*Research article*

# Pesticide Distribution in the Namphong River NE Thailand Arising from Land Use and Other Practices

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**Abstract** Large quantities of pesticides and herbicides are used in the Namphong River catchment, NE Thailand for protection of crops and agro industrial production. The aim of this study was to screen pesticides in waters of the Namphong River from in-situ river aquaculture, surface runoff and agro industrial discharges to identify if pesticide levels pose significant risk to the aquatic ecosystem. A passive sampling technique was used to estimate the level of pesticides in the river water. Pesticides were accumulated on polydimethyl siloxane (PDMS) strip passive samplers during 29 days deployment in January-February 2012, and then sent to Australia for analysis of pesticides at the University of Queensland and Queensland Health Laboratories. The PDMS passive samplers were deployed at 5 sites in the Namphong River from below the Ubonratana Dam, the tributary downstream of the paper mill and vegetable and paddy fields down to the Chi River above the junction of Namphong River. Atrazine, ametryn, chlorpyrifos and oxadiazon were found at all sites at elevated levels associated with vegetable and paddy field areas indicating their extensive application. Terbuthylazine, terbuphos and phosphate tri-n-butyl were found only in the paper mill discharge. Traces of galaxolide were found at all sites but only in significant amounts (30 times higher) just below the paper mill. Comparison of pesticides between the present and an earlier 2005 study of the paddy field ecosystem 50 km N from Khon Kaen show a shift from organochlorine use to low persistence pesticides, particularly chlorpyrifos. The results confirm that a range of pesticides are being used in the Namphong river catchment able to be detected downstream, though at low levels. These data provide a baseline, showing the need exists for more systematic and complex assessment of the catchment to develop a tool for pollution control in the catchment and to identify major sources of contamination and for ongoing environmental risk management.

**Keywords** pesticides, herbicides, passive sampling, land use practices, environmental risk management

## 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 which use irrigation from dam storage and some supplementary groundwater supply. Pesticides and herbicides from agro-industry activities are identified as potential risks to human health and the environment and as significant pollutants (Somparn et al., 2014). Of all pesticides in use, chlorpyrifos was identified as the highest volume of insecticide importation in Thailand (Department of Agriculture, 2012). The aquatic ecosystem of the Namphong River is a critical aspect for the evaluation of the effects of pesticides dispersed in the environment. Ecotoxicological effects from pesticides on aquatic organisms may be observed via biomonitoring with both individual organisms and ecosystem function and structure. The Namphong River also supports extensive cage aquaculture which may be affected by pesticides. In 2010, 209 cages produced 1536 tonnes of Nile tilapia in Khon Kaen province (Department of Fisheries, 2010).

Key questions are: (i) what are the effects of pesticides in the Namphong River?; and (ii) 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 addition, of particulate and organic matter from soil transferred directly to river water can absorb pesticides. Potential effects are therefore possible from pesticides added to river water during the annual cycle that may arise from agricultural, aquaculture and other urban discharges from Khon Kaen city.

## OBJECTIVE

This study aims to identify if pesticides and herbicides from multiple agro-based activities comprising agro-industry and small-scale farming activities along the Namphong River, are environmental and health risks, causing any impact to the Namphong River water body at different sample locations, and compares data from the 2012 dry season with existing data and criteria.

## METHODOLOGY

Pesticides and herbicides were accumulated on polydimethylsiloxane (PDMS) strip passive samplers during 19 January-23 February 2012 at 5 sites at the Namphong River from below the Ubonratana Dam, the tributary downstream of the paper mill and vegetable and paddy fields down to the Chi River above the junction of Namphong River (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. 1C). Prior to application each PDMS sampler (strips 2.5 cm x 92 cm and thickness about 400 µm) was cleaned on a horizontal shaker in fresh redistilled hexane for three consecutive 24 h periods at the pesticide analytical laboratory followed by drying under high purity nitrogen gas steam, wrapping in acetone rinsed aluminium foil and stored in the refrigerator until dispatched to Khon Kaen. The PDMS samplers were placed under water at a depth of 0.50 m and left in place for 29 days. Following collection, the PDMS samplers were placed in pre-cleaned acetone rinsed aluminium foil envelopes and kept refrigerated until dispatched with quarantine clearance details from Khon Kaen to Australia for sample processing and analysis using the routine procedures of Queensland Health Organic Chemistry Laboratory. Prior to PDMS extraction in hexane and following instrumental analysis each of them was cleaned by scrubbing with water, dipping in redistilled hexane for 30 seconds and 0.5M HCL for 20 seconds followed by rinsing with acetone and isopropanol. Water quality measured using standard techniques described (Komarova et al., 2012, 2013).

Passive samplers using polydimethylsiloxane are low cost and have an improved affinity for polar compounds relative to other samplers (Rusina et al., 2007). Comparative studies (Shaw et al., 2010) showed that PDMS samplers accumulated a larger number of compounds with log Kow 2.9 to 6.4 dissolved in water. At log Kow of 4.7 (chlorpyrifos) and 4.27 (trifluralin) the mass captured was 6 times higher in PDMS compared with other samplers with the same surface area.

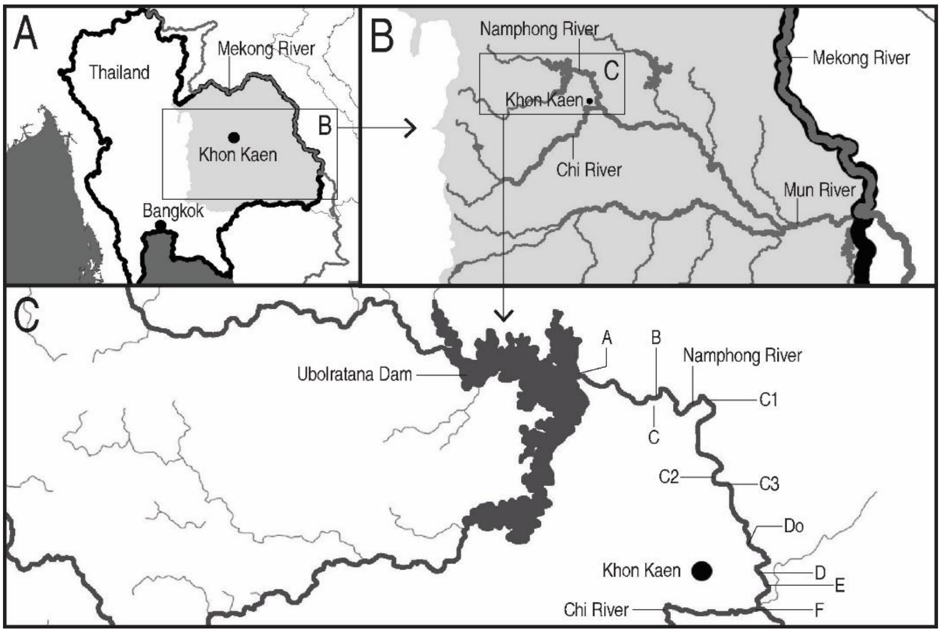


**Fig. 1 Location of study site in the Mekong River basin NE Thailand (Maps A and B) and sampling sites along the Namphong River (Map C)**

[*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*]

Well developed and validated procedures are used at all steps of PDMS passive sampler application (Shaw, 2005). The mass of contaminants accumulated in a PDMS sampler are converted to their concentrations in water (Cw, ng/L) using a sampling rate (Rs in $Ld^{-1}$) that is estimated for different pesticides at different environmental conditions in laboratory calibration study (Huckins et al., 2002) by Eq. 1.

$$C_w = M_{PDMS} / Rs\ t \tag{1}$$

where $M_{PDMS}$ is the mass of a pesticide found in the PDMS sampler after deployment (ng) and t is the deployment time in days. Method detection limits are calculated from the lowest mass per sampler detected on analytical equipment (LCMS, GCMS) and the respective compound sampling rate (e.g. <50 ng/mL for the extracted volume in the laboratory and 0.001 ng/L for chlorpyrifos in PDMS samplers for 29 day deployment). These detection limits are an order of magnitude lower than reported for pesticide concentrations using grab sampling techniques (Shaw, 2005). The linearity of the relationship between log $K_{ow}$ and sampler to water partition coefficients has been demonstrated over a wide range of compounds for PDMS (Yates et al., 2007).

Following preparation, extraction of samples and extensive clean-up procedures using size exclusion chromatography, pesticide and herbicide are analysed by different instrumental analytical methods: these are gas chromatography (GC), high performance liquid chromatography (HPLC), GC/MS and LC/MS-MS undertaken in the Queensland Health NATA accredited laboratory (according to ISO 17025) and based on USEPA Method EPA 503/6-90-004. All standards (3 external standards) and samples are spiked with an internal standard just prior to analysis.

## RESULTS AND DISCUSSION

Table 1 gives the pesticide and herbicide concentrations that have the highest inputs for effluent at Site C (Paper Mill) when compared with Table 2. Galaxolide, terbuthylazine, phosphate tri-n-butyl, tonalid and terbutryn are added in paper mill effluent (Table 1) but only galaxolide remains detectable at much lower concentration (1:35) showing dilution down to Site F at the Chi River; tonalid is diluted 1:10 at Site C3 (Fig. 1C) but is then undetectable downstream.

**Table 1 Pesticide and herbicide concentrations for 19-23 January 2012 showing Site C (Paper Mill) effluent with highest input (average of 2 PDMSs per site)**

| Sampling site | Galaxolide[a] | Terbuthylazine | Terbuphos | Phosphate Tri-n-Butyl | Tonalid | Terbutryn |
|---|---|---|---|---|---|---|
| A. Ubolratana (ng/L) | 0.201 | <0.001 | <0.001 | <0.001 | <0.001 | 0.069 |
| C. Pulp mill (ng/L) | 26.8 | 3.1 | 1.1 | 0.18 | 0.17 | 0.34 |
| C3. Corn (ng/L) | 0.68 | <0.001 | <0.001 | <0.001 | 0.017 | <0.001 |
| D. Vegetable/ paddy field (ng/L) | 0.81 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| F. Vegetable (ng/L) | 0.89 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| Guideline or acute toxicity | | | | | | |
| Algae, protozoa LC50 (ng/L) (WHO, 1991) | - | - | - | 3.2-100 x $10^6$ | - | - |
| Fish LC50 (ng/L) (PAN, 2014) | - | 0.16-90 x $10^6$ | 2340 – 20000 | - | - | 0.8 – 10.0 x $10^6$ |
| Fish LC50 (ng/L) (PFW Aroma Chemicals, 2007) | - | - | - | - | 0.318 x $10^6$ | - |

*Note: a. Not toxic to aquatic species, with low toxicity to terrestrial species [Rat Acute: >5000 mg/kg rat (Spectrum, 2009)]*

Table 2 gives the pesticide and herbicide concentrations for all sites upstream or lower downstream; i.e. below Site C2. Ametryn, oxadiazon, chlorpyrifos, prometryn and atrazine are all found at measureable concentrations at Site A below Ubonratana Dam (Fig. 1C) indicating that application of these pesticides and herbicides has occurred in the upper Namphong River catchment above Ubonratana dam and contribute to the downstream river load. Fig. 1 shows that about 60% of the Namphong River catchment is associated with the two branches above Ubonratana dam. At Site C3 (Fig. 1C), ametryn, oxadiazon, chlorpyrifos, prometryn and atrazine all show increased or similar concentrations indicating extensive insect and weed control from agricultural activities in the upper Namphong catchment. The trend continues at Sites D and F with significant (2-7 times) increases in concentrations of ametryn, oxadiazon, chlorpyrifos, prometryn and atrazine in river water (Table 2) where the observed levels of pesticides and herbicides are associated with vegetable and paddy field areas indicating their extensive application. At Site D (Fig. 1C) the application of trifluralin is observed, indicating a particular crop application, but was then undetectable at Site F (Table 2).

The comparison of measured concentrations of pesticides and herbicides for all sites in Tables 1 and 2 with compiled details of guidelines and LC50 values for fish and other freshwater species shows that all compounds are well below concentrations that will induce a toxic response. While all compounds excepting chlorpyrifos are present at exceedingly low concentrations, chlorpyrifos is only 10-20 times lower than the validated Australian aquatic guideline (Table 2 – note no Thai guideline available). The application of chlorpyrifos is associated with insect control of vegetable and paddy field areas in line with the highest volume of insecticide importation in Thailand cited above (Department of Agriculture, 2012). The pesticides and herbicides that were detected at the sampling sites of the Namphong River in January 2012 are all low persistent compounds and indicate recent applications. Comparison of the observed pesticides and herbicides identified in this study with an earlier 2005 study of paddy fields, horticulture and vegetable farming in the

Namphong River basin sediment, water samples and PDMS samplers (Boonthai-Iwai et al., 2007) showed that the pesticides and herbicides in use at that time included atrazine, oxadiazon and the organochlorines dicofol and endosulfan; comparison with Tables 1 and 2 levels shows there was no detection of organochlorines in 2012 but that chlorpyrifos is used extensively together with a range of herbicides. If the application rate of chlorpyrifos increases, the level in Namphong River may increase and exceed the threshold of toxicity for fish and be a threat to cage aquaculture. Thus there needs to be a more systematic and complex assessment of chlorpyrifos in the Namphong River basin to develop a tool for its control and environmental risk management.

**Table 2 Pesticide and herbicide concentrations for 19-23 January 2012 showing inputs at all sites upstream or below site C downstream** (average of 2 PDMSs per site)

| Sampling site | Ametryn | Oxadiazon | Chlorpyrifos | Prometryn | Atrazine | Trifluralin |
|---|---|---|---|---|---|---|
| A. Ubolratana (ng/L) | 2.6 | 0.46 | 0.061 | 0.23 | 0.10 | <0.001 |
| C. Pulp mill (ng/L) | 0.12 | 0.75 | 0.24 | <0.001 | 0.10 | <0.001 |
| C3. Corn (ng/L) | 1.7 | 1.0 | 0.45 | 0.14 | 0.29 | <0.001 |
| D. Vegetable/ paddy field (ng/L) | 2.7 | 6.7 | 0.79 | 0.30 | 0.40 | 0.062 |
| F. Vegetable (ng/L) | 2.6 | 7.2 | 0.88 | 0.28 | 0.40 | 0.18 |
| Guideline or acute toxicity | | | | | | |
| 95% protection aquatic freshwater species (ANZECC/ARMCANZ, 2000) (ng/L) | - | - | 10 | - | 13000 | 4400 |
| Nile tilapia LC50 (ng/L) (PAN, 2014) | - | 60000 | - | - | - | - |
| Fish LC50 (ng/L) (EXTOXNET, 2014a,b) | $3.2 – 8.8 \times 10^6$ | - | - | $2.5 – 10.0 \times 10^6$ | - | - |

## CONCLUSION

This paper identified that the Namphong River basin can absorb current inputs of pesticides and herbicides that arise from the agro-based activities and is not causing any impact to the water quality in the Namphong River itself. Measured pesticides and herbicides except chlorpyrifos were present at exceedingly low concentrations in Namphong river water. However chlorpyrifos is only 10-20 times lower than the Australian aquatic guideline (noting no Thai guideline) for protection of aquatic species and was identified as the highest volume of insecticide importation in Thailand. If the application rate of chlorpyrifos is increased, the level in Namphong River may increase and exceed the threshold of toxicity for fish and other species and be a threat to cage aquaculture. Although there does not appear to be a current contamination problem there is a potential issue with chlorpyrifos in water which is identified as having higher risk and requiring further data and information. Thus there needs to be a more systematic and complex assessment of chlorpyrifos in the Namphong River basin to develop a tool for its control and environmental risk management.

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