Research article

Metals and Nutrient Seasonal Variations in the Namphong River NE Thailand and Land Use Practices

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Abstract The Namphong river catchment in NE Thailand, part of the Mekong River catchment, has agro-industrial activities, dry land farming, rice cultivation and river cage aquaculture. Most utilize irrigation while larger industrial activities extract groundwater. The tropical wet and dry seasons cause variation in river flow. Potential effects of water quality may arise annually from constituents introduced by agricultural and other practices. Nutrients are added to soil to improve agricultural production and directly to the river in cage aquaculture from fish feed. The seasonal variations were considered from heavy metals (cadmium, copper, iron, manganese, lead and zinc) and nutrients in the Namphong River during one annual cycle and their relationships to water quality. Water samples were collected from 10 sites along the Namphong River in January 2012 (dry season mean flow 8 sec/m) and 9 sites in September 2012 (wet season mean flow 28 sec/m). Labile metals estimated by the Diffusive Gradient in Thin Films (DGT) technique showed no toxicity to aquatic biota. Most metals showed concentration and location consistency in both seasons. Iron and manganese in pulp mill discharge and vegetable cultivation downstream showed high concentrations in September indicating a groundwater or saturated soil seepage source from reducing conditions. Nutrients decreased by half from January to September; total N was higher at upstream sites in January while nitrate and orthophosphate were not significant and pH and electrical conductivity were consistent for both seasons. Hardness and alkalinity increased in September and were highest in pulp mill discharge indicating a groundwater source. Total and suspended solids were affected by wet season runoff. Variations in metals and nutrients in January and September were attributed to differences in Namphong River flow and from seasonality and agricultural activities. Large agro-industries, particularly pulp, contributed the highest concentrations of nutrients and metals to the river.

Keywords metals, nutrients, seasonal, variations, river flow, land use practices

INTRODUCTION

The Namphong River in the NE part of Thailand is within a sub-catchment of the Mekong River (Fig. 1). The Namphong River flows to the Chi River and via the Mun River to the Mekong River. Below Ubolratana Dam, there are extensive agro-industry and farming activities along the Namphong River. The wet-dry agricultural activities use irrigation from dam storage and some supplementary groundwater supply. A key question is: what are the effects of seasonal variations of heavy metals and nutrients in the Namphong River and their relationships to other water quality parameters associated with agro-industry and farming activities. The prevailing tropical wet and dry seasons cause variation in river flow. The background water quality is influenced by water seepage through geological strata and soil before entry to the main river channel. Nutrients are added to soil to improve agricultural production and in river cage aquaculture are transferred directly from fish feed to the river water. Potential effects are therefore possible from constituents added to river water during the annual cycle that may arise from heavy metals and nutrients introduced by agricultural, aquaculture, urban discharges from Khon Kaen to tributaries and other practices.

OBJECTIVE

This study aimed to understand the effects of seasonal variations of heavy metals and nutrients in the Namphong River during one cycle and their relationships to other water quality parameters associated with land use practices comprising agro-industry and small-scale farming activities along the Namphong River, a sub catchment of the Mekong River located in NE Thailand. The study compares water quality data with existing water quality criteria during one annual wet-dry season cycle.

METHODOLOGY

Water samples were collected from 10 sites along the Namphong River in 19-23 January 2012 and 9 sites 20-24 September 2012 (Fig. 1). Site C is on a small tributary less than a few km to the Namphong River from the pulp and paper mill (Fig. 1.C). Water quality parameters including heavy metal and nutrient concentrations were measured using standard techniques (APHA-AWWA-WEF, 1998). Concentrations of labile metals were estimated by the Diffusive Gradient in Thin Films (DGT) technique (Komarova et al. 2012, 2013). The DGT accumulates labile metal species in waters (Davison and Zhang, 1994; Davison et al. 2000; Zhang and Davison, 1995; Zhang and Davison, 2000). The DGT technique incorporating passive sampling gives an integrated concentration measurement (Davison and Zhang 1994) and was previously described for measurement of labile metal forms in water and predicting their toxicity to aquatic biota (Komarova et al. 2012, 2013).

The DGT passive samplers were deployed to accumulate labile heavy metals at the 10 sites (Fig. 1) and were used to measure labile metal forms in waters at sub-nanogram per liter levels. Passive samplers are defined as human-made devices where sample collection is completely passive (Komarova et al. 2012). Measurements were made of pH, electrical conductivity (EC), temperature, dissolved oxygen (DO) concentration in river water using field equipment. Active (direct) sampling was employed to collect water samples (1L) before and after DGT deployment at each site in January and September for total dissolved solids (TDS), suspended solids (SS), total alkalinity (mg/L $CaCO_3$), hardness (mg/L $CaCO_3$), nutrients [total N and P, nitrate (NO_3^-) and ortho-phosphorus (P)] and dissolved organic carbon (DOC). All measurements on the active water samples were undertaken in the field or at the Division of Land Resources and Environment, Department of Plant Sciences and Agricultural Resources, Faculty of Agriculture, Khon Kaen University. Following deployment, DGTs were sent by air courier to the Queensland Health Forensic and Scientific Services (QHFSS), Inorganic Chemistry laboratory at Coopers Plains, Australia, for the extraction of the heavy metals from the gel and analysis by inductively-coupled plasma mass spectrometry (ICPMS). The time-averaged concentration of dissolved heavy metal species in the bulk solution, C, is then calculated using the DGT equation derived from Fick's first law of diffusion (Komarova et al. 2012, Zhang and Davison, 1995).

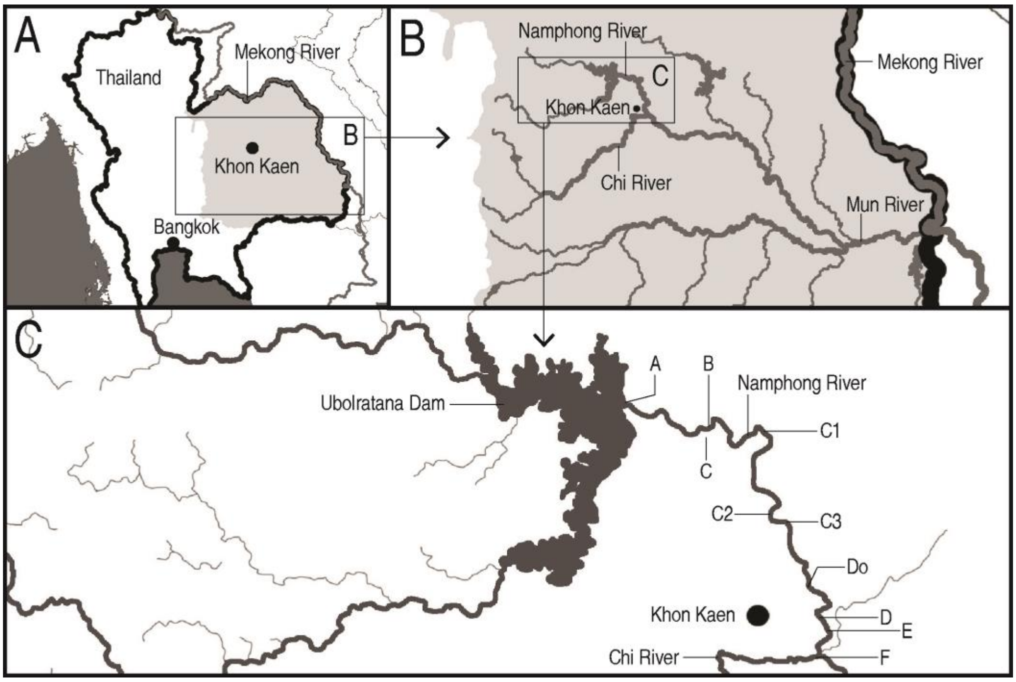

Fig. 1 Location of study site in the Mekong River basin NE Thailand (Maps A and B) and sampling sites along the Namphong River (Map C)

Sites A – Ubolratana Dam; B – fish cage (in-river cage aquaculture for Tilapia production); C – pulp/paper industrial plant (discharge via small tributary to main river); sugar industrial plant; C2 cucumber culture; C3 corn culture; Do vegetables culture; D vegetable culture and paddy fields; E vegetables culture; and F – vegetables culture, residential discharge to Chi River just upstream from confluence with Namphong River

Water quality was assessed by comparison with the Water Quality Standards of the Pollution Control Department, Ministry of Natural Resources and Environment, Thailand and the protection of the aquatic ecosystem of the Australian ANZECC/ARMCANZ (2000) decision tree process for assessing heavy metal toxicity in water. Site-specific trigger values for metals were calculated by using a correction for hardness (mg/L $CaCO_3$) to the default ANZECC/ARMCANZ (2000) heavy metal guideline value. Aquatic metal toxicity decreases with increasing water hardness as soluble metal is precipitated. The metal concentrations in labile or bioavailable forms (DGT technique) and metals in particulate and insoluble colloidal fractions were also measured following filtration (<0.45µm membrane) and were shown to be much higher compared with the bioavailable fractions of metals in Namphong river water (Komarova et al. 2013).

RESULTS AND DISCUSSION

Tables 1 and 2 give average water quality and nutrient data for January and September at the 10 sampling sites (Fig.1). The Namphong River mean flow was 3.6 times lower in January (dry season mean flow 8 sec/m) compared with September (wet season mean flow 28 sec/m). Table 3 gives average labile metal concentration data using DGTs [cadmium (Cd), copper (Cu), iron (Fe), manganese (Mn), lead (Pb) and zinc (Zn)] for each sampling period at the 10 sampling sites.

The water quality shows little difference in pH, DO and DOC between January and September. Temperature was lower in January (mean 24 ^{0}C) compared with September (mean 32 ^{0}C) (Tables 1 and 2). Mean EC (TDS) in January was 65% of September and indicated wet season flushing of salts or groundwater contribution to the river; both alkalinity and hardness showed the same feature. Mean SS in January was 51% of September indicating wet season runoff of solids and an association with EC. DOC was higher in September showing the effect of runoff or biological activity in the river. Total N in January and September were similar but in January the contribution from upstream was higher and was subsequently diluted moving further downstream. Nitrate was lower in September indicating dilution with wet season flow. Total (not shown) and ortho-P were both similar in January and September but localized additions to river water were apparent. Water quality standards for Thailand (Tables 1 and 2), excepting SS, were not exceeded.

Table 1 Seasonal variations of water quality in the Namphong River

Sampling site	pH		EC(µS/cm)		Temp (^{0}C)		DO (mg/L)		SS (mg/L)		TDS (mg/L)	
	Jan	Sep	Jan	Sep	Jan	Sep	Jan	Sep	Jan	Sep	Jan	Sep
A. Ubolratana	7.4	7.4	94	116	23.0	31.9	6.28	5.20	53	213	46	59
B. River cage aquaculture	7.7	7.4	86	106	23.0	32.3	5.45	5.78	80	274	47	52
C. Pulp mill	8.2	8.4	1250	1040	25.0	31.7	5.88	4.60	1790	1067	672	508
C1.Sugar mill	7.8	7.4	97	143	25.0	32.8	5.29	5.18	360	314	52	62
C2.Cucumber	7.9	7.5	80	154	23.0	32.2	7.65	6.20	107	264	47	76
C3. Corn	7.7	7.4	99	122	23.0	32.7	7.31	5.62	80	290	51	61
Do.Vegetable	7.9	7.3	102	164	25.0	32.6	5.46	5.20	133	210	55	80
D. Vegetable/ paddy field	7.9	7.4	106	191	25.0	33.1	5.75	5.44	120	287	55	95
E. Vegetable	7.7	7.5	109	171	25.0	33.4	5.54	5.05	150	244	57	84
F. Vegetable	7.8	7.4	110	181	25.0	30.8	5.47	4.72	150	317	57	89

Note: Water Quality Standards Pollution Control Department, Ministry of Natural Resources and Environment, Thailand Freshwater animal Temperature (^{0}C) 23-32, pH 5-9, Dissolved Oxygen (mg/L) 3 min., Suspended solids (mg/L) 25 max.

Table 2 Seasonal variations of water quality and nutrient content in the Namphong River

Sampling site	Alkalinity (mg/L $CaC0_3$)		Hardness (mg/L $CaC0_3$)		DOC (mg/L)		Total N (mg/L)		NO_3^- (mg/L)		Ortho-P / Total P (mg/L)	
	Jan	Sep	Jan	Sep	Jan	Sep	Jan	Sep	Jan	Sep	Jan	Sep
A. Ubolratana	18	65	64	684	2.3	4.6	23	10	1.8	1.2	0.04/ 0.34	0.004/ 0.40
B. River cage aquaculture	31	63	66	745	1.9	8.8	26	11	2.8	1.0	0.05/ 0.36	0.002/ 0.26
C. Pulp mill	131	190	227	1289	2.3	22.5	28	8	2.5	0.5	0.22/ 1.31	0.024/ 2.6
C1.Sugar mill	24	59	70	532	3.4	3.7	19	11	3.1	1.1	0.05/ 0.39	0.002/ 0.25
C2.Cucumber	29	74	69	613	1.9	5.3	23	12	2.9	1.4	0.04/ 0.37	0.008/ 0.88
C3. Corn	12	65	67	412	1.8	4.0	12	10	2.0	1.1	0.04/ 0.33	0.008/ 0.94
Do.Vegetable	18	70	65	839	1.3	4.1	13	12	1.9	1.1	0.04/ 0.35	0.007/ 0.72
D. Vegetable/ paddy field	23	55	69	549	3.6	6.2	12	12	3.0	1.0	0.04/ 0.33	0.006/ 0.64
E. Vegetable	30	61	61	377	2.9	5.9	12	10	2.2	0.8	0.04/ 0.36	0.006/ 0.53
F. Vegetable	30	65	66	499	3.1	3.2	7	9	2.4	1.2	0.03/ 0.36	0.006/ 0.68

Note: Water Quality Standards Pollution Control Department, Ministry of Natural Resources and Environment, Thailand protecting Water Source Class 3 (applies to Namphong River). NO_3-N 5 mg/L; Effluent Standard B Point Source Total TKN (mg/l) 35, Total N (mg/L) 410, Total P (mg/L) 0.5.

The labile metal DGT concentrations for Cd, Cu, Pb and Zn are very low and do not exceed the Water Quality Standard Class 3 (Table 3). Comparison of Cd, Cu, Pb and Zn labile concentrations against the ANZECC/ARMCANZ (2000) criteria adjusted for hardness (Table 3) indicates that these metals are not likely to be toxic to aquatic biota in the Namphong River.

Table 3 Seasonal variations of labile metal concentrations using DGT (passive) sampling (average of before and after DGT sampling for 19-23 January and 20-24 September 2012, respectively)

Sampling site	Cd (µg/L) DGT conc.		Cu (µg/L) DGT conc		Fe (µg/L) DGT conc		Mn (µg/L) DGT conc		Pb (µg/L) DGT conc		Zn (µg/L) DGT conc	
	Jan	Sep	Jan	Sep	Jan	Sep	Jan	Sep	Jan	Sep	Jan	Sep
A. Ubolratana	0.021	0.00	0.39	0.37	0.68	4.80	1.19	9.17	0.032	0.00	2.96	3.86
B. River cage aquaculture	0.021	0.01	0.30	0.40	2.43	4.03	6.76	27.9	0.024	0.00	2.75	2.90
C. Pulp mill	0.020	0.00	0.24	0.41	34.3	31.5	269	106	0.049	0.00	2.16	4.08
C1.Sugar mill	0.021	0.00	0.22	0.02	2.19	1.39	13.0	8.62	0.026	0.00	2.08	2.04
C2.Cucumber	0.021	-	0.19	-	27.8	-	21.5	-	0.040	-	1.68	-
C3. Corn	0.021	0.01	0.23	1.71	15.5	35.2	20.6	66.7	0.042	0.05	3.82	6.08
Do.Vegetable	0.020	0.00	1.45	0.23	8.23	18.5	23.9	126	0.031	0.00	1.42	2.65
D. Vegetable/ paddy field	0.020	0.00	0.25	0.36	4.84	5.26	30.8	32.1	0.13	0.00	9.25	0.93
E. Vegetable	0.020	0.00	0.21	1.17	3.00	9.23	16.9	36.4	0.17	0.05	8.53	1.40
F. Vegetable	0.027	0.00	0.28	0.19	8.00	3.31	26.9	16.8	0.50	0.00	1.47	1.33

Note: Water Quality Standards Pollution Control Department, Ministry of Natural Resources and Environment, Thailand protecting Water Source Class 3 (applies to Namphong River): Cd 5 µg/L (hardness <100 mg/L $CaCO_3$) or 50 µg/L (hardness >100 mg/L $CaCO_3$); Cu 100 µg/L, Pb 50 µg/L and Zn 1000 µg/L. Trigger value (µg/L) 95% of aquatic species protection (adjusted for hardness) Cd (0.5 µg/L), Cu (3.5 µg/L), Fe (-), Mn (-), Pb (13.6 µg/L) and Zn (20.0 µg/L) (ANZECC/ARMCANZ, 2000).

The Mn and Fe DGT concentrations show high levels in the pulp mill effluent at Site C and at downstream Namphong River Sites C2, C3 and Do (Fig. 1.C). Below Site Do labile Fe decreases to levels similar to upstream while labile Mn decreases but remains higher than found upstream. It is clear that the source of labile Fe and Mn at and below Site C2 is different from Site C and the location of Site C2 is more than 20 km downstream from Site C (Fig 1.C). Thus there is a different source of labile Fe and Mn at and below Site C2 which may be shallow seepage from water-saturated soil, including paddy fields as there is no increase in total alkalinity and hardness as observed at Site C (Table 2). The Cu DGT concentrations are low but show some increase at Sites C3 (September), Do (January) and Site (E) (September) (Fig. 1.C).

Wet season transfer of particulate and soluble constituents is a key feature of the water quality data from this study. The industrial area (Sites C and C1 - pulp and sugar mills) was a major potential source of contamination of the Namphong River associated with increased levels of labile heavy metals in both sampling periods. The increase of total alkalinity, hardness and EC (Tables 1 and 2) for both periods confirms that groundwater was being used in the pulp mill (Site C). The release of Cu and Pb in the Namphong River occurred in the area of rice and mixed vegetable cultivation (Sites C3 - E) and was most likely related to extensive pesticide use (metals in the pesticides used such as carbamates). At Site F in the Chi River labile metal levels were low, excepting for Fe and Mn, and were similar to the Namphong River at the upstream Site A (Fig 1.C).

The overall finding is that there is little effect on the water quality of the Namphong River from upstream to downstream, from the extensive river cage aquaculture and vegetable farms, and paddy fields and taking account of dilution removing observed additions of suspended solids and labile metals from the major agro-industrial activities located upstream.

CONCLUSION

Variations in the levels of heavy metals and nutrients were observed in the Namphong River in January and September 2012. These variations could be attributed to differences in river flow and associated with seasonality and agricultural activities in the catchment. Although the industrial area (pulp and sugar industries) is a major source of contamination of the Namphong River with heavy metals, there is sufficient dilution from the Namphong River to give safe levels downstream for protection of aquatic species. The outcome of this study will help to develop more focused monitoring of specific toxic heavy metals at particular locations on the Namphong River.

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