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LEAD CONTAMINATIONS IN THE CHANTHABURI RIVERAND VICINITY AREAS, CHANTHABURI PROVINCE, THAILAND.

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ABSTRACT

This research was conducted to investigate lead (Pb) contaminations in water and sediment in the Chanthaburi River and surface soil in the vicinity areas along the river. The samples were collected to estimate Pb concentrations found in river water and sediment and potential environmental risks by Hazard Quotient Equation (HQ). The results revealed that the distribution of Pb in surface soils from orchards located on the bank along the river in dry and wet seasons were in the ranges of 4.06 to 4.67 and 4.60 to 4.80 mg/kg, dry weight (dw), respectively, while the potential environmental risks of those surface soil were not at risks (HQ < 0.1). The Pb concentrations in the water of the Chanthaburi River from upstream down to estuaries in both seasons were ranged from not detectable (ND) to 0.002 and ND to 0.005 mg/l, respectively. Likewise, the potential environmental risks of water were not at risks. Also, the concentrations of Pb in sediment collected in dry and wet seasons were in the ranges of 2.20 to 4.24 and 2.46 to 4.34 mg/kg, dw, respectively. The potential environmental risks of sediment were not at risks as well. It could be concluded that this project area was still not at risks.

Keywords: Lead (Pb), environmental risks, hazard quotient (HQ), and the Chanthaburi River.

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INTRODUCTION

The Chanthaburi River is originated from Soi-Dao Mountain, where the water current flows through Ma-Kham district, which is the first community area located in and around the origin of the river. The water current is flowing through the orchard plantation area, which is the major activity of plant cultivations. The water current runs through Mueang district, which is a high-density community, and through Laem-Sing district, which is subsequently run to the Gulf of Thailand. The major geological characteristics of this province consist of the mountains, forestlands, and highlands at the elevation of 30-190 meters above the sea level.

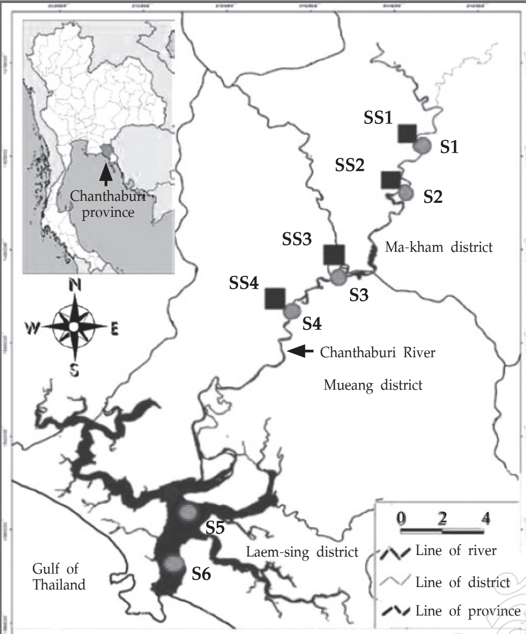
Most agricultural areas are located along the river bank, which the rainwater runoff washes away the pesticides into the river and estuaries. Most of factories in this province are medium and small size factories dealing with transportation and food production. The others include non-ferrous metal industry, timber industry, wood products, and industrial agriculture (Ministry of Industry, Thailand, 2007).

The popular and effective pesticides used in agriculture about three decades ago were those in which the active component was lead (Pb). Lead arsenate, which had been used for many decades, was banned in Thailand on 1st December 2001 by Ministry of Industry (Ministry of Industry, Thailand, 2001). At present, the contaminations of pesticides, especially Pb, in the water of the Chanthaburi River are presumably coming from domestic and industrial sources, i.e., batteries, gasoline, paint products, and gunpowder's. Lead is known as one of the most toxic heavy metals, which is stable and persistent environmental contaminant, because it cannot be degraded or destroyed. Therefore, it will be accumulated in various environmental constituents, i.e., soil, water, and sediment, which can affect infants and young children in the development of brain and nervous system. It has been shown that high levels of lead can cause an adverse effect against kidneys of adults and children (CDC, 2000). The information concerns the contamination of Pb in the Chanthaburi River and its vicinity areas has not been studied.

MATERIALS AND METHODS

Sampling procedure

The sampling was conducted in both dry season (March 2011) and wet season (May 2011) in several locations along the river bank of the Chanthaburi River, as shown in Figure 1. Surface soil samples were randomly collected using a spade at three depth levels, i.e., at 0-5, 6-10, and 11-15 cm of the open pits or small creaks in the orchards near the sampling locations along the Chanthaburi River. Three grab samples of surface soils were randomly collected in each sampling station/plot. Each composite soil sample was collected for one kg and kept in plastic bags until use. The sites for collection of water and sediment samples in the Chanthaburi River and its estuary were randomly selected from various locations that carried several activities, i.e., stations 1 and 2 were related to agricultural activities, station 3 was related to water supply intake, station 4 was related to water running through high density communities, while stations 5 and 6 were the water running along aquaculture activities. Stations 1 to 3 were located upstream of the Chanthaburi River and were unlikely to be contaminated with seawater, since there was a rubber dam blocking the seawater to overflow into those agricultural areas. Stations 4 to 6 were located downstream of the Chanthaburi River where the water current runs to the mouth of the river and the Gulf of Thailand. Water samples were randomly collected using Kemmerer sampler at the mid-depth of the stream and kept in HDPE bottles until use. Water samples for the detection of Pb must be preserved with conc. HNO_3 acid ($pH < 2$). Two grabs of sediment samples were randomly collected from each station at the bottom of the river within the same locations as did for water samples using Ekman dredge (size 20x20 cm^2). All samples were kept in an icebox at 4 °C and then transported to the laboratory for analyses.



No.	Locations by GRS	
	Surface soil (SS- ■)	Water/Sediment (S- ○)
1	N 12 ° 41'482" E 102 ° 10'382"	N 12 ° 41'482" E 102 ° 10'400"
2	N 12 ° 40'081" E 102 ° 10'006"	N 12 ° 40'247" E 102 ° 09'951"
3	N 12 ° 38'401" E 102 ° 08'385"	N 12 ° 38'381" E 102 ° 08'394"
4	N 12 ° 36'879" E 102 ° 06'901"	N 12 ° 36'844" E 102 ° 06'893"
5	-	N 12 ° 31'237" E 102 ° 04'060"
6	-	N 12 ° 29'780" E 102 ° 03'779"

Figure 1. Showing sampling locations of study sites in the Chanthaburi River and vicinity areas (modified from the Region of Environmental Office 13, 2010).

The quality control of laboratory

Paraquat measurement was calibrated against three replicated samples of standard concentrations of paraquat dichloride, reference materials (SRM 1646a for sediment) from the U.S. Department of Commerce, National Institute of Standard and Technology (NIST) and four samples of blank. The Method Detection Limit (MDL) was calculated by using 3.143 multiplies the standard deviation of the seven reagent blank samples in the sample batch and used as a tool for verification of all Pb analyses.

Sample analyses

Water: The physical and chemical characteristics of the river water were measured both in the field and in the laboratory (APHA, 1998). The determination of Water Quality Index (WQI) consisted of eight parameters, i.e., dissolved oxygen (DO), fecal coliform bacteria (FCB), pH, biochemical oxygen demand (BOD), total phosphate, NO_3^--N, turbidity, and total solid (TS). The WQI was calculated using the following equation:

$$WQI = \sum_{i=1}^{n} w_i \; q_i \qquad (1)$$

n = number of parameter

w_i = unit weight of parameter

q_i = the quality of parameter (PCD, 2010)

Surface soil/sediment: The preparation of surface soil and sediment samples were air dried under shade around two days, crushed by using a porcelain pestle and mortar, and subsequently sieved with stainless sieve to remove the particles greater than 2 mm. The physical and chemical analyses of surface soil and sediment samples were measured for pH, organic matter (Walkley and Black, 1934), texture (Sheldrick and Wang, 1993), and cation exchange capacity (Chapman, 1965) in the laboratory.

Total lead contents of water samples were carried out using the method of nitric acid digestion (APHA, 1998). Likewise, total lead contents of surface soil and sediment samples were also carried out using the method of nitric acid digestion (USEPA, 1996). All surface soil and sediment samples were dried at 103°C for 24 hours prior to digestion. Varian SpectrAA-600 Atomic Absorption Spectrophotometer was used to determine Pb concentrations in the samples, where the limit of detection was 1.0 μg/l.

An evaluation of the potential environmental risks could be estimated numerically using the Hazard Quotient (HQ)(USEPA, 2006). The HQ was a ratio, which could be used to estimate whether risk to harmful effects was likely or not due to the contamination at the site of collection. The HQ was calculated using the following equation:

$$HQ = EEC/\text{Screening benchmark} \qquad (2)$$

EEC = estimated (maximum) environmental contaminant concentration in the soil, sediment, or water at the site of collection (e.g., mg contaminant/kg soil).

Screening benchmark = maximum allowable of lead concentration; if the contamination concentration was below this level, the contaminant was not likely to cause harmful effects.

If: HQ < 0.1, no hazard exists
HQ = 0.1-1.0, hazard is low
HQ = 1.1-10, hazard is moderate
HQ > 10, hazard is high

Statistical analysis of data was carried out with the SPSS statistical program for Window (version 18.0). The comparison of lead mean value between the selected seasons was significant at the level of $p < 0.05$.

RESULTS AND DISCUSSION

The accuracy of the analytical procedure for the detection of Pb, which was calibrated against standard reference material by the percentage recovery, was at 98.29, whereas the method detection limit (MDL) was at 0.0012 mg/l.

The physical and chemical characteristics of surface soil are summarized in Table 1. The concentrations of Pb in surface soils both in dry and wet seasons were in the ranges of 4.06 to 4.67 and 4.60 to 4.80 mg/kg, dw, respectively, as shown in Figure 2.

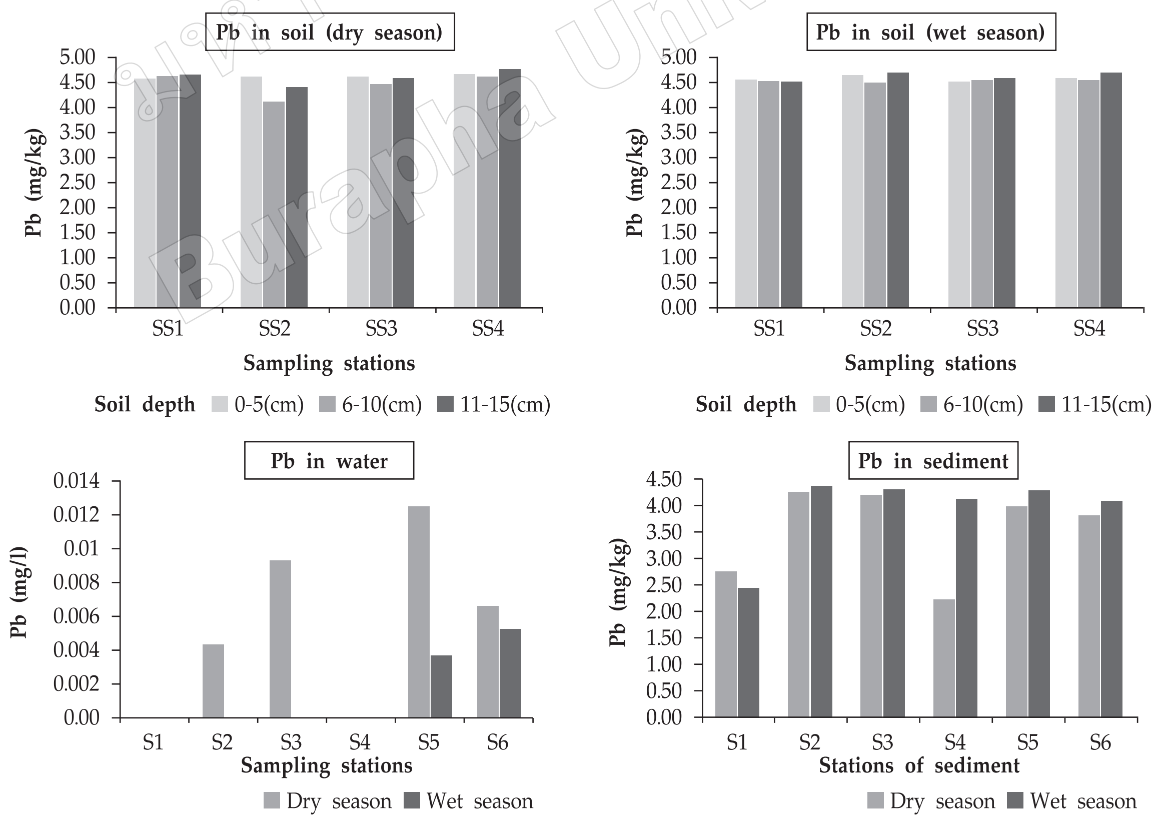


Figure 2. Showing the concentrations of Pb in soil, water, and sediment samples.

Table 1. The physical and chemical characteristics of surface soil samples.

Stations (depth in cm)	Sand (%)	Silt (%)	Clay (%)	Texture	pH	OM (%)	CEC (cmol/kg)
Dry season							
SS1 (0-5)	22.8	52.9	24.3	Silt loam	5.7	5.67	14.69
(6-10)	21.3	52.8	25.9	Silt loam	5.6	4.90	14.31
(11-15)	23.3	51.4	25.3	Silt loam	5.1	3.48	12.16
SS2 (0-5)	28.7	48.2	23.1	Loam	5.7	5.45	14.67
(6-10)	24.9	50.7	24.4	Silt loam	5.6	3.51	12.22
(11-15)	25.0	49.8	25.2	Loam	5.2	2.50	9.84
SS3 (0-5)	43.5	39.3	17.2	Loam	5.4	3.77	9.58
(6-10)	38.6	42.5	18.9	Loam	4.8	2.31	7.86
(11-15)	41.3	39.3	19.4	Loam	4.8	2.07	7.78
SS4 (0-5)	27.6	45.7	26.7	Loam	5.1	4.63	14.69
(6-10)	29.1	44.4	26.5	Loam	4.3	3.51	11.38
(11-15)	28.8	45.3	25.9	Loam	4.4	2.95	11.06
Wet season							
SS1 (0-5)	24.2	50.5	25.3	Silt loam	5.0	4.96	13.83
(6-10)	24.8	48.3	26.9	Loam	4.9	3.05	12.65
(11-15)	25.0	48.2	26.8	Loam	4.9	2.14	10.42
SS2 (0-5)	25.3	49.5	25.2	Loam	5.6	4.78	13.98
(6-10)	26.2	48.9	24.9	Loam	5.2	2.92	11.17
(11-15)	26.9	47.4	25.7	Loam	5.0	2.27	10.10
SS3 (0-5)	47.8	35.2	17.0	Loam	4.7	2.51	8.21
(6-10)	41.9	35.8	22.3	Loam	4.6	3.70	10.52
(11-15)	43.2	38.4	18.4	Loam	4.6	1.76	7.28
SS4 (0-5)	43.8	37.0	19.2	Loam	5.9	4.13	17.25
(6-10)	43.6	37.5	18.9	Loam	4.8	5.52	7.63
(11-15)	35.9	41.1	23.0	Loam	5.2	3.70	3.18

OM = organic matter; CEC = cation exchange capacity

Lead in surface soil sample was found at high concentration only in the sample collected at the depth of 11-15 cm regarding to Pb related to agricultural and industrial activities, which was banned in Thailand many years ago. Lead was previously added to gasoline used for gasoline-powered machines that had been employed in several agricultural operations for cultivation, i.e., water pumping, and harvesting (Wenzhong et al., 2010), which were the major activities of this province. The results of statistical analyses for comparisons of Pb concentrations between seasons in surface soil were significant difference.

The characteristics of water are summarized in Table 2. The concentrations of Pb in water samples collected in both dry and wet seasons were in the ranges of ND to 0.002 and ND to 0.005 mg/l, respectively, as shown in Figure 2. The concentrations of lead were decreased as the period of time was increased, which were based on the annual water quality report during the years 2004-2010 in the Chanthaburi River (Region of Environmental Office 13, 2010).

Table 2. The physical and chemical characteristics of water samples.

Stations	Turbidity (NTU)	TS (mg/l)	pH	DO (mg/l)	BOD (mg/l)	Total Phosphate (mg/l)	NO_3^--N (mg/l)	FCB (MPN/100ml)
Dry Season								
S1	2.56	26.00	8	6.78	1	0.0108	0.17	40
S2	3.89	28.00	7.5	5.54	2	0.0038	0.19	70
S3	3.26	32.00	7.1	4.29	2	0.0073	0.07	40
S4	5.59	21152.00	6.9	3.16	8	0.0231	0.07	150
S5	4.57	35397.33	7.5	5.69	7	0.0038	0.08	300
S6	3.78	37225.33	8	4.60	9	0.0021	0.10	<30
Wet Season								
S1	4.60	188.00	7.5	7.28	4	0.0401	0.39	2670
S2	4.56	205.33	7.5	6.39	4	0.0821	0.27	≥24000
S3	5.52	222.67	7.5	5.50	4	0.0576	0.24	1650
S4	9.65	12078.67	7.2	6.33	4	0.0471	0.17	930
S5	14.50	34657.33	7.8	5.44	4	0.1468	0.73	≥24000
S6	3.85	25268.00	7.5	7.85	3	0.0725	0.13	2100
Thai Surface Water Quality Standard (PCD, 1994)	-	-	5-9	2-6	1.5-4.0	-	5.0	1000-4000

TS = total solid; DO = dissolved oxygen; BOD = biological oxygen demand
FCB = fecal coliform bacteria; NO_3^--N = nitrate-nitrogen

It was found that the concentration of Pb in water sample was high in dry season, and that in wet season it was high only at stations S5 and S6. This was probably due to those stations received runoff rainwater from contaminated areas. Statistical analysis of the comparison between the concentrations of Pb in the water samples collected during different seasons showed no significant difference. Most of the water qualities of the river are classified as good (as calculated WQI of the Chanthaburi River), as shown in Table 3. The classification for lower quality of water from stations 4 and 5 might be due to activities in communities and in aquaculture, respectively. These results were consistent with the annual water quality reports during the years 2008 to 2010, which revealed that the water quality was likely to decrease gradually (Region of Environmental Office 13, 2010).

The physical and chemical characteristics of sediment samples are summarized in Table 4. It was found that the concentrations of Pb in sediment samples collected both in dry and wet seasons were in the ranges of 2.20 to 4.24 and 2.46 to 4.34 mg/kg, dw, respectively, as shown in Figure 2. The concentrations of Pb in samples were increased as the clay content was. It was also shown that levels of organic compounds, nutrients, phosphate, and organic matter were increased, and the level of salinity was decreased during the monsoon period, which enhanced the formation and deposition of metals in the sediment that corresponded to the report of Seralathan et al. (2008). However, there was no significant difference in sediment samples collected in different seasons.

Table 3 Water Quality Index (WQI) of the Chanthaburi River.

Stations (Dry season)	WQI	Criteria	Class	Stations (Wet season)	WQI	Criteria	Class
S1	94	Good	2	S1	85	Good	2
S2	90	Good	2	S2	74	Good	2
S3	87	Good	2	S3	84	Good	2
S4	69	Fairly	3	S4	80	Good	2
S5	78	Good	2	S5	63	Fairly	3
S6	73	Good	2	S6	82	Good	2
Water quality criteria (based on WQI) (PCD, 2010).				71-100 Good	61-70 Fairly	31-60 Bad	0-30 Very bad

Table 4 The physical and chemical characteristics of the collected sediment samples.

Stations	Sand (%)	Silt (%)	Clay (%)	Texture	pH	OM (%)	CEC (cmol/kg)
Dry season							
S1	99.3	0.2	0.5	Sand	6.2	0.11	1.25
S2	46.9	31	22	Loam	5.3	1.58	7.75
S3	14.5	61	24	Silt loam	5.1	4.26	12.87
S4	98.8	0.2	1	Sand	5.5	0.07	2.75
S5	22.9	53	24	Silt loam	6.4	5.89	20.75
S6	78.3	11	11	Sandy loam	7.0	1.78	7.11
Wet season							
S1	97.9	1.1	1	Sand	7.0	0.13	1.57
S2	27.7	49	24	Loam	5.5	4.50	12.11
S3	64.8	17	19	Sandy loam	5.4	3.47	10.95
S4	22.4	50	28	Clay loam	5.5	1.85	7.35
S5	33.3	36	30	Clay loam	6.7	5.16	17.81
S6	74.3	15	11	Sandy loam	7.2	1.73	7

OM = organic matter; CEC = cation exchange capacity

Results of Hazard Quotient (HQ) of surface soil, using the screening benchmark based on the Thai Soil Quality Standards for residential and agriculture established by the Pollution Control Department (PCD, 2004), showed that the soils in selected sites were not at risks with the value of HQ = 0.01, where there was no hazard existed with the value of HQ < 0.1 in both seasons. Results of HQ in water, using the screening benchmark based on the Thai Surface Water Quality Standard established by the Pollution Control Department (PCD, 1994) was used to calculate HQ, revealed that therewas no hazard effect (HQ < 0.1) in the water current collected upstream of the river. Nevertheless, the hazard still existed in water current collected downstream of the river, but it was low with the values of HQ = 0.1-1.0. Likewise, results of HQ of sediment samples, using the screening benchmark based on the Draft Interim Thai Sediment Quality Standard established by the Pollution Control

Department (PCD, 2009), showed that the potential environmental risks were almost the same as those water samples collected from the study areas.

It can be concluded that the environmental compartments in the selected areas of the Chanthaburi River and its vicinity are not at risks although they have been exposed to Pb containing pesticides that have been applied for several years.

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