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Impact of Long-term and Intensive Rice Cultivation on Heavy Metal Accumulation in Soil: An Observation from Mae La River Basin, Central Thailand

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Abstract

Intensive rice cultivation relies greatly on chemical fertilizers and pesticides, some of which contain heavy metals as impurities. Application of these agrochemicals can result in heavy metal accumulation in soil. This research discusses the current concentrations and migration pathways of heavy metals (Cu, Pb and Zn) in paddy soil subjected to long-term use of chemical fertilizers and pesticides. The study of soil pH and metal concentrations in 60 surface and subsurface samples from a relatively small river basin revealed that although highly varied, pH values and metal concentrations in topsoil were significantly different from values in subsurface soil. The soil pH as low as 5.4 was observed in topsoil. Although the observed levels in topsoil were in within safe limits according to the Dutch standard, they were significantly elevated above the subsurface concentrations. Evidence on the differences between their concentrations in paddy soil and river sediments suggests that considerable amount of metals in paddy fields have been transported into the river. A detailed study of input inventory, fluxes and migration pathways of these metals in the river basin can provide a better understanding of their mobility and measures that might needed to safeguard aquatic habitats, especially the well-known striped snakehead fish in Mae La River.

Keywords: Heavy metals, Agrochemicals, Accumulation, Migration pathway, Paddy soil

Introduction

Soil provides many functions vital for healthy ecosystems and food production. It, therefore, plays an essential role in a country's economy, especially in agricultural countries, such as Thailand. As one of the world's major rice exporters, Thailand has gradually moved from traditional to intensive farming and relied significantly on agrochemicals during the last 50 years [1]. This can be seen in the amount of chemical fertilizers and pesticides imported to Thailand, which has rose from ca. 3.6 million tons in 2006 [2] to 5.8 million tons in 2018 [3], i.e. an increase of 61 % in 12 years. This intensive use of agrochemicals raises concerns about pesticide residues and heavy metals accumulation in agricultural soil, which can be transferred to human through food chains. In agricultural systems, heavy metals are introduced to soil through several sources including atmospheric deposition, irrigation waters, use of composts and soil amendments, and use of agrochemicals such as phosphate fertilizers (PFs) and pesticides [4].

A number of studies suggested that the application of PFs is one of the major sources of heavy metal inputs to agricultural soil [4-7]. For example, Alloway [4] pointed out that Cd, Pb, and As concentrations in topsoil were associated with the application of PFs. Similar results were reported by Kassir *et al.* [7], who found that Cu, Cd, Zn and Pb in topsoil increased after the application of PFs.

In addition to PFs, heavy metals can enter agricultural soil through the application of pesticides (including insecticides, fungicides and herbicides), many of which contain metalloid As [8] and heavy metals, such as Cu and Zn [4,9-11]. A recent study on heavy metal contaminants in pesticides was carried out by Defarge *et al.* [10]. They reported that 11 glyphosate-based herbicides and 11 other pesticides marketed mostly in France contained up to 53, 40, 62 and 11 times over the permitted levels for As, Cr, Ni and Pb, respectively. As a result, their application can lead to higher heavy metal concentrations in soil. For example, Patinha *et al.* [9]; Mirlean *et al.* [11] pointed out that elevated Cu concentrations in vineyard topsoil were resulted from the application of pesticides.

The fact that most agriculture lands receives both PFs and pesticides. This can intensify the accumulation of heavy metals in agricultural soil. As a result, it is often found that heavy metal contents in agriculture areas are elevated over non-agriculture ones [12-14]. For example, Toth *et al.* [14] pointed out that agricultural land in the EU has higher percentage of samples with concentration above the threshold value than other land uses. These findings highlight the need to study the impact of long term agricultural practices, especially those involves the application of agrochemicals.

Rice cultivation in Central Thailand has long been subjected to intensive use of agrochemicals. However, the impact of their application on heavy metals in agricultural soil is not well documented. This research aims to assess the current concentrations of Cu, Pb and Zn in paddy soil in relation to their risk to human health and the environment, and examine the impact of long-term application of agrochemicals on heavy metals in paddy soil in term of contamination factor. It also seeks to explore the link between the heavy metals in paddy soil and river sediments. The assessment was achieved through the study of pH and metal concentrations in 60 soil samples collect from 15 boreholes at various depths alongside the river bank.

Materials and methods

Study area

Mae La River basin is the area that drains into Mae La River in Sing Buri Province, Central Thailand. It originates from Mae Nam Noi River, a tributary of Chao Phraya River, the largest river in Thailand. It flows southeast in between Chao Phraya River to the east, and Mae Nam Noi River to the west (**Figure 1**). With the length of ca. 18 km and the width between 40 - 60 m, Mae La River flows through an alluvial plain of Chao Phraya River and its tributary before discharging into Chao Phraya River. Besides being a fertile plain for rice production, Mae La River is also famous for its striped snakehead fish, a delicacy of unique taste.

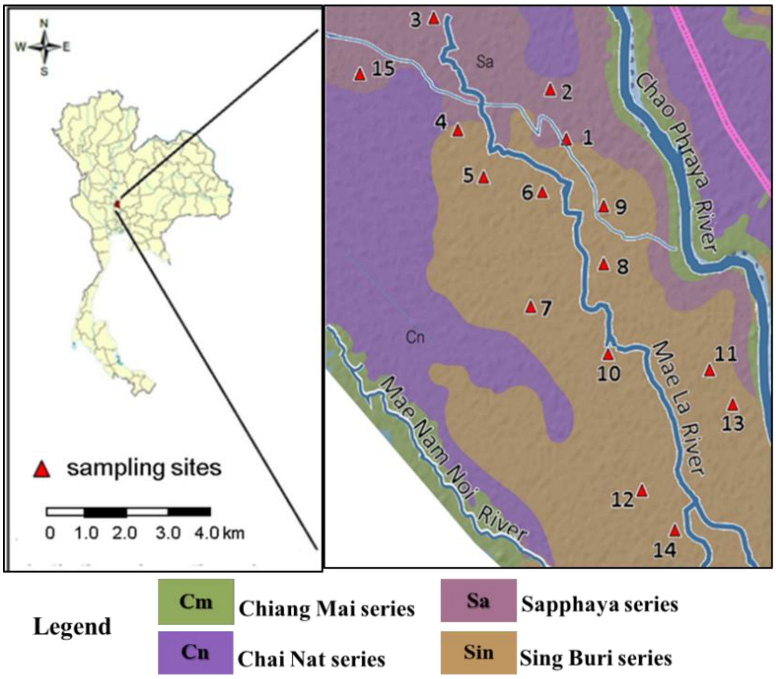

Figure 1 The study area and sampling sites. The geographic coordinates of the sampling sites are: (1) = 14.979600N 100.322545E; (2) = 14.987916N 100.319472E; (3) = 14.998572N 100.297656E; (4) = 14.979623N 100.298127E; (5) = 14.968219N 100.306994E; (6) = 14.965412N 100.317363E; (7) = 14.944376N 100.314539E; (8) = 14.952438N 100.333434E; (9) = 14.965565N 100.331460E; (10) = 14.938340N 100.334471E; (11) = 14.934284N 100.352407E; (12) = 14.922591N 100.342573E; (13) = 14.928350N 100.365311E; (14) = 14.908594N 100.349523E; (15) =14.991150N 100.278613E.

Mae La river basin is a well irrigated paddy floodplain in Central Thailand. It has been subjected to intensive rice cultivation since 1957, after the completion of Chao Phraya Dam and the Greater Chao Phraya Irrigation Project, which makes intensive rice cultivation (2 - 3 crops per year) possible. To date, most of rice cultivation in the area is non-organic and the application of agrochemicals is a common practice. Farmers in the study area usually apply NPK or NP blends about 20 - 30 days after seed sowing at the rate of 125 - 156 $kg \cdot ha^{-1}$ and nitrogen fertilizers about one month before flowering at the rate of 125 - 250 $kg \cdot ha^{-1}$, depending on soil properties and rice varieties [15]. About 87 % of the farmers use pesticides in rice cultivation. Generally, herbicides were used by most of the farmers before, during and about 10 days after germination. Their application rate varies, depending largely on field preparation and types of weeds. Insecticides are used only at pest outbreaks. The most often used herbicides in rice cultivation include glyphosate, followed by 2, 4-D, paraquat and bispyribac-sodium respectively; while the most often used insecticides include abamectin followed by chlorpyrifos, cypermethrin and dinotefuran, respectively [16].

The soil in the study area are alluvial soil in Chao Phraya River flood floodplain. Most of the soil samples are Sing Buri series. It is a poorly drained of very-fine, mixed, semiactive, nonacid, isohyperthermic Vertic Endoaquepts. The rest of the samples are Sapphaya series. It covers the northern part of the study area. It is a moderately to poorly drained of fine-loamy, mixed, active, nonacid, isohyperthermic Aquic (Fluventic) Haplustepts [17]. Soil series map of the study area is given in **Figure 1**.

Sampling protocol and sample treatment

Soil samples were collected from 15 boreholes on 9 - 11 May 2017. The sampling sites were located within 3 km from the river bank (**Figure 1**). Each borehole was drilled using a hand auger to a depth of ca. 150 cm, and the soil profiles were divided into 4 layers using soil colour and texture (feeling method). A composite sample from each layer was then taken using the quartering method until the required amount was obtained (ca. half of a 7”×10” Kraft paper bag). This summed up to a total of 60 samples. Once returned to the laboratory, the samples were dried at 40 ℃ until constant weights were obtained. The samples were then disaggregated and particles > 2 mm were removed. For heavy metal analysis the particles < 2 mm were ground until 90 % of grounded sample were smaller than 180 µm (80 mesh).

Reagents

All aqueous solutions were prepared with 18.2 MΩ water (LaboStar™). Unless stated otherwise, AR grade acids (Univar, Ajax Finechem) were used for preparation of standard solutions, acidification, digestion and cleaning processes. Standard calibration curves were prepared from 1,000 $mg \cdot L^{-1}$ standard solutions for AAS (Spectrosol, Ajax Finechem) and diluted appropriately. Sampling bottles, containers, equipment were rinsed and washed with detergent followed by rinsing with tap water before subjected to double acid washing (24 h in 1:1 HCl, followed by 24 h in 1:1 HNO_3,) before the final rinse with distilled water.

Determination of soil pH

Ten grams of each sample (< 2 mm fraction) was made up into soil suspensions with 10 mL of 18.2 MΩ water in a 50 mL centrifuge tube. The samples were then shaken rigorously for 5 min and allowed soil suspensions to settle for 10 min. The pH of the samples were then measured using pH metre (Mettler Toledo) after calibration with pH 4 and 7 buffers (Mettler Toledo).

Determination of pseudo-total metals

Duplicate samples (1.0 g, < 180 µm) were digested with 30 mL 1:1 HNO_3 (v/v) in 60 mL glass vessels using a digestion block system (DigiBlock, Lab Tech). The sample was gently boiled until the solution was reduced to ca. 5 mL, followed by another 10 mL 1:1 HNO_3 and repeated. The sample was then cooled to room temperature and filtered (Whatman no. 542) and adjusted to 25 mL [18] before being analysed for total metals with flame-AAS (Shimadzu, AA 6200). The accuracy of analytical methods was verified against certified reference material (CRM) TMDA 53.3 lot number 1011 (Environment Canada). For every individual analysis protocol, the CRM was tested until satisfied (typically < 10 % RSD). The wavelength, linear ranges, linearity, the limit of detection (LOD) and CRM recoveries for each element are given in **Table 1**.

Table 1 Operating conditions, the limit of detection (LOD) and the percentage recovery of CRM for each element. *LOD in mg·L^{-1} were from 3SD; **LOD in mg·kg^{-1} were calculated from LOD in mg·L^{-1}, final volume adjusted (25 mL) and weight of soil used (1.0 g).

Metals	Wavelength (nm)	Linear Range (mg·L^{-1})	Average Linearity	Analysis Limit of Detection (LOD)* (mg·L^{-1})	Analysis Limit of Detection (LOD)** (mg·kg^{-1})	CRM's recovery (%)
Cu	324.7	0.1 - 2.0	> 0.998	0.0534	1.33	90.4 - 112.9
Pb	217.0	0.1 - 2.0	> 0.999	0.5614	14.03	90.6 - 108.4
Zn	213.9	0.05 - 1.0	> 0.997	0.1282	3.20	99.5 - 104.7

Assessment of heavy metal accumulation

Heavy metal accumulation in soil and sediments associated with anthropogenic activities can be assessed by contamination factor (CF). Defined by Hakanson [19], CF is the ratio of the concentration of the metal of interest in the soil samples (C_m) to the background concentration (C_b). It can be expressed as:

$$CF = \frac{C_m Sample}{C_m Background} \quad (1)$$

where CF < 1 indicates low contamination; 1 < CF < 3 refers to moderate contamination; 3 < CF < 6 is considerable contamination; and CF > 6 means very high contamination.

Results and discussion

Soil pH

Soil pH is the most important variable influencing metal-solution and soil-surface chemistry [20]. In general, at low pH, heavy metals tend to be in free ion form, hence adsorption is small. The pH of paddy soil from 15 boreholes are given in **Figure 2(a)**. The results showed that, although highly varied, the pH increased with increasing depth, in other words, topsoil were more acidic than subsurface soil. Since the depths of soil layers varied among each borehole, new groups were assigned for data interpretation and statistical analysis. Based on pH profiles, a topsoil or plough layer (0 - 30 cm) and 2 subsurface layers of 30 - 80 cm and 80 - 150 cm depths were classified. The latter 2 layers were distinguished based on the pH variation, the upper layer showed higher variation compared to the bottom layer. The descriptive statistics (minimum, q1, q2, q3, maximum and mean) of the pH values of each layer are illustrated in **Figure 2(b)**.

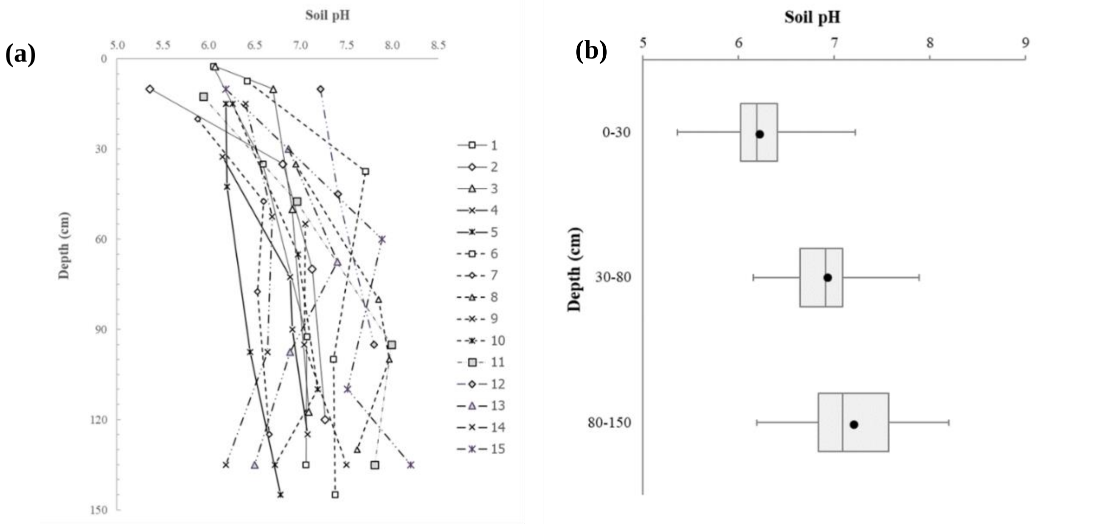

Figure 2 Soil pH $_{(KCl)}$ (a) variation of soil pH values of individual borehole at varied depth; (b) box plots and mean values (●) of pH in topsoil and subsoil layers.

The box plots and the mean (●) values (**Figure 2(b)**) shows obvious progression of pH from surface toward deeper soil. The topsoil pH (5.36 - 7.22; 6.22 ± 0.46) were lower than the pH in 30 - 80 cm layer (6.15 - 7.89; 6.93 ± 0.45) and the pH in 80 - 150 cm layer (6.19 - 8.20; 7.21 ± 0.52). One-way analysis of variance confirmed that the soil pH were significantly different among those 3 layers ($p < 0.000$). The Tukey-Kramer Post Hoc analysis suggested that the pH of topsoil were significant lower than the 2 subsoil layers. However, the pH of 2 subsoil was not significance, suggesting that the 2 subsoil layers are from the same soil. According to the observed soil pH, about 25 % of topsoil can be classified as moderately acidic (pH 5.6 - 6.0) and about 83 % of topsoil are slightly acidic (pH 6.1 - 6.5. In general, a low pH tends to lead to an increase in solubility, bioavailability and mobility for most metals [21].

Soil acidification resulting from nitrification of ammonium and urea based fertilizers has been discussed in several studies. For example, Schroder *et al.* [22] observed that acidification of surface soil (0 - 15 cm) was significantly related to the application rates of nitrogen fertilizers; Cai *et al.* [23] reported the decrease in pH values by 1.2 - 1.5 units after soil was continually received 300 $kg \cdot N \cdot ha^{-1} \cdot year^{-1}$ for 8 years and remained constant afterward throughout the study period of 19 years. Similar findings were reported by several studies [24-26]. As for this study, the change in pH values by 0.2 - 0.8 with an average of 0.5 units were observed from the application rate of 50 - 80 $kg \cdot N \cdot ha^{-1} \cdot crop^{-1}$, which summed up to 100 - 160 $kg \cdot N \cdot ha^{-1} \cdot year^{-1}$ for 2 crops $year^{-1}$. Although, it is likely that the decrease in topsoil pH observed in this study was contributed by excessive use of nitrogen fertilizers. It should also be noted that soil acidification occurs naturally at very slow rate due to carbonic acid in rainfalls, and soil acidification due to leaching is a common phenomenon in tropical regions. Because of this reason and due to the lack of information on soil pH in the study area prior to an intensive use of nitrogen fertilizers, nor the soil pH from control sites in the same soil series nearby that are not subjected to nitrogen fertilizers, it is impossible to quantify and separate the impact caused by nitrogen fertilizers and from natural processes.

Heavy metal concentrations in paddy soil

Various methods have been used to extract metals in soils. The choice of method used, however, depends on the nature of metals of interest. This study used the pseudo-total digestion obtained from a mixture of 1:1 HNO_3. This method is not able to extract the metals that associated with silicates, however, it gives reliable measurements of non-silicate metals [18]. This method is considered adequate for this study because, the aim of the study is to investigate the metals that can be released under normal environmental conditions with respect to pH, temperature and pressure.

Among metals studied, Cu and Zn are essential elements required for biological processes, but excessive dosage can be harmful. In plants, Cu and Zn are required for many enzymes essential for plant growth and development. Among other things, Cu is a key component for chlorophyll and seed production, while Zn plays important roles for plant hormone balance and auxin activities. In comparison to mammals, Cu is highly toxic to aquatic organisms [27,28]. This reflects in higher limit Cu levels in drinking water in many standards (e.g. 1 $mg \cdot L^{-1}$ for the Thai standard) [29] compared to guideline concentrations in water quality for protecting aquatic life (e.g. 0.005 - 0.012 $mg \cdot L^{-1}$ for hardness < 10 to > 300 $mg \cdot L^{-1}$ $CaCO_3$ for the EU directive on Freshwater Fish 2006/44/EC) [30]. In contrast to Cu and Zn, Pb is a non-essential and toxic element, whose known effects on biological systems are deleterious [31].

The pseudo-total concentrations of Cu, Pb and Zn obtained by acid extraction of 60 samples collected from 15 boreholes are presented in **Figures 3 - 5**, respectively. It is clear from the figures that metal concentrations in soil samples varied between each borehole and at depth. In general, concentrations in topsoil samples were higher than those in subsoil samples for the metals studied, which followed the order of Zn > Pb > Cu.

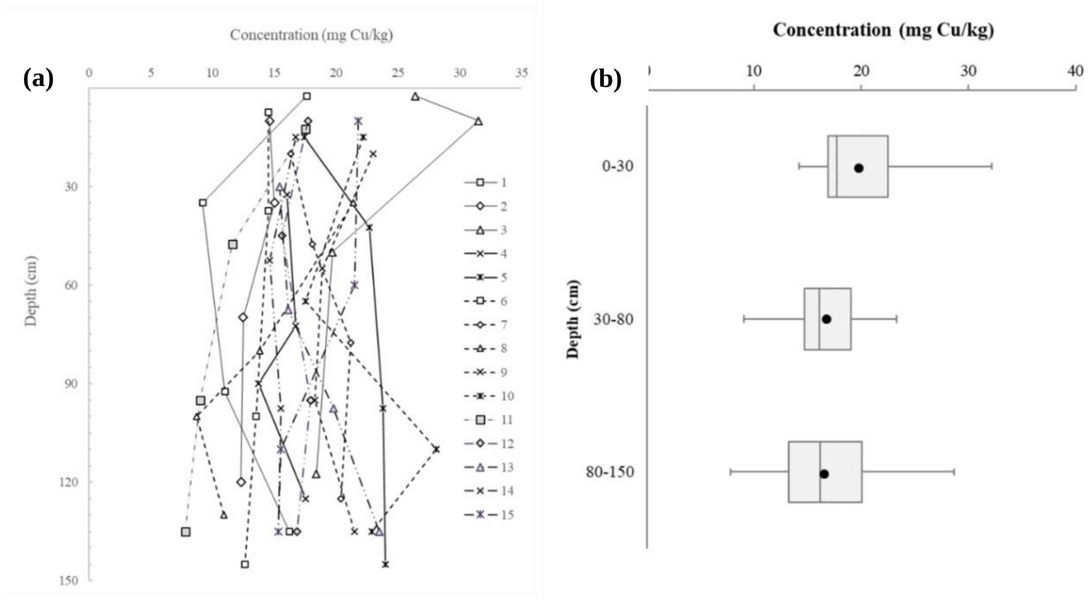

Figure 3 (a) variation of Cu concentrations of individual borehole at depths; (b) box plots and mean values (●) of Cu concentrations in topsoil and subsoil layers.

As can be seen from **Figure 3**, Cu concentrations were ranging from 14.2 to 32.2 mg·kg^{-1}, with an average of 19.8 ± 4.9 mg·kg^{-1} in topsoil layer, from 9.1 to 23.3 mg·kg^{-1} with a mean of 16.8 ± 3.6 mg·kg^{-1} in 30 - 80 cm layer and from 7.8 to 28.7 mg·kg^{-1} with an average of 16.6 ± 5.1 mg·kg^{-1} in 80 - 150 cm layer.

Interestingly, the mean concentrations of all metals studied (Cu, Pb and Zn) in samples from a 30 - 80 cm layer and a 80 - 150 cm layer were almost identical (**Figures 3(b)** – **5(b)**), suggesting that these 2 layers were from the same sources and represented uncontaminated soil. For this reason, they were grouped together as 1 and the concentrations determined in this new layer are considered as the background concentrations of the study area, which will be used for calculating accumulation indices. The background concentrations (16.64 ± 4.53) observed in this study were comparable with the mean concentrations for uncontaminated paddy soil, and within the ranges for worldwide normal surface soil suggested by Satpathy *et al.* [32] (**Table 2**). In their study, they reviewed the heavy metals in natural soils from several sources. Student's t test showed that Cu in topsoil were significantly higher than in subsoil ($p < 0.00$).

Table 2 Heavy metals concentrations of this study compared to other studies. All values are in mg·kg^{-1}.

Metals	Mean values for uncontaminated paddy soil [32]	Mean values for worldwide normal surface soil [32]	The Dutch SGVs (Target values) [33]	Thai standard for agricultural soil [34]	Investigation values for Thai soil [13]	This study	
						Topsoil	Subsoil
Cu	20.7	13-24	36	-	45	19.8	16.6
Pb	23.3	22-44	86	400	55	24.1	20.6
Zn	61	45-100	140	-	70	42.1	38.2

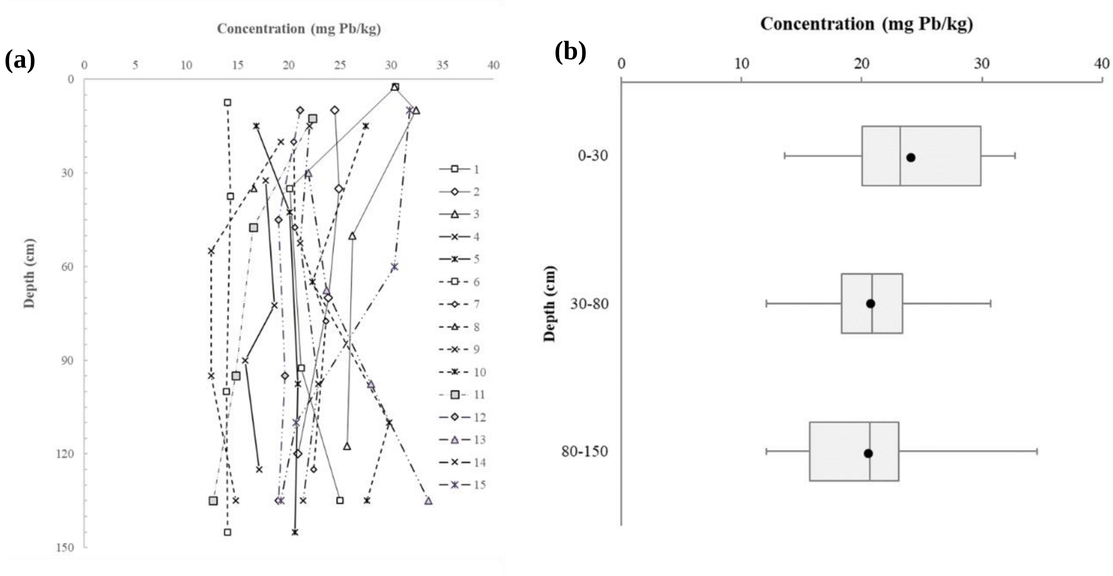

Figure 4 (a) variation of Pb concentrations of individual borehole at depths; (b) box plots and mean values (●) of Pb concentrations in topsoil and subsoil layers.

It is clear from **Figure 4** that Pb concentrations varied both laterally and vertically. The concentrations in a topsoil layer ranged from 13.6 to 32.7 mg·kg^{-1} with a mean of 24.1 ± 5.9 mg·kg^{-1}, whereas the concentrations observed in subsoil (30 - 150 cm) ranged from 12.0 to 34.6 mg·kg^{-1} with an average of 20.6 ± 5.0 mg·kg^{-1}. Statistical analysis (Student's t test) indicated that metal concentrations in topsoil were significantly higher than that in subsoil ($p < 0.00$).

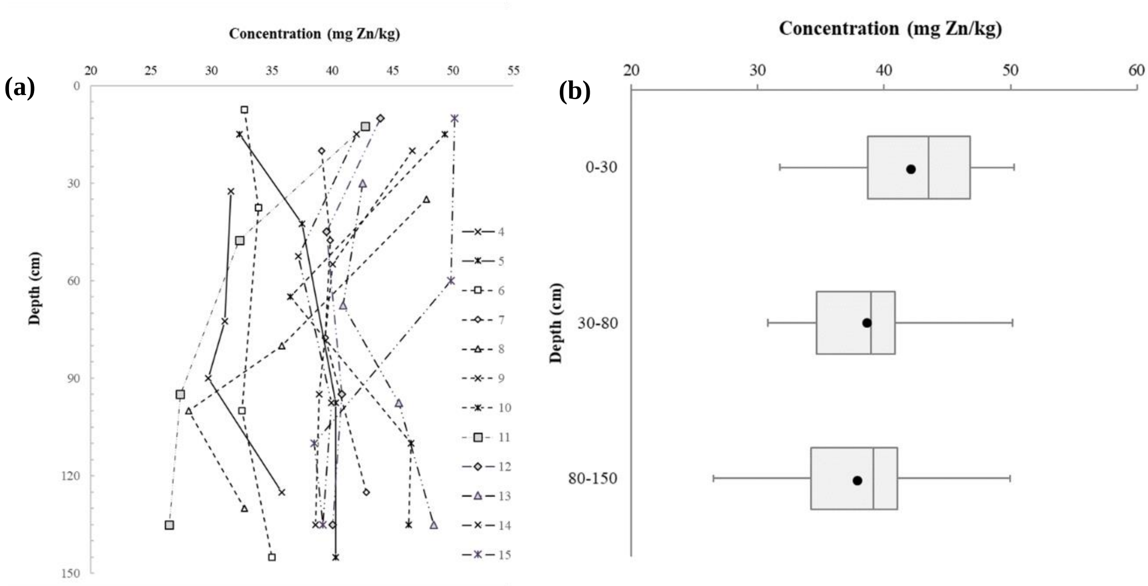

Figure 5 (a) variation of Zn concentrations of individual borehole at depths; (b) box plots and mean values (●) of Zn concentrations in topsoil and subsoil layers (excluding boreholes1, 2 and 3).

Similar to Cu and Pb, concentrations of Zn in the study area (**Figure 5**) varied with location and depth. For unknown reason, Zn in samples from boreholes 1, 2, 3 (116 - 130 mg·kg^{-1}, n = 12) were markedly higher than the rest (26.5 - 50.1 mg·kg^{-1}, n = 48; $p < 0.000$). As a result, samples from boreholes 1 - 3 were excluded from data interpretation. The Zn concentrations in topsoil (31.8 to 50.3 mg·kg^{-1} with an average of 42.1 ± 6.4 mg·kg^{-1}) were significantly higher than that in subsoil (26.5 to 50.2 mg·kg^{-1} with a mean of 38.2 ± 5.8 mg·kg^{-1}; $p < 0.02$)

To the author knowledge, there is no data on heavy metal concentrations in the study area prior to this study. Heavy metal contents in paddy soil in the central Thailand, approximately 250 km from the study area were reported by Kingsawat and Roachanakanan [35]. They reported the metal contents of 17.0 - 19.9 mgCu·kg^{-1} and 57.1 - 65.4 mgZn·kg^{-1} before cultivation and the values of 16.4 - 21.0 mgCu·kg^{-1} and 55.2 - 66.8 mgZn·kg^{-1} after cultivation in paddy soil in Samut Songkhram province, which were comparable to this study.

Heavy metal accumulation in paddy soil

In order to assess the degree of contamination of the surface soil, this study used the Dutch standard instead of the Thai standard for agricultural soil. This was due to: 1) The Dutch offers standards for more elements than the Thai standard; and 2) The Thai standard does not provide the target value, which is an acceptable risk or natural concentrations in soil like the Dutch standard (**Table 2**). As can be seen from the table, the mean concentrations for Cu, Pb and Zn in topsoil determined in this study were lower than the target values of the Dutch standard, indicating that metal contents in the study area were within acceptable limits.

Soil contamination was also evaluated based on the investigation values for Thai soil, which was established by Zarcinas *et al.* [13] (**Table 2**). They conducted a reconnaissance geochemical survey of Thai soil from 318 topsoil samples (0 - 15 cm) collected throughout the country; and suggested that the 95th percentile concentration represents an investigation level or a minimum concentration of a heavy metal for a soil to be considered contaminated. Metal contamination assessment using these values also suggested that soil in the study area were not considered contaminated.

Although, assessment based on the Dutch standard and the investigation values suggested that soil metal concentrations in the study area were within acceptable ranges, it is clear from **Figures 3 - 5** and statistical analysis results that concentrations of Cu, Pb and Zn in in topsoil were significantly elevated above the subsurface concentrations. By using the background concentrations represented by subsoil concentrations in this study, the contamination factor of topsoil in the study area were 0.70 to 1.9 (1.2 ± 0.31) for Cu, from 0.78 to 1.5 (1.2 ± 0.23) for Pb and from 0.82 to 1.5 (1.10 ± 0.19) for Zn. The contamination factors observed indicated that the study area is low to moderate contaminated.

Because there is no industry in the study area, accumulation of Cu, Pb and Zn in topsoil is most likely to be contributed by long-term use of agrochemicals in rice cultivation. The Cu, Pb and Zn contents in PFs marketed in Thailand and other countries are given in **Table 3**. The table suggests that Zn content in PFs can be up to 3 - 15 times higher than Cu and 10-over 100 times higher than Pb. However, the Zn contamination factors (1.10 ± 0.19) determined in this study were relatively similar to that of Cu (1.2 ± 0.31) and Pb (1.2 ± 0.23). This suggested that, in the study area, Zn was more mobile compared than Cu and Pb.

Table 3 Heavy metals (mg·kg^{-1}) in NP and NPK blends marketed in Thailand and other countries.

Elements	Thailand		Abroad		
	[36]	[37]	EU (P^{50} - P^{95}) [38]	China [39]	Germany [40]
Cu	6.85 - 19.2	9.0 - 25.0	-	14.3 ± 42.5	39 ± 96
Pb	0.20 - 0.35	5.0 - 25.0	2.1 - 7.5	8.3 ± 21.8	1.5 ± 1.3
Zn	9.4 - 320	-	115 - 516	176 ± 620	111 ± 162

It is possible that low accumulation of metals observed in this study area, Zn in particular, is associated with relatively low pH (4.6 - 6.5; 5.6 ± 0.28) in topsoil layer, at which may promote metal mobility. In general, mobility of metals increases with decreasing pH [21,41,42]. For example, Cottenie and Verloo [41] reported that at pH values below 6, the relative mobility, expressed as percentage of total content dissolved, is in the order of Zn > Cu > Pb. High mobility of Zn was also reported by other studies [35,43].

The heavy metals in the study area can also derive from the application of pesticides, particularly herbicides, which applied regularly before, during and ca. 10 days after the germination of rice. Several studies have pointed out the association between pesticides and heavy metal contamination [9-12]. However, it is difficult to justify their impact in this study. This is due to: 1) while there are numerous formulations of pesticides marketed worldwide, information on their heavy metal contents is relatively scarce; 2) limitation of information on quantity and formulations of herbicides and insecticides used in the study area.

Heavy metal concentration in Mae La river sediments were studied by Mighanetara [42], who reported that sediment samples contained 26.2 ± 7.0 mgCu·kg^{-1}, 30.7 ± 3.2 mgPb·kg^{-1} and 72.0 ± 27.3 mgZn·kg^{-1}, while the concentrations in topsoil identified in this study are 19.8 ± 4.9 mgCu·kg^{-1}, 24.1 ± 5.9 mgPb·kg^{-1} and 42.1 ± 6.4 mg·kg^{-1}. It can be seen that concentrations in river sediments followed the same order with that in paddy soil (Zn > Pb > Cu). The result from Student t's test also suggested that metal concentrations in sediment samples were significantly higher than those in topsoil samples (p < 0.000 for all metal studied). The contamination factors of metals in river sediments were calculated using the same background concentrations used in the calculation for paddy soil. The results showed that the contamination factors of Cu, Pb and Zn in river sediments (1.6, 1.5 and 1.9, respectively) were higher than their contamination factors in paddy soil (1.2, 1.2, and 1.1, respectively). This illustrated that metal accumulation, Zn in particular, was more pronounce in the sediments than in the paddy soil. Relatively higher contamination factor of Zn in sediment samples may explain the disagreement between high Zn contents in PFs and low Zn accumulation in paddy soil.

Mae La river basin is rural and the main land use is rice cultivation. Therefore the application of agrochemicals is a major source of heavy metal in the area. Once applied to paddy fields, heavy metals in agrochemicals will redistribute in receiving soil and water depending on physiochemical conditions in paddy fields. They may dissolve or suspend in submergence water, accumulate onto soil particles, bioaccumulation by organisms, or migrate from receiving soil and water to adjacent environments.

According to soil series map, the study area consist very fine to fine loamy soil of poorly to moderated drained soil. As a result, migration of metals to deeper layer is relative low. It is likely that heavy metals retain in topsoil and remobilize by either flood waters as fine particulates and/or through ploughing. This explain an elevated metal content in a plough layer.

Mae La River receives both surface water (runoff and submergence) and groundwater from paddy fields in the basin. As a result, heavy metals in paddy fields, either in dissolved or particulate forms are major sources of heavy metals to Mea La River. Proposed migration pathway of heavy metals in Mae La river basin is illustrated in **Figure 6**.

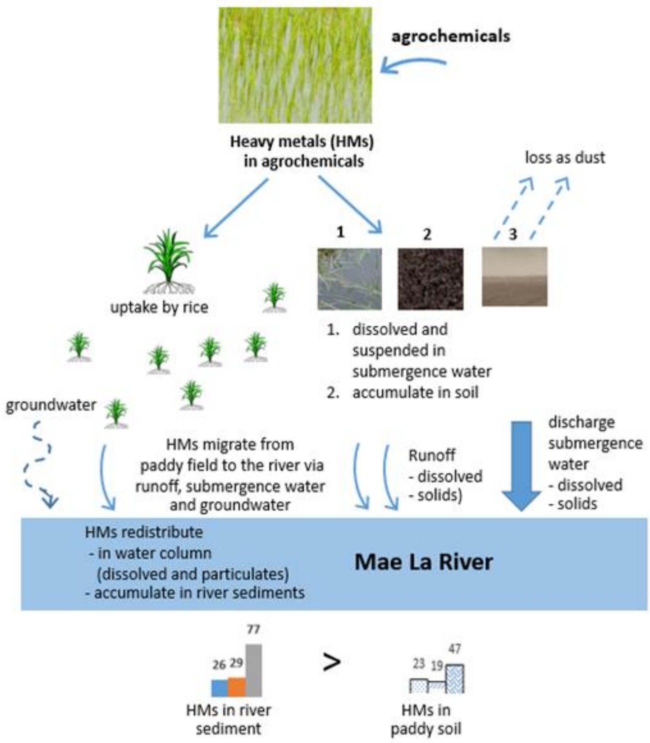

Figure 6 proposed migration pathway of heavy metals form agrochemicals to Mae La river.

Additionally, it should be noted that Cu concentrations in river sediments (11.4 - 38.8 mg·kg^{-1} with an average of 26.2 ± 7.0 mg·kg^{-1}) were close to the Threshold effect level of the Dutch Sediment Quality Guidelines (36 mg·kg^{-1}) [33]. This highlights the need for further studies. This is because Cu is highly toxic to most aquatic organisms [27,28]. Further use of agrochemicals may lead to higher Cu accumulation in the river sediments and eventually exceed the Threshold value at which low effect begins. This can have adverse effects on the Mae La striped snakehead fish, which is a local delicacy and has long been associated with the community in many aspects. Therefore, a detailed study of its potential sources and migration pathways in a river basin is a key information to assess the risk of Cu in river sediments on the Mae La striped snakehead fish and develop remediation strategies in case of need.

Conclusions

In this study, a total of 60 soil samples from 15 boreholes at different depths were collected from paddy fields in Mae La River basin. The pH and heavy metals (Cu, Pb and Zn) concentrations were determined in order to investigate the effects of long-term application of agrochemicals used in rice cultivation on metal accumulation. It is likely that long-term application of nitrogen fertilizers has resulted in significant decrease in topsoil pH. The concentrations of Cu, Pb and Zn in topsoil samples were significantly higher than that in subsoil, which is likely to result from long-term application of agrochemicals. The amount of Cu, Pb and Zn in subsoil, considered as background concentrations of the study area, were within normal range for uncontaminated paddy field. Although the concentrations observed in topsoil are safe according to the Dutch standard, evidence on heavy metal accumulation in river sediments demonstrates that the impact of agrochemical use extends beyond their receiving soil. Therefore, impact assessment of their application should cover all major components in the basin. Detailed studies on heavy metal input inventory, mass balance and migration pathways can provide a better understanding of their mobility in the river basin. Priority attention should be given to Cu due to its toxicity to aquatic organisms and its concentrations are approaching the Threshold limit of the Sediment Quality Guidelines. The information obtained will provide a better prediction model for risk assessment of long-term application of agrochemicals and remediation measures, if needed.

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