Introduction
Cadmium (Cd) is considered one of the most toxic heavy metals, and is a non-essential element to all living organisms [1]. It is usually found together with zinc ore and is recovered as a by-product of zinc mining [2]. Cadmium from industrial discharges is deposited into different components of the aquatic ecosystem such as water bodies, suspended particulate matter, sediment, and biota [3]. Consequently, cadmium can be accumulated and magnified in aquatic insect tissue through ingesting food and via water. Cadmium, even at very low concentrations, can be strongly accumulated through the aquatic food-web [4-5]. Many small aquatic organisms spend the majority of their life-cycle in water, living on or in sediments, and may provide a pathway for chemicals to be accumulated and consumed by higher organisms [6]. Adult aquatic insects, which form a significant portion of the diet of some terrestrial organisms [7], inevitably emerge from contaminated sediments and transfer body burden to the terrestrial

Original Research

Monitoring Cadmium Concentrations in Sediments and Aquatic Insects (Hydropsychidae: Trichoptera) in a Stream near a Zinc Mining Area

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Abstract
Aquatic insects can accumulate pollutants such as cadmium from stream sediments. This research aimed to monitor cadmium concentrations in both larvae and adult Hydropsychidae (Trichoptera, Insecta) in Mae Tao (MT1 to MT5) and Mae Ku (MK2 and MK8) watersheds in northern Thailand. Samples were collected twice a month from July 2011 to May 2012 at seven sampling sites. The cadmium concentrations in the stream sediments ranged from 0.12 to 21.5 mg kg⁻¹ wet weight. The highest concentration was recorded from the MT3 sampling site (21.5 mg kg⁻¹), which is also closest to a mining area. The lowest concentration was recorded from the MK2 sampling site (0.12 mg kg⁻¹). Cadmium concentrations in both larvae and adult Hydropsychidae were not significantly different at all sampling sites. However, the cadmium concentrations in Hydropsychidae larvae that ranged from 0.07-1.70 mg kg⁻¹ were higher than the detected cadmium in adult samples (average 0.020 mg kg⁻¹). There was no significant correlation between cadmium concentrations in sediments, and in both larvae and adult Hydropsychidae. Concentrations of cadmium in adult Hydropsychidae in this study were low. Even though the contamination of heavy metals was low in adult Hydropsychidae, long-term exposure to heavy metals could seriously impact terrestrial animals such as birds and bats that consume these insects.

Keywords: cadmium, aquatic insects, sediment, mining area

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environment either directly as prey items to insectivores, or indirectly through the detritus food chain [8]. A number of studies [9-10] have shown that both immature and emerging insects play a crucial role in determining metal contaminants in the environment. Currie et al. [11] collected emerging insects (Diptera, Odonata, Ephemeroptera, and Trichoptera) from lake water in order to quantitatively estimate the export of cadmium by aquatic insects from a natural system having elevated cadmium concentrations in the water and sediment.

In the Mae Tao watershed, Mae Sot District, Tak Province, Thailand, cadmium residues were found in the environment and in products such as rice, aquatic animals, and drinking water, which is likely due to nearby mineral extraction activities [12]. These activities include drilling, material transfer, and the removal of mine tailings and drainage [13]. Simmons et al. [14] studied the cadmium concentrations of 154 soil samples collected from the Huai Mae Tao area and found cadmium levels in rice field soils of 3.40-284 mg kg\(^{-1}\) soil, which is 94 times higher than the European Economic Community's maximum permissible concentration in soil (3 mg kg\(^{-1}\) soil) [14]. Krissanakriangkrai et al. [15] investigated the magnitude of cadmium pollutants in water, sediment, fish, and shellfish from nine sites along Mae Tao Creek. They found that cadmium levels in the river sediment exceeded the allowable standard. The highest concentrations of cadmium were detected in Swamp eel (0.27 mg kg\(^{-1}\) wet weight). Concentrations of cadmium in pond snail were 0.13 mg kg\(^{-1}\) wet weight. In the same year, Othman et al. [16] determined that cadmium accumulation and bioconcentration factors affect the whole organism. The liver, kidney, ovary, and testis of *Fejervarya limnocharis* are exposed to different environmental cadmium levels. Frogs from contaminated sites had significantly higher hepatic (1.939 mg kg\(^{-1}\)), renal (7.253 mg kg\(^{-1}\)), and testicular (1.462 mg kg\(^{-1}\)) cadmium levels than those from the reference sites (0.205, 0.783, and 0.379 mg kg\(^{-1}\), respectively).

Trichoptera (also known as caddisfly) is one of the largest groups of aquatic insects. They are holometabolous insects with aquatic larvae and pupae with terrestrial adults [17]. Most species of caddisfly in the Hydropsychidae family spend their larval lives in running water and have been reported to be excellent bioindicators of trace element pollution in aquatic ecosystems [18]. They take up trace elements directly from water, sediments, and diet, and serve as a trophic link to higher food chain organisms such as fish and aquatic birds [19]. Therefore, this study aimed to monitor cadmium concentrations in both larvae and adult Hydropsychidae, and cadmium concentrations in stream sediments in close proximity to zinc mines. The Huai Mae Tao site runs through a mine, whereas the Huai Mae Ku site has a mine parallel to the stream.

### Materials and Methods

#### Study Area

Mae Tao and Mae Ku watersheds are located in the lower part of Mae Sot district, Tak Province, northern Thailand, in the mountain area of the border between Thailand and Myanmar. Mae Tao Stream is vital for life in Mae Sot District and is the main freshwater resource for many villages, meeting nearly all the demands for drinking water, irrigation, and agricultural. There is the zinc mine upstream of Mae Tao Stream. The zinc mine began operating in 1982, and this area has been affected by the adverse impacts of heavy metals, especially cadmium. Cadmium contamination has been reported in rice, soil, and sediment in and around Mae Tao Stream [14, 20]. About 69.2% of the sediment samples of the stream exceeded the European maximum permissible level of 3.0 mg kg\(^{-1}\) [21-23]. Cadmium concentrations were low in the sediments before reaching the zinc area, but became much higher when the stream passed through this area.

The seven sampling sites were selected from both watersheds in this study. Study sites in the Mae Tao watershed (MT1, MT2, MT3, MT4, and MT5; Fig. 1) run through a mine, while MK2 and MK8 both flow parallel to the mentioned stream located in Mae Ku watershed, which is surrounded by agricultural areas. The main agricultural products in this area are rice, soybean, sugar cane, and garlic. Mining activity contributes significantly to metal contamination due to the discharge and the natural spread of mine wastes by wind, water, and rainfall into adjacent agriculture soils, food crops, and water ecosystems [24]. The streams from Mae Tao and Mae Ku watersheds flow to the Moei River – a 327 km-long borderline between Myanmar and Thailand. At each site, the sample was collected two times per month from July 2011 to May 2012.

#### Sample Collection

Hydropsychidae larvae are distinguished from all other caddisfly larvae by the sclerotization of the dorsum of each thoracic segment and branched gills on the ventral surface of the abdomen and the last two thoracic segments, usually with a tuft of long setae near the apex of each anal proleg [25]. The sclerotized plates of the mesonotum and metanotum do not have a median dorsal ecdysial line, although the line does occur on the pronotal plates; in some subfamilies, the last two thoracic notal sclerites have a transverse ecdysial suture [25]. Hydropsychidae larvae for cadmium analysis were collected using a D-frame aquatic net (mesh sieve 250 μm), as described in Prommi and Permkam [26], and by hand from the surfaces of stones, stone crevices, gravel, and woody debris at each collection site. Samples were collected until there was enough biomass for laboratory analysis (at least 2.0 g). Specimens were immediately
Monitoring Cadmium Concentrations... categorized into family level upon sample collection, frozen using dry ice, and then kept on ice during transportation to the laboratory in order to perform cadmium analysis. Additionally, at each collection site adults were collected using portable blacklight traps (10-W fluorescent tube, 12-volt DC battery) suspended across a white pan containing a detergent solution.

Surface sediments were collected from the same depositional areas of shallow, slow-moving water near the water's edge forming one composite sample.

Fig. 1. Map showing the sampling stations (MT1-MT5, MK2, MK8) at Mae Tao and Mae Ku watersheds.
These areas were directly adjacent to riffle areas where Hydropsychidae larvae samples were collected. A 5 cm depth of sediment samples from several areas were collected and immediately sieved with native river water through a 60-μm nylon mesh, transported to the laboratory on ice, and then dried at 60°C. Radziemska and Fronczyk [27] revealed that the highest concentration of cadmium in the analyzed soil samples were noted at a depth of 0.00-0.10 m; a reduction of approximately 19% occurred at 0.90-1.00 m at the sampling location 4.5 m from the pollution site.

Cadmium concentrations of all samples were analyzed by an inductively coupled plasma mass spectrophotometer (ICP-MS). The limit of cadmium detection was <0.020 mg kg^{-1}. Results were expressed as milligrams of metal per kilogram wet weight.

**Statistical Analysis**

Analysis of variance (ANOVA) was used to test for statistical differences between the means of cadmium concentration from the seven sampling sites. Duncan's multiple range test (DMRT) was also used for multiple comparisons of the means of the cadmium concentration in order to measure similarities of the sampling points. Cadmium concentrations in sediments were correlated with those in both larvae and adult Hydropsychidae using the nonparametric Spearman's correlation to evaluate the response of the biota to metals in sediments. All statistical tests were applied using SPSS software (version 15).

**Results and Discussion**

The cadmium concentrations obtained were in the 0.11-3.46 mg kg^{-1} range, with an average of 0.99 mg kg^{-1} at MT1; MT2 values were in the 0.12-0.50 mg kg^{-1} range, with an average of 0.32 mg kg^{-1}; MT3 values were in the 2.43-76.45 mg kg^{-1} range, with an average of 21.50 mg kg^{-1}; MT4 values were in the 2.47-11.80 mg kg^{-1} range, with an average of 8.56 mg kg^{-1}; MT5 values were in the 1.59-16.98 mg kg^{-1} range, with an average of 9.29 mg kg^{-1}; MK2 values were in the <0.020-0.20 mg kg^{-1} range, with an average of 0.12 mg kg^{-1}; and MK8 values were in the 0.67-6.01 mg kg^{-1} range, with an average of 3.44 mg kg^{-1} (Table 1). Cadmium concentration in stream sediment was significant at sites MT1, MT2, MK2, MK8, and MT3 ($P<0.05$).

At the upstream site (MT2), the stream that flows through the zinc mines had lower levels of cadmium, which amassed into 21.5, 8.56, and 9.29 mg kg^{-1} sediments downstream (MT3-MT5). The samples at MK8 situated on the other side of the mountain had cadmium concentration of 6.01 mg kg^{-1}, perhaps from phosphate fertilizers [28]. Roberts [29] reported that the phosphate fertilizers were generally the major source of trace metals among all inorganic fertilizers, and much attention had also been paid to the concentration of Cd in phosphate fertilizers. The use of fertilizers containing different concentrations of metals in different periods of cultivation, in addition to the deforestation of riparian vegetation, impacted the hydric resources of the adjacent areas, leading to contamination of the aquatic sediments. Metals introduced in the aquatic environment by agricultural activities around these areas can be absorbed and incorporated into the sediments. Every year, agricultural activities are carried out using fertilizers. This process causes severe damage to aquatic communities [30]. The stream sediment that was collected from MT1, the northeastern highland of zinc mining, found cadmium at a quantity of 0.99 mg kg^{-1}. MK2, a stream in the southwestern highland, had a cadmium level of only 0.12 mg kg^{-1} (Table 1).

Although cadmium was detected in both larvae and adult Hydropsychidae, the obtained cadmium concentrations in hydropsychidae adults were negligible (<0.020 mg kg^{-1}; Table 1). There were no significant differences of cadmium concentration in both larvae and adult Hydropsychidae from all sampling sites ($P>0.05$; Table 1). The highest values for cadmium...
Monitoring Cadmium Concentrations...

Concentrations in the hydropsychidae larvae were detected at site MK8 (mean concentration of approximately 1.70 mg kg\(^{-1}\)). Cadmium was detected at very low values (<0.020 mg kg\(^{-1}\)) in the hydropsychid larvae at site MT3.

Fig. 2 shows the distribution of cadmium levels in stream sediments and aquatic insect samples during the dry and rainy seasons in 2011-12 from the Mae Tao and Mae Ku watersheds. When cadmium concentrations were compared according to season, higher cadmium concentrations were found during the rainy season (July to November 2011) than the dry season (January to May 2012). The seasonal mean values of cadmium concentrations in stream sediment and aquatic insects ranged from 4.50, 0.40, and <0.020 mg kg\(^{-1}\) in the dry season to 8.20, 0.70, and <0.020 mg kg\(^{-1}\) in the rainy season. Krissanakriangkrai et al. [15] reported that cadmium concentrations in the rainy season were higher than in the dry season because of heavy rainfall leaching cadmium into the creek. The increased volume of cadmium from agricultural and mining waste entering the creek in the rainy season could have elevated metal bioavailability in water, which could in turn lead to increased bioaccumulation in aquatic insects.

No significant correlation was observed between aquatic insect and sediment cadmium concentrations (Table 2).

Table 2: Spearman’s correlation between cadmium concentrations in stream sediment, and in both larvae and adult Hydropsychidae in Mae Tao and Mae Ku watersheds from July 2011 to May 2012.

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Conclusions

The results show the problems of cadmium accumulation caused in streams receiving mining effluence. This process may instigate severe harm to aquatic communities in the near future. In Thailand, there are no reference values for cadmium concentration in sediments and for aquatic fauna. However, the results presented in this work uncovered high values of cadmium in the impacted areas, compared to the reference values for stream sediments. This work also tries to show the importance of the elaboration of a monitoring system that uses sediment as a compartment in environmental studies. Moreover, cadmium contamination in aquatic insects with a terrestrial adult life cycle, such as Trichoptera organisms, represent an important link for the transference of cadmium to upper trophic levels as fish, reptiles, birds, and mammals.

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