Research article

Passive Sampling Approach to Identify Contaminants in a Tropical Freshwater River System

TATIANA KOMAROVA*
Queensland Health Forensic and Scientific Services (QHFSS), Brisbane, Australia
Email: Tatiana_Komarova@health.qld.gov.au

CHULEEMAS BOONTHAI IWAI
Faculty of Agriculture, Khon Kaen University, Khon Kaen, Thailand

ATCHARAPORN SOMPARN
Faculty of Agriculture, Khon Kaen University, Khon Kaen, Thailand

NATSIMA TOKHUN
Faculty of Agriculture, Khon Kaen University, Khon Kaen,Thailand

BARRY NOLLER
Centre for Mined Land Rehabilitation (CMLR), Sustainable Minerals Institute, The University of Queensland, Brisbane, Australia

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Abstract This study aimed to understand labile metal distribution and water quality associated with agro-industry and farming activities along the Namphong River, a sub catchment of the Mekong River located in NE Thailand. An integrated sampling program was designed to identify the range of potential contaminants in the Namphong River by incorporating active or grab sampling along with passive sampling using the diffuse gradients in thin films technique (DGTs) for the bio available heavy metal forms, field measurement of pH, electrical conductivity, temperature and dissolved oxygen and laboratory-based measurement of total solids, total alkalinity, hardness, nutrients and dissolved organic carbon concentration together with heavy metals (total and filtered (< 0.45 µm) fractions). The DGTs were deployed at 10 different sites along approximately 50 km of the Namphong River for 4 days to enable sufficient integrative sampling of heavy metals. One liter of water samples were collected from the sites before and after deployment of the DGTs. Although total and filtered (<0.45 µm) concentrations of cadmium, chromium, copper, lead and zinc in the Namphong River from active sampling significantly exceeded the trigger values of water quality guidelines for protection of freshwater aquatic species, the concentration of metals estimated from DGT data indicated more accurately that the bio available metal levels were below the trigger values and that there were no predicted effects on aquatic species. The agro-industrial area (pulp and sugar mills) was a major potential source of contamination of the Namphong River associated with increased levels of heavy metals (aluminium, chromium, cobalt, iron and manganese) but diluted to insignificant levels in the Namphong River. The release of copper, nickel and lead to the downstream Namphong River occurred in the area of rice and mixed vegetable cultivation and was most likely related to extensive pesticide use. The outcome of this study will help to develop more focused monitoring of specific toxic heavy metals at particular locations on the Namphong River.

Keywords active and passive sampling, aquatic ecosystem, DGT, heavy metals, bioavailability

INTRODUCTION

The NE part of Thailand is the location of extensive wet-dry agricultural activities with major use of irrigation from dam storage and some supplementation of water supply from groundwater sources. The rivers systems of NE Thailand are also part of the sub-catchment of the Mekong River (Fig. 1). One of the sub-catchments of the Chi River is that of the Namphong River. Below the Ubolratana Dam there are extensive agro-industry and farming activities along the Namphong River which flows to the Chi River and via the Mun River to the Mekong River. A key question was the extent and the effects on aquatic species of heavy metal additions to the river system that result from the collective of agricultural activities. River water may also be used for human consumption and recreational activities.

The Diffusive Gradients in Thin-films (DGT) technique uses passive sampling to give an integrated concentration measurement (Davison and Zhang 1994). The DGT technique was previously described for measurement of labile metal forms in water and predicting their toxicity to aquatic biota (Komarova et al. 2012). In contrast, active sampling collects a grab sample at a fixed time. This paper uses passive sampling techniques to measure dissolved inorganic compounds in waters at sub-nanogram per liter levels. “Passive” samplers are defined as human-made devices where sample collection is completely passive. The DGT technique is designed to accumulate labile metal species in environmental systems including from water (Davison and Zhang, 1994; Davison et al. 2000; Zhang and Davison, 1995; Zhang and Davison, 2000).

OBJECTIVE

This study aimed to understand the labile metal distribution associated with agro-industry and farming activities along the Namphong River a sub catchment of the Mekong River located in NE Thailand. The study addressed the following questions: (i) to compare passive DGT and active sampling techniques for heavy metals and associated water quality in the Namphong River water body for different locations; (ii) to compare labile heavy metal concentration data from the DGT technique with water quality guidelines that can be incorporated into the trace metal monitoring programs in water together with traditional methods and replace them in the future; and (iii) to use DGT analysis for labile metals to assess bioavailability to aquatic freshwater species.

METHODOLOGY

The DGT technique employed an ion exchange resin (Chelex-100) that was immobilized in a polyacrylamide gel (the binding or resin gel), to exchange analytic species from solution (Davison and Zhang 1994). Chelex-based resins can be used for simultaneous collection of many metals in water including aluminium (Al), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni) and zinc (Zn) (Komarova et al. 2012). The binding gel was separated from the bulk solution by a permeable polyacrylamide gel (the diffusive gel) and a solution diffusive boundary layer.

An integrated sampling program was designed to identify the range of potential contaminants in the Namphong River by using diffuse gradients in thin films technique (DGTs) for the passive (integrated) sampling of labile heavy metal forms, field measurements of pH, electrical conductivity (EC), temperature and dissolved oxygen (DO) concentration and active sampling for total solids (TS), total alkalinity (mg/L $CaCO_3$), hardness (mg/L $CaCO_3$), nutrients, dissolved organic carbon (DOC) and heavy metal concentrations for the total and filtered (< 0.45 µm) fractions. DGTs were deployed for 4 days from 19-23 January 2012 to accumulate labile heavy metals at 10 different sites along approximately 50 km of the Namphong River (Fig. 1).

One liter of grabbed water samples were collected before and after DGT deployment; the mean concentrations of metals were calculated from the measured parameters. 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 Division laboratory at Coopers Plains, Australia to separate the gels and elute the accumulated analyte from the binding gel using dilute nitric acid. The concentrations of metals in the eluant were then determined by inductively-coupled plasma mass spectrometry (ICPMS). The time-averaged concentration of dissolved metal species in the bulk solution, C, is then calculated using Eq. (1), which is derived from Fick's first law of diffusion (Zhang and Davison, 1995): M is the accumulated mass of a metal on the binding gel; Δg is the thickness of the diffusive gel, D is the diffusion coefficient of a specific metal in the diffusive gel, t is the deployment time, and A is the surface area of the diffusive gel exposed to the bulk solution.

$$C = M\,\Delta g / D\,t\,A \qquad (1)$$

The assessment of water quality for the protection of the aquatic ecosystem made use of a combination of analytical methods based on following the Australian ANZECC/ARMCANZ (2000) decision tree process for assessing metal toxicity in water. An initial step was to calculate site-specific trigger values for metals by using a correction for hardness, calculated from the calcium plus magnesium concentrations expressed as mg/L $CaCO_3$, to the default ANZECC/ARMCANZ (2000) guideline value. This more accurately predicts aquatic metal toxicity which decreases with increasing water hardness as soluble metal is precipitated. The next step in the decision tree process used the measurements of metals in labile or bioavailable forms and metals in particulate and insoluble colloidal fractions that could be measured through filtration (<0.45 µm membrane) to predict the bioavailable fractions of metals in waters. Thus DGT samplers offered an alternative to conventional water sampling techniques for measuring labile trace metals.

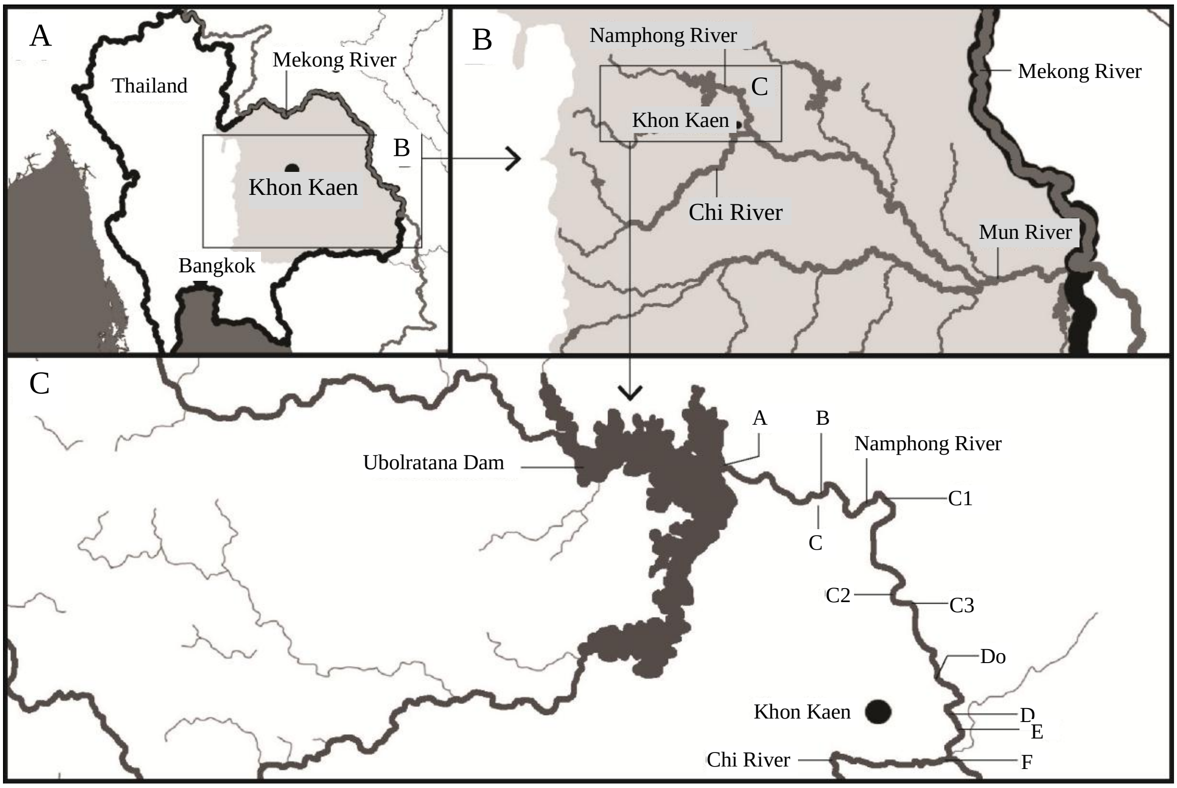

Fig. 1 Location of study site in the Mekong River basin NE Thailand (Maps A and B) and sampling sites along the Namphong River (Map C)

Sites A – Ubolratana Dam; B – fish cage (in-river cage aquaculture for Tilapia production); C – pulp/paper industrial plant (discharge via 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

RESULTS AND DISCUSSION

Tables 1 and 2 give the water quality data (mean (±sd) of before and after DGT sampling) for the 10 sampling sites along the Namphong River below the Ubolratana dam (Fig.1).

Table 1 Field water quality data (mean of before and after DGT sampling)

Sampling site	pH	EC (μS/cm)	Temp (^{0}C)	DO (mg/L)	Sat (%)
A. Ubolratana	7.0	94	23.0	6.28	76.4
B. River cage Aquaculture	7.0	86	23.0	5.45	62.8
C. Pulp mill	7.7	1250	25.0	5.88	75.1
C1. Sugar mill	7.3	97	25.0	5.29	70.3
C2. Cucumber culture	7.4	80	23.0	7.65	91.4
C3. Corn culture	7.4	99	23.0	7.31	90.1
Do. Vegetable culture	7.3	102	25.0	5.46	69.6
D. Vegetable culture and paddy field	7.3	106	25.0	5.75	70.5
E. Vegetable culture	7.2	109	25.0	5.54	69.6
F. Vegetable culture	7.3	110	25.0	5.47	69.7

Table 2 Water quality data (mean±sd of before and after DGT sampling)

Sampling site	TS (mg/L)	TDS (mg/L)	Alkalinity (mg/L $CaCO_3$)	Hardness (mg/L $CaCO_3$)	DOC (mg/L)	Total N (mg/L)	NO_3^- (mg/L)
A. Ubolratana	53± 2	46±3	18±1	64± 4	2.3	23±4	1.8±0.2
B. River cage aquaculture	80± 4	47±1	31±1	66± 4	1.9	26±4	2.8±0.3
C. Pulp mill	1790±80	672±7	131±1	227± 5	2.3	28±7	2.5±0.5
C1. Sugar mill	360±20	52±0	24±0	70± 7	3.4	19±8	3.1±0.2
C2. Cucumber culture	107±10	47±4	29±7	69± 4	1.9	23±8	2.9±0.3
C3. Corn culture	80± 0	51±3	12±0	67± 5	1.8	12±2	2.0±0.1
Do. Vegetable culture	133±19	55±0	18±1	65± 7	1.3	13±2	1.9±0.6
D. Vegetable culture and paddy field	120± 0	55±0	23±3	69± 3	3.6	12±4	3 ±1
E. Vegetable culture	150±19	57±0	30±2	61±13	2.9	12±4	2.2±0.7
F. Vegetable culture	150±19	57±0	30±0	66± 7	3.1	7 ±0	2.4±0.1

Generally good water quality was found. The Namphong River water pH (range 7.0-7.4) and hardness (range 64-70 mg/L as $CaCO_3$) were consistent and electrical conductivity showed slight increase in proceeding downstream, apart from Site C (pulp mill) which was a tributary receiving discharge to the main river and indicated that groundwater may be used in the processing. Sites C and C1 also showed that increased total solids in water were associated with these agro-industries. Nitrate was consistent travelling downstream while dissolved organic carbon (DOC) tended to increase downstream and total-nitrogen decreased downstream (Table 2). Total and filterable phosphorus (ranges 0.33 - 0.39 mg/L and 0.03 - 0.05 mg/L respectively, excluding Site C) showed no change from upstream to downstream Namphong River.

The total and filtered (<0.45 μm) concentrations of cadmium, chromium, copper, lead and zinc in the Namphong River were measured from before and after sampling and significantly exceeded the ANZECC/ARMCANZ (2000) the hardness-adjusted trigger values of water quality guidelines (Table 3). However, the concentration of metals estimated from the DGT data were below the hardness-adjusted trigger values (Table 3) and indicated (more accurately) that the labile (bioavailable) metal concentrations in the Namphong River were not significant to freshwater aquatic biota. The industrial area (Site C - pulp and sugar mills) was a major potential source of contamination of the Namphong River associated with increased levels of heavy metals (aluminium chromium, cobalt, iron and manganese). Confirmation that groundwater was being used in the pulp mill (Site C) was indicated by the increased total alkalinity, hardness, electrical conductivity (Tables 1 and 2) and the presence of iron and manganese from the total, <0.45 µm filtered and DGT concentration data (Table 3 and Fig. 2). Comparison of the DGT and active sampling (<0.45 µm filtered) data for manganese (Fig. 2) at Site C suggested that there was a high short term release of manganese into the tributary of the Namphong river during DGT deployment. Active sampling technique data (Fig. 2) showed only a slight elevation in manganese concentration as sampling was undertaken before and after the release.

Table 3 Mean concentrations of heavy metals in Namphong River and trigger values for 95% level of aquatic species protection (ANZECC/ARMCANZ 2000)

Metal	Cmax (µg/L) DGT conc.	Cmin (µg/L) Total conc.	Cmin (µg/L) Filtered (0.45 µm) conc.	Trigger value (µg/L) 95% of aquatic species protection (adjusted for hardness)
Cd	0.03	57.9	11.5	0.5
Co	0.2	0.3	0.1	ID
Cr	0.2	58.7	48.0	2.5
Cu	1.5	42.2	19.2	3.5
Fe	34.3	470.0	77.0	ID
Pb	0.5	64.0	28.0	13.6
Zn	3.8	223.0	32.2	20.0

ID; insufficient data to derive reliable trigger value

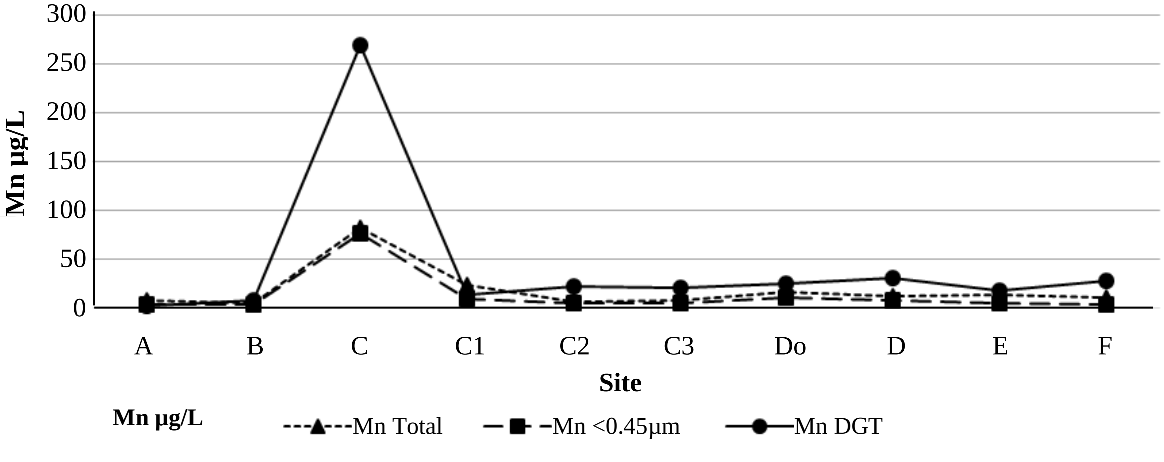

Fig. 2 Manganese (µg/L) in total, 0.45 µm filtered water fraction by active sampling and passive DGT technique from the Namphong River

The release of copper, nickel and lead in the Namphong River occurred in the area of rice and mixed vegetable cultivation (Sites Do − F) and was most likely related to extensive pesticide uses (metals in the pesticides used such as carbamates).

The overall finding is that there is little effect on the water quality of the Namphong River from upstream to downstream and taking into account of dilution removing observed additions of suspended solids and metals from the major agro-industrial activities located upstream. In addition the Namphong River water is considered safe for human consumption and recreational activities based on comparison with relevant guidelines.

CONCLUSION

Active and passive sampling methods produce similar trends with results when used simultaneously at the same sites. DGTs were shown to be effective for measuring ultra-trace levels of the labile fraction of heavy metals in water. DGTs offer an extra cost effective and sensitive method for the independent evaluation of environmental sites. DGTs help to estimate the actual levels of toxicities of metals under the specific environmental conditions and measure time integrated average water concentrations of metals over the deployment time where active sampling represents single points in time. Concentrations of Cd, Cr, Cu, Pb, and Zn in the Namphong River by active sampling significantly exceeded the hardness-adjusted ANZECC/ARMCANZ (2000) trigger value for 95% protection of aquatic species. Concentration of metals estimated from DGT data were far below the trigger values and indicated more accurately that there were no predicted toxicity effects on aquatic biota in the Namphong River from dissolved metals. Although the industrial area (pulp and sugar industries) is a major source of contamination of the Namphong River with heavy toxic metals (aluminium, cobalt, chromium, iron and manganese), 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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