from 0.01 to 0.15 mg L^{-1}; nitrite and nitrate were 0.01-0.85 mg L^{-1} and 0.01-1.75 mg L^{-1}, respectively; orthophosphorus were 0.01-0.71 mg L^{-1}; electrical conductivity values were 140-350 µs cm^{-1}; COD varied extremely from 2.86-5.28 mg L^{-1} and BOD varied from 0.19 to 3.22 mg L^{-1}. There were no differences among stations for pH, water temperature, ammonia and COD ($P > 0.05$). On the other hand, seasonal variation in DO, BOD and Total-P was found. Water temperatures were high in summer and lower in winter because of annual cycle characteristics. COD is commonly used for municipal and industrial waste determination. The higher values of COD were recorded at stations 2 and 3, where might affect from industrial sites. Most environmental scientists in each plant concern only their own effluents to meet the standard requirement, but they do not pay attention on the overall wastewaters from all industries. The BOD in the Mae Kuang River varied from 1.54-2.18 mg L^{-1} in the rainy season, from 2.19 to 2.81 mg L^{-1} in the winter season and from 1.50 to 1.97 mg L^{-1} in the summer season. Increased values of BOD in stations 2, 3 and 4 were observed in this River because of pollutant combination including urban and industrial sewage. In summer, the water flow velocity decreased dramatically, while there were still a lot of high organic drainages without treatment. As a result, DO were in un-acceptable levels in summer and subsequently resulted in fish death.

Surface inland water quality standards in Thailand were classified into five classes. Class 1 refers to extra clean natural water without any effluent that is able to be used for domestic consumption after simple disinfection, for recreation, or for aquatic organism breeding and conservation. Class 2 refers to clean water that can be used as domestic water after treatment, for recreational purposes or for fishing, farming, aquatic organism conservation, swimming. Class 3 includes polluted water, which can be used after water improvement. This water can also be used for agricultural purpose. Class 4 includes polluted water, which can only be used as industrial water after treatment.

Table I: Physical-chemical parameters and total metal concentrations in water from Mae Kuang River during June, 2008-July, 2009

Season	Station	pH	Dissolved oxygen (mg L^{-1})	T (°C)	BOD (mg L^{-1})	COD (mg L^{-1})	NH_3 (mg L^{-1})	PO_4 (mg L^{-1})
Rainy	1	7.42 ± 0.47a	3.68 ± 1.54a	27.70 ± 0.67a	1.54 ± 0.59 a	3.34 ± 0.69a	0.0382 ± 0.02a	0.0995 ± 0.05a
	2	7.44 ± 0.43a	4.42 ± 0.41ab	28.15 ± 0.86a	2.01 ± 0.38 ab	3.41 ± 0.77a	0.0333 ± 0.02a	0.2106 ± 0.12b
	3	7.41 ± 0.43a	4.60 ± 0.67ab	28.53 ± 0.97a	2.18 ± 0.34 b	3.62 ± 0.62a	0.0529 ± 0.02a	0.1412 ± 0.08ab
	4	7.38 ± 0.40a	4.37 ± 0.68ab	28.54 ± 0.96a	2.02 ± 0.20 ab	3.50 ± 0.56a	0.0392 ± 0.02a	0.1389 ± 0.05ab
	5	7.48 ± 0.41a	4.11 ± 0.50ab	28.45 ± 1.33a	1.78 ± 0.58 ab	3.42 ± 0.52a	0.0447 ± 0.02a	0.1447 ± 0.04ab
	6	7.45 ± 0.40a	4.95 ± 0.30b	28.75 ± 1.07a	1.93 ± 0.51 ab	3.38 ± 0.61a	0.0453 ± 0.03a	0.1594 ± 0.07ab
Winter	1	8.97 ± 2.17c	6.36 ± 0.80c	22.92 ± 1.54c	2.62 ± 0.44cd	3.11 ± 0.69c	0.0679 ± 0.05c	0.6339 ± 0.70c
	2	8.15 ± 0.10c	6.25 ± 0.70cd	23.43 ± 1.30c	2.81 ± 0.41d	3.25 ± 0.38c	0.0729 ± 0.05c	0.7073 ± 0.63c
	3	8.02 ± 0.13c	5.62 ± 0.52cde	24.04 ± 1.53c	2.58 ± 0.40cd	3.37 ± 0.46c	0.1503 ± 0.24c	0.6577 ± 0.65c
	4	8.08 ± 0.15c	5.47 ± 0.74de	24.18 ± 1.50c	2.39 ± 0.23cd	3.37 ± 0.56c	0.0740 ± 0.04c	0.6793 ± 0.70c
	5	7.99 ± 0.11c	4.80 ± 0.80e	24.38 ± 1.53c	2.19 ± 0.43c	3.31 ± 0.63c	0.0830 ± 0.04c	0.6728 ± 0.70c
	6	8.09 ± 0.22c	6.17 ± 0.71cd	24.54 ± 1.63c	2.74 ± 0.27d	3.36 ± 0.44c	0.0686 ± 0.04c	0.7312 ± 0.67c
Summer	1	7.41 ± 0.47f	2.21 ± 1.02g	29.63 ± 1.52g	1.79 ± 0.38f	2.86 ± 1.50f	0.0112 ± 0.02f	0.1743 ± 0.15f
	2	7.66 ± 0.46f	2.22 ± 1.17g	29.62 ± 1.08g	1.96 ± 0.36g	3.49 ± 1.50f	0.0127 ± 0.02f	0.1242 ± 0.11f
	3	7.85 ± 0.79f	2.08 ± 0.59g	29.61 ± 1.22g	1.97 ± 0.45g	3.01 ± 1.07f	0.0177 ± 0.01f	0.1795 ± 0.23f
	4	7.64 ± 0.55f	2.05 ± 0.87g	29.92 ± 0.77g	1.92 ± 0.41g	2.93 ± 1.73f	0.0208 ± 0.02f	0.1773 ± 0.24f
	5	7.58 ± 0.51f	1.90 ± 1.42g	29.97 ± 1.72g	1.67 ± 0.26f	2.21 ± 0.87f	0.0187 ± 0.02f	0.2791 ± 0.38f
	6	7.59 ± 0.40f	1.91 ± 0.89g	30.16 ± 1.70g	1.50 ± 0.49f	3.61 ± 1.07f	0.0109 ± 0.01f	0.2305 ± 0.30f

*Different letters in same column in each season indicate significant differences at P < 0.05 (ANOVA)
BOD = Biochemical Oxygen Demand; COD = Chemical Oxygen Demand

Class 5 refers to heavily polluted water that can be only used for navigation. Referring to pH, BOD and DO parameters, water in the Mae Kuang River was classified as class 3-4, according to Thailand National Environmental Quality Act (1992). That means this water can also be used for consumption after water improvement and disinfection. However, the sewage treatment processing must be carried out and sources of pollution must be reduced. Drought crisis, industrial development and un-controlled city expansion make this problem more serious. Mechanical aeration and sewage treatment is recommended to reduce this problem. A high nutrient disposal also causes massive water hyacinth expansion, affects the aquatic organisms and increases the cost of tap water preparation. Community participation must be applied for river clean-up. Prasopkeatpoka (2008) surveyed the willingness to pay of the local residents was about 5 $US/month for the Mae Kuang River conservation.

Pb and Cd concentrations in water were below detection limits, while the concentrations of Zn in water were 0.01-0.11 mg L^{-1}. Pb, Cd and Hg in surface water of the Ping River were below than detection limit (Traichaiyaporn & Chitmanat, 2008). Similar to study of Bordalo *et al*. (2001), Cd in water was not always found in the Bangpakong River, one of the most important rivers in the Eastern Thailand. The levels of zinc, lead and cadmium in this study should not present any hazard for fish. However, villagers usually believe the fish death phenomenon in Mae Kuang River is caused by heavy metals from industrial effluents. For this reason, they always ignore to reduce or treat their own wastewater after daily uses.

Metal concentrations in sediment: In some cases, sediments hold greater than 99% of total quantity of a metal present in an aquatic system (Netpae & Phalaraksh, 2009). Generally, content of metal in sediment were higher than content of metal in water and fish (Demark *et al.,* 2006; Klavin *et al.,* 2000) The heavy metal concentrations were 100-10,000 times greater in the sediment than in the water (Yi *et al*., 2008). Pb, Cd and Zn concentrations in sediment were 3.13-27.56, <0.02-0.43, 3.42-10.32 mg kg^{-1}, respectively (Table II). Higher mean metal concentrations were found in sampling sites near industrial community. Especially, Pb is usually used in a large number in industrial process. Clearly, Zn, Cd and Pb levels in sediment were much lower than global standards. However, there were great variations in heavy metal concentrations due to a large water flows and sediment in this river. Rauf *et al.* (2009) suggest that a big part of heavy metals in sediments are likely to release back to water compartment; for this reason, special attention must be given to the remobilization issue.

Metal concentrations in fish: Jullien's mud carp (*Henicorhynchus siamensis*), Smith's barb (*Puntioplites proctozysron*) and snakehead (*Channa striatus*) were most abundant indigenous fish species. The levels of zinc, lead and cadmium in muscles of snakehead fish (*C. striatus*) are given in Table II. The highest Zn (12.19 mg kg^{-1} wet weight) concentration was detected in rainy season and Cd (0.24 mg kg^{-1}) and Pb (2.37 mg kg^{-1}) were highest in summer and winter seasons, respectively. A fluctuation of heavy metal concentrations in fish was observed since different temperature in each season affects the metal uptake and fish metabolism. Heavy rainfall increases metal concentrations in water by agricultural waste runoff leading to higher metal accumulation in wet seasons (Dural *et al*., 2007). Priprem *et al*. (2007) stated that the average metal concentrations in fish tissues were Zn > Pb> Cd, which were similar to our investigation.

Differences in metal accumulation between fish species were observed due to different physiology, size and feeding habits. No Cd and Pb residues were found in

Table II: Heavy metal concentration in water (mg L^{-1}), sediment (mg kg^{-1}), fish (mg kg^{-1}) from Mae Kaung River (All results are given as mean value standard deviation of three determinations)

Samples	Zn	Pb	Cd
	Rainy		
Water			
Site 1	0.03 ± 0.01a	<0.005	< 0.002
Site 2	0.03 ± 0.00ab	<0.005	< 0.002
Site 3	0.06 ± 0.01bc	<0.005	< 0.002
Site 4	0.07 ± 0.03c	<0.005	< 0.002
Site 5	0.04 ± 0.00abc	<0.005	< 0.002
Site 6	0.04 ± 0.01abc	<0.005	< 0.002
Sediment			
Site 1	6.17 ± 0.17a	10.81 ± 1.49a	0.14 ± 0.02ab
Site 2	6.34 ± 0.81a	16.51 ± 3.45b	0.16 ± 0.10ab
Site 3	10.55 ± 0.29b	18.24 ± 0.87b	0.33 ± 0.04c
Site 4	6.10 ± 0.29a	17.65 ± 5.82b	0.24 ± 0.06bc
Site 5	4.21 ± 0.37c	13.40 ± 0.82b	0.07 ± 0.06a
Site 6	1.12 ± 0.12d	4.86 ± 0.46b	0.04 ± 0.05a
Fish			
Site 1	9.25 ± 0.961ab	1.48 ± 0.51a	0.08 ± 0.02a
Site 2	8.36 ± 1.55a	1.70 ± 0.69a	0.14 ± 0.02a
Site 3	12.19 ± 1.07b	1.79 ± 0.18a	0.15 ± 0.05a
Site 4	8.33 ± 1.05a	1.56 ± 0.59a	0.09 ± 0.01a
Site 5	7.50 ± 0.65a	1.09 ± 0.15a	0.10 ± 0.05a
Site 6	6.63 ± 1.98a	1.04 ± 0.31a	0.07 ± 0.02a
	Winter		
Water			
Site 1	0.04 ± 0.01a	<0.005	< 0.002
Site 2	0.07 ± 0.04a	<0.005	< 0.002
Site 3	0.08 ± 0.02a	<0.005	< 0.002
Site 4	0.05 ± 0.01a	<0.005	< 0.002
Site 5	0.07 ± 0.01a	<0.005	< 0.002
Site 6	0.04 ± 0.01a	<0.005	< 0.002
Sediment			
Site 1	1.86 ± 0.03a	4.68 ± 0.19a	< 0.02
Site 2	2.05 ± 0.10a	6.47 ± 0.83b	0.11 ± 0.03a
Site 3	5.00 ± 0.38c	10.36 ± 0.51c	0.17 ± 0.01a
Site 4	6.32 ± 0.36d	12.78 ± 1.94c	0.15 ± 0.08a
Site 5	1.63 ± 0.10a	4.07 ± 0.20a	0.08 ± 0.01a
Site 6	3.87 ± 0.51b	9.67 ± 0.88c	< 0.02
Fish			
Site 1	4.07 ± 1.32b	0.41 ± 0.15a	0.14 ± 0.05a
Site 2	4.82 ± 0.45b	1.16 ± 0.38ab	0.14 ± 0.08a
Site 3	4.46 ± 0.63b	1.56 ± 0.42bc	0.11 ± 0.05a
Site 4	3.37 ± 0.50a	2.13 ± 0.21bc	0.07 ± 0.06a
Site 5	4.60 ± 1.21b	2.37 ± 0.24c	0.24 ± 0.12a
Site 6	6.06 ± 1.11c	0.49 ± 0.38a	0.21 ± 0.02a
	Summer		
Water			
Site 1	0.03 ± 0.01ab	<0.005	< 0.002
Site 2	0.07 ± 0.03cd	<0.005	< 0.002
Site 3	0.07 ± 0.01d	<0.005	< 0.002
Site 4	0.06 ± 0.01bcd	<0.005	< 0.002
Site 5	0.02 ± 0.01a	<0.005	< 0.002
Site 6	0.04 ± 0.01abc	<0.005	< 0.002
Sediment			
Site 1	4.70 ± 0.56a	6.73 ± 0.37a	< 0.02
Site 2	6.24 ± 0.19a	23.34 ± 1.66c	0.14 ± 0.02a
Site 3	14.16 ± 5.11b	12.13 ± 4.62b	0.19 ± 0.03ab
Site 4	6.92 ± 0.32a	6.42 ± 0.67a	0.21 ± 0.03ab
Site 5	3.38 ± 0.31a	5.09 ± 0.26a	0.25 ± 0.03b
Site 6	5.77 ± 0.89a	26.44 ± 1.12c	< 0.02
Fish			
Site 1	7.07 ± 1.26a	1.40 ± 0.07a	0.09 ± 0.01ab
Site 2	8.32 ± 1.95a	1.43 ± 0.31a	0.18 ± 0.06ab
Site 3	10.02 ± 1.15a	1.65 ± 0.03a	0.21 ± 0.05b
Site 4	7.70 ± 2.16a	1.58 ± 0.61a	0.11 ± 0.07ab
Site 5	7.17 ± 0.94a	1.22 ± 0.17a	0.12 ± 0.04ab
Site 6	6.07 ± 2.14a	1.07 ± 0.34a	0.06 ± 0.03a
Background concentrations in water* (world average)	10	0.2	0.02
Tolerance level in fish**	50	0.5	0.1

*Klavin *et al.* (2000); **Demirak *et al.* (2006); ***Different letters in same column in each season indicate significant differences at P < 0.05 (ANOVA)

Henicorhynchus siamensis and *Puntioplites proctozysron* flesh, while the concentrations of Zn in these fish were 4.57-6.58 mg kg^{-1}. Although Pb is toxic metal, it poorly accumulates in fish muscle (Erdoğrul & Erbilir, 2006). This study conflicted with Mzimela *et al*. (2003), which reported that Pb concentrations in fish reflected increased concentrations in water. As there was no metal detection in these fish muscles (*H. siamensis* & *P. proctozysron*), they cannot be used as bioindicators for metal pollution in aquatic environment.

However, Cd and Pb are accumulated in human that could be hazardous to health (Van Oostdam *et al*., 1999). The fish muscle results were compared with limit values found in the bibliography using wet weights. International Standards for Trace Elements in edible portion of freshwater fish based on Compilation of Legal Limits for Hazardous Substances in Fish and Fishery Products, Food and Agriculture Organization of the United Nations (Nauen, 1983) were 40-100, 2-10 and 0.05-2 mg kg^{-1} (wet weight) for Zn, Pb and Cd, respectively. The Joint FAO/World Health Organization suggested the provisional tolerable weekly intakes are 0.007 and 0.025 mg kg^{-1} body weight for cadmium and lead, respectively (Castro-González & Méndez-Armenta, 2008). As there are different in standard levels, it is difficult to justify that snakehead fish from some sample site were safe for consumption or not. It could inform local population that eating fish from the Mae Kuang River is at your own risk. This result was in agreement with recommendation of French, which is to consume fish from various sources and avoid eating fish captured from heavily contaminate sites especially in Adour-Garonne Rivers (Shinn *et al*., 2009). Usero *et al*. (2004) noted that metal concentrations in fish muscles were significantly lower than those found in fish livers and enrichment factors in the livers for Zn, Cd and Pb were around 5. The study undergoes to determine the relationship between heavy metals in different fish tissues and biological responses of fish.

Fig. 1: Map of the sampling stations in the Mae Kuang River

The concentrations of heavy metals in water, sediments and fish from sampling stations near industrial park were quite higher than other samples. As, toxic metals including Cd and Pb were not detected in water samples, sometimes people neglect to pay attention on accumulation of these toxic substances in sediment and fish. In addition, a potential health risk may generate in near future because of the un-planned rapid expansion of agricultural, provincial and industrial development.

CONCLUSION

Anthropogenic pollution from urban sewage, industrial effluent and agricultural runoff was clearly seen between the sampling stations 02 and 04 of the Mae Kuang River. Seasonal variations and flooding affected water flow rate and subsequently led to pollutant dilution. Even though heavy metal contents in water and sediments were below the acceptable levels, a hazardous possibility may generate depending on rapid expansion of urban and industrial development in near future. The heavy metal concentrations varied among fish species. Moreover, Pb levels in snakehead fish from some sites were greater than acceptable standard for consumption. Eating high contaminated fish could result in adverse effects although fish is one of healthy foods.

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