App. Envi. Res. 37 (1): 1-10

Applied Environmental Research

Journal homepage : http://www.tci-thaijo.org/index.php/aer

Fractionation and Mobility of Lead in Klity Creek Riverbank Sediments, Kanchanaburi, Thailand

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Article History
Submitted: 25 May 2014/ Accepted: 30 September 2014/ Published online: 15 February 2015

Abstract

The sequential extraction method was employed to investigate the distribution and chemical fractions of lead (Pb) in Klity Creek sediments, Kanchanaburi, Thailand with the main objective to define the lead mobility in sediment and potential bioavailability in relation to sediment contamination levels. Samples were collected from a total of twelve sampling sites distributed from upstream of the polluted zone until the final downstream point at Srinakarin Reservoir. The results showed that the background value of total lead concentration in the sediments from this area was higher than those reported from other locations in Thailand. Sequential extraction results revealed that lead was mainly associated with the reducible fraction especially in the polluted zone in the vicinity of the ore dressing plant. This is different from the distribution of lead fractions upstream and downstream of the polluted area, i.e. reducible fraction was the major component upstream whereas strongly dissociated fractions (oxidizable and residual) were the major components for the downstream samples (at Srinakarin Reservoir). A significant amount of the lead fraction in the study area was rather mobile, suggesting it as readily available to living organisms. Most samples exhibited a medium risk level with Risk Assessment Code (RAC) values of more than 10%.

Keywords: Lead concentration; sediment fractions; mobility, risk assessment code (RAC); Klity Creek

Introduction

Lead-ore tailing contamination from metalliferous mining and processing into Klity Creek has attracted considerable public attention in recent decades as hundreds of tons of ore tailing were believed to contaminate this creek sediment. Klity Creek canal is the one of the water sources of the Meklong river basin which is the main water resource in the western region of Thailand. In 1998, the Pollution Control Department reported lead contamination in Klity Creek, especially in sediment samples collected from the vicinity of the ore dressing plant. The highest lead concentrations were found to be as high as 65,771–143,097 mg kg^{-1} which is 20–100 times higher than the surrounding area without mining. Lead levels in fish were ten times higher than the allowable maximum level in food (1 mg kg^{-1}) [1]. Lead contamination was found all along the 20 km length of the creek [1, 2, 3].

Metal extraction methods for environmental samples have been extensively studied [4]. Heavy metal accumulation in soils takes various forms, i.e. exchangeable, carbonate bound or acid extractable, Fe-Mn oxides bound or reducible, organic bound and residual forms. The exchangeable fraction is considered to be bioavailable; carbonate bound, Fe-Mn oxides bound and organic bound may be potentially bioavailable, while the residual fraction is mainly unavailable to either plants or animals [5,6]. Metal ions bound to the solid phase can be dissolved through changes in soil pH, temperature, redox potential, soil organic matter decomposition, leaching and ion exchange and microbial activity [7]. The sequential extraction method is typically used to determine the various chemical forms of heavy metals, and is recognized as an important and effective approach.

Although the studies of lead contamination in Klity Creek sediments have been investtigated by many researchers [1, 2, 3, 8, 9], none have reported the various forms of lead species. Therefore it was the aim of this work to examine the various lead species in the contaminated sediments in Klity Creek using the sequential extraction technique to evaluate mobility factors in the creek and downstream sediments. The results provide useful supporting information in the mitigation management of the contaminated site at Klity village.

Materials and Methods

1) Study area

Klity Creek is located in Klity village, Cha Lea Sub district, Thong Pha Phum District, Kanchanaburi, Thailand, which is approximately 450 km northwest of Bangkok. This area was an important lead source during 1960s to 1980s. The area of Bor Ngam open pits mine is 47.84 km^2. Lead in this area is in the form of cerussite ($PbCO_3$) [9]. Crude ore was transported to the ore dressing plant located 6 km south of the mining area. Lead was extracted by the flotation process to the 60% mineral ore and ore tailings; there was no smelting process in this area. Klity stream flows southward past upper Klity Village, Klity ore dressing plant area, Thidadoy Waterfall, lower Klity Village, Klity Waterfall and finally reaches Srinakarin Reservoir. The stream consists of 2 sub-streams: one is from the east; the other is from the north. The northern stream goes past Bor Ngam Mine whereas the eastern stream, which passes through the lime-stone full of lead, is originally generated from Pung and Deka swamps [10] at the location of 14^o 95' to 14^o 75' N and 98^o 89' to 89^o 97' E (Figure 1). Mining activities ended and the ore dressing plant was terminated in 1999 following leakage of ore tailings from sediment pond which contaminated the Klity canal, by an injunction by Thailand's Department of Mineral Resources and the Pollution Control Department.

2) Sample collection and preparation

From January to April 2012, river bank sediment samples were collected from 12 locations (Figure 1) within the polluted areas and utilization zone. Sample sites were selected considering the need for vehicular access to the sampling location. The section of creek that runs through the forest was not sampled. Five samples were collected from upper Klity village (S1 to S5), one from lower Klity village (S6) and six from downstream of Klity Creek in Srinakarin Reservoir (S7 to S12). Details of these 12 locations are provided in Table 1. The sediment samples were collected in polyethylene bottles and promptly returned to the laboratory for analysis.

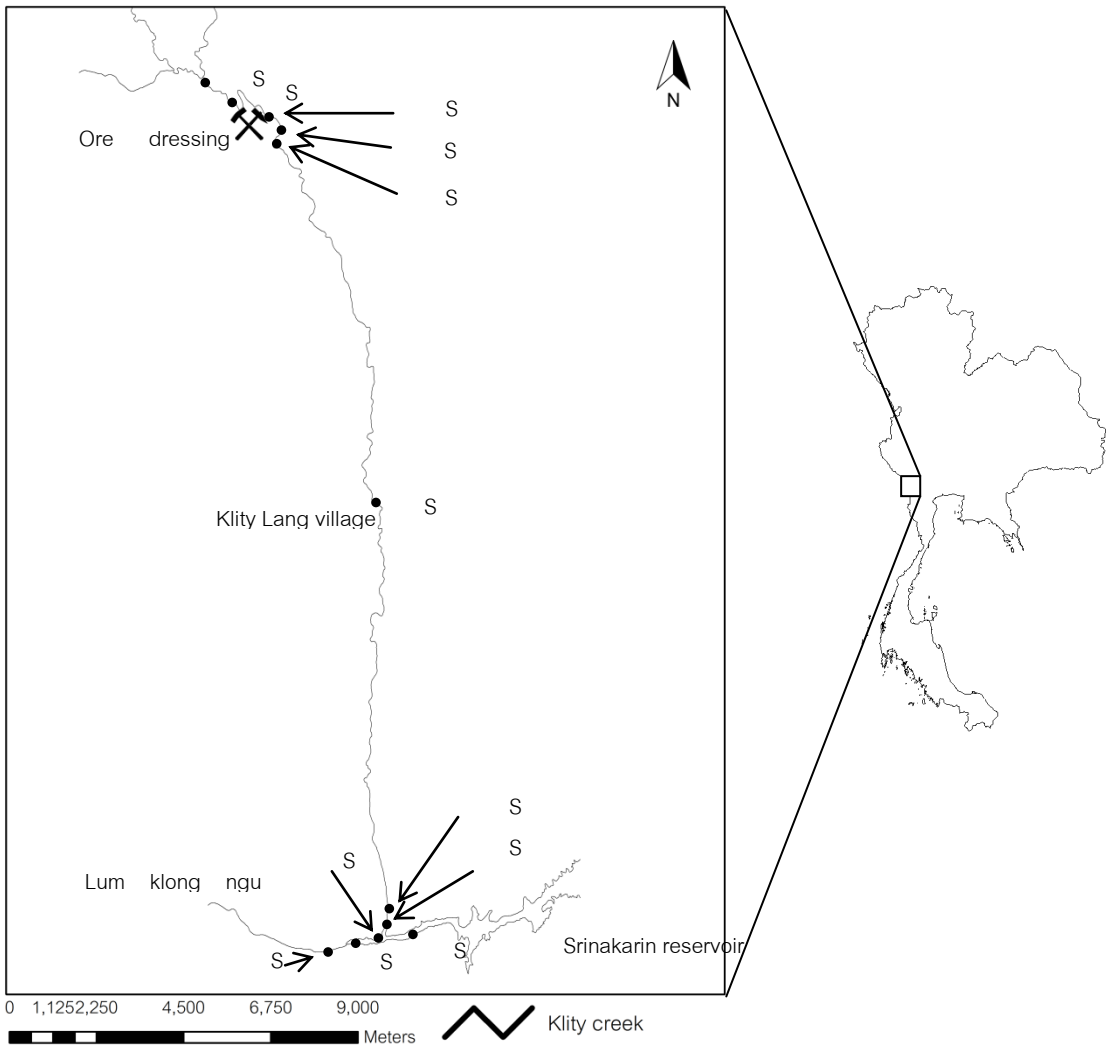

Figure 1 Map of sediment samples collecting along Klity Creek

3) Sample analysis

The riverbank sediment was collected by 1 kg grab sampling from the top layer (20 cm depth), placed in a plastic bottle and sent to the laboratory. Sediment samples were air-dried at ambient temperature for 4 days and homogenized by grinding, mixing then sieving through a 2 mm sieve. Sieved samples were dried in a hot-air oven at 80^{o}C to constant weight and placed in closed plastic bags until analysis.

Table 1 Description of Klity Creek sediment sample sites

Site	Site Description	North	East
S1	1,500 meters upstream from discharge point	14° 96' 16"	98° 90' 98"
S2	500 meters upstream from discharge point	14° 95' 56"	98° 92' 16"
S3	200 meters downstream from discharge point	14° 95' 55"	98° 92' 20"
S4	250 meters downstream from discharge point	14° 95' 57"	98° 92' 24"
S5	300 meters downstream from discharge point	14° 95' 58"	98° 92' 28"
S6	Tidadoy waterfall, Klity Lang village	14° 87' 86"	98° 94' 89"
S7	Klity water fall (upstream from water fall)	14° 76' 50"	98° 95' 35"
S8	Klity water fall (downstream from water fall)	14° 76' 49"	98° 95' 35"
S9	Downstream of Klity Creek into Srinakarin Reservoir	14° 76' 34"	98° 95' 23"
S10	Srinakarin Reservoir	14° 76' 14"	98° 95' 33"
S11	Downstream of Lum Klong Ngu canal into Srinakarin	14° 76' 05"	98° 94' 76"
S12	Reservoir	14° 75' 91"	98° 93' 41"
	Lum klong Ngu canal		

The five-step sequential extraction procedure was carried out to define the various forms of lead present in the samples. This procedure was performed according to the method proposed by Tessier et al (1979) [11]. Each chemical fraction was extracted as follows: (F1) Exchangeable : 1 M $MgCl_2$ extraction at pH 7; (F2) Acid extraction : 1 M NaOAc extraction at pH 5 adjusted by HOAc; (F3) Reducible : 0.04M $NH_2OH{\cdot}HCl$ at pH 2 in 25% HOAc; (F4) Oxidzable : 30% H_2O_2/0.02M HNO_3 and (F5) Residual : mixture of HNO_3 and HCl. The extracted solutions were brought to a 50 ml final volume with DI water and then filtered using 0.45 µm Whatman filter. The solutions were stored in polyethylene bottles. The lead content was measured by atomic absorption spectroscopy (Thermo Scientific AAs ICE 3000).

The mobility factor (MF) of heavy metal in the samples was examined where the mobile fraction in sediment was accessed by comparing the exchangeable and acid extraction fractions with the total lead concentration [7]. The mobility factors (MF) are calculated according to Kabala and Singh (2001) [12].

$$MF = \frac{F_{exc} + F_{aci}}{\text{Total concentration}} \times 100 \quad (1)$$

Results and discussion

1) Total lead concentration in sediments

Table 3 demonstrates that the lead content in Klity Creek sediments ranges from 299.1–58,952 mg kg^{-1}. The concentrations downstream from the discharge point (S3, S4, S5, S6, S7 and S8) were higher than those of upstream samples (S1 and S2), which was estimated to be around 3–100 times of non-polluted values in Klity Creek [1, 2, 3]. Note that in this study, sampling sites S1 and S2 represent the background values in Klity Creek sediment, with an average concentration of 443.6 mg kg^{-1}. The highest concentration was found at Tidadoy waterfall sediment (S6) followed by the samples S4, S5, S3, S8 and S7 (58,952, 11,127, 8,792, 8,213, 1,833 and 1,248 mg kg^{-1}, respectively). This observation shown the highest lead concentration in lower Klity village sample because the absence of remediation actions to treat polluted sediments, in contrast to upper Klity village, where sediment dredging for landfill was enforced. Most of the non-polluted samples contained lead at concentrations below 500

mg kg^{-1}, such as those observed in Sinakarin Reservoir and Lum Klong Ngu canal (S9, S10, S11 and S12). This demonstrates that lead contamination remains high in the vicinity of the polluted area, but that contamination levels declined further downstream (Figure 2).

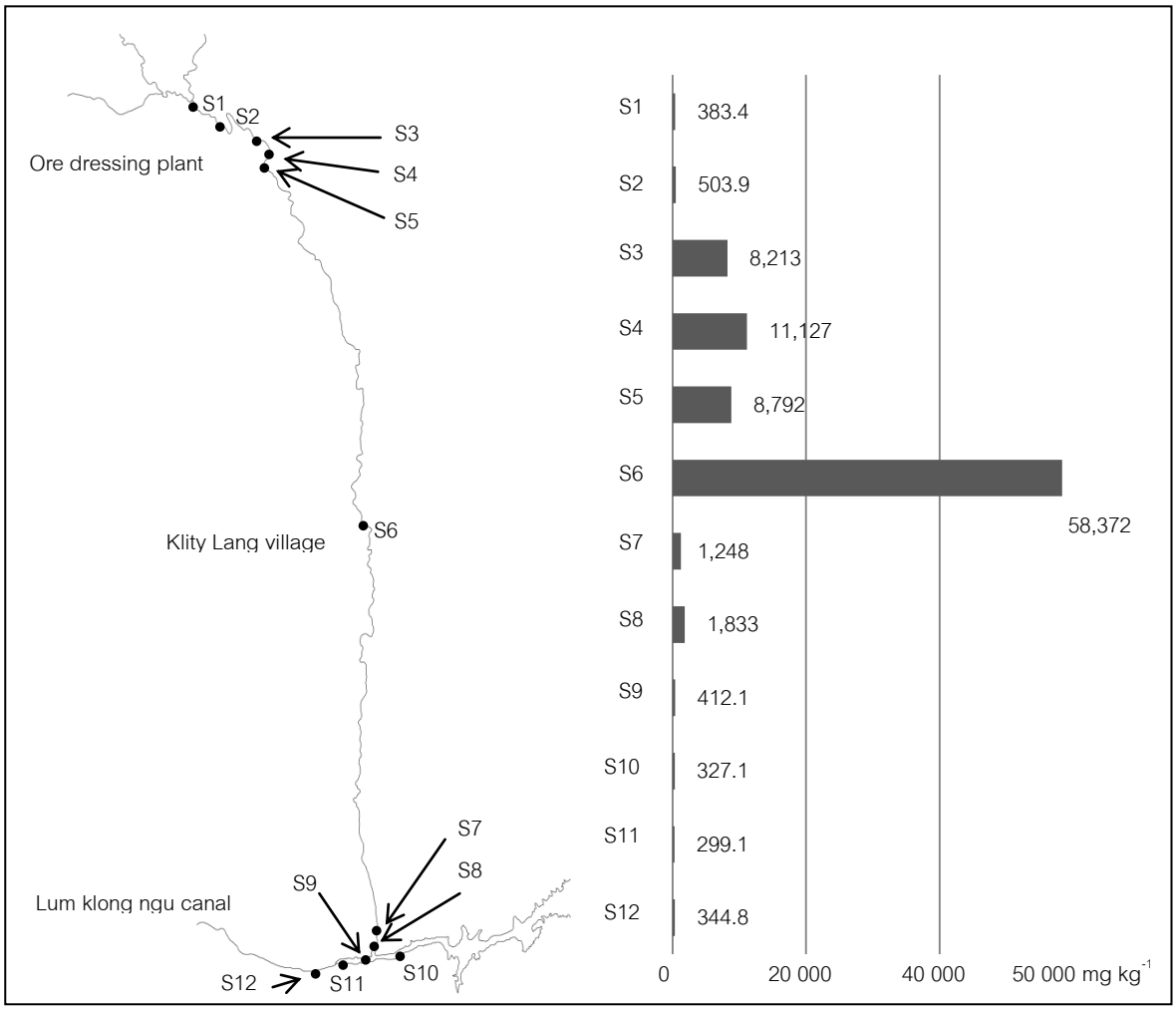

Figure 2 Total lead concentrations in Klity Creek sediment samples

It is interesting to note that, due to the existence of natural lead ore, soils/sediments in Klity area without anthropogenic contamination are naturally high in lead, with average concentrations exceeding typical values reported from other areas of the country. For example, lead concentrations in soil samples from the Pattani river estuary [13], Saensab Canal in Bangkok [14], the upper Gulf of Thailand [15] and Bung Boraphet Reservoir [16] had mean values of only 32, 203.8, 28.19 and 26.89 mg kg^{-1}, respectively. In addition, this level of non-polluted samples in Klity sediment are much greater than the background value reported in the World Surface Rock Average (WSA) and the World Common Trace Metal Range in lake sediments (WCTMRL) (Table 2).

2) Lead fractions in sediments

It was demonstrated that metal speciation and solubility affected the mobility, bioavaila bility and toxicity of metals significantly [19, 20, 21]. To assess the mobility and bioavailability of lead in this work, the five-step sequential extraction method was performed to

determine lead fractions in sediments according to the Tessier method [11]. Table 3 reports analytical fractions of lead in sediment samples, whereas the distribution of lead speciation in sediment samples is illustrated in Figure 3.

Table 2 Statistical summary of lead concentrations from non-polluted sites (n=6: S1, S2, S9, S10, S11 and S12)

	Lead concentration (mg kg^{-1})
Mean	378.4
Maximum	504
Minimum	299.1
SD	73.5
WAS [a]	20
WCTMRL[b]	10-100

[a] World surface rock average [17]
[b] WCTMRL: World common trace metal range in lake sediment [18]

2.1) Exchangeable fraction

It is generally accepted that the exchangeable metal in sediments is the most labile, the most bioavailable and the most toxic fraction [22]. This study reveals that the exchange able fraction ranged from 0.9–19.3%. The lowest levels (0.9–1.5%) were measured in the polluted zone (samples S3 to S6) located downstream from the discharged point (Table 3). An increase in the exchangeable fraction downstream from the discharged point was observed. The findings from non-polluted samples (S1, S2 and S10-S12) display the range of the exchangeable fraction from 11.4–19.3% with an average of 16.36%; the highest levels for this fraction occurred in the Srinakarin Reservoir sampling sites, indicating a background level of the exchangeable fraction in Klity Creek and its vicinity.

2.2) Acid extraction fraction

The acid extraction fraction (metals bound to carbonate, and metallic ions adsorbed into the surface of carbonate minerals), can be released into solution under lower pH conditions, and thus becomes bioavailable. Table 3 illustrates that this fraction ranged from 8–51.4% with an average value of 19.04%, and the highest was found in S6 sample (Tidadoy waterfall, lower Klity village)

2.3) Reducible fraction

The reducible fraction refers to lead which is bound to Fe and Mn as metal oxides. It has been well established that Fe and Mn oxides exist as nodules, concretions, cement between particles, or simply as a coating on particles. These oxides are scavengers for trace metals and thermodynamically unstable under anoxic conditions [11]. The sequential extraction results revealed that this fraction was predominant especially in heavily polluted zone (S3, S4, S5 and S6 in Table 3 and Figure 3) which constitutes 51.4, 68.4, 66.5 and 25.1% of the total lead in the sample, respectively. This fraction was the highest proportion in the Klity Creek sediments (average 28.8%). This is in agreement with analogous studies which stated that the reducible fraction was a dominant species on lead smelter-impacted tilled soils and mining areas [12, 13].

2.4) Oxidizable fraction

Organic matter and sulfides are important factors controlling the mobility and bioavailability of heavy metals, which are mainly bound to various forms of organic compounds by bioaccumulation in certain living organisms through various pathways. Current opinions differ on the toxicity of heavy metals influenced by organic matters [24]. This study found low values of oxidizable fraction in the polluted area (S3, S4, S5 and S6) while high values were found

downstream in the area before Srinakarin Reservoir (S7, S8 and S9) with values ranging from 3.9 to 21.4% and 31.4 to 37.1%, respectively. The result indicates that lead had been accumulating in living organisms throughout the length of the creek, especially at the end of the creek which might have accumulated a higher organic matter load.

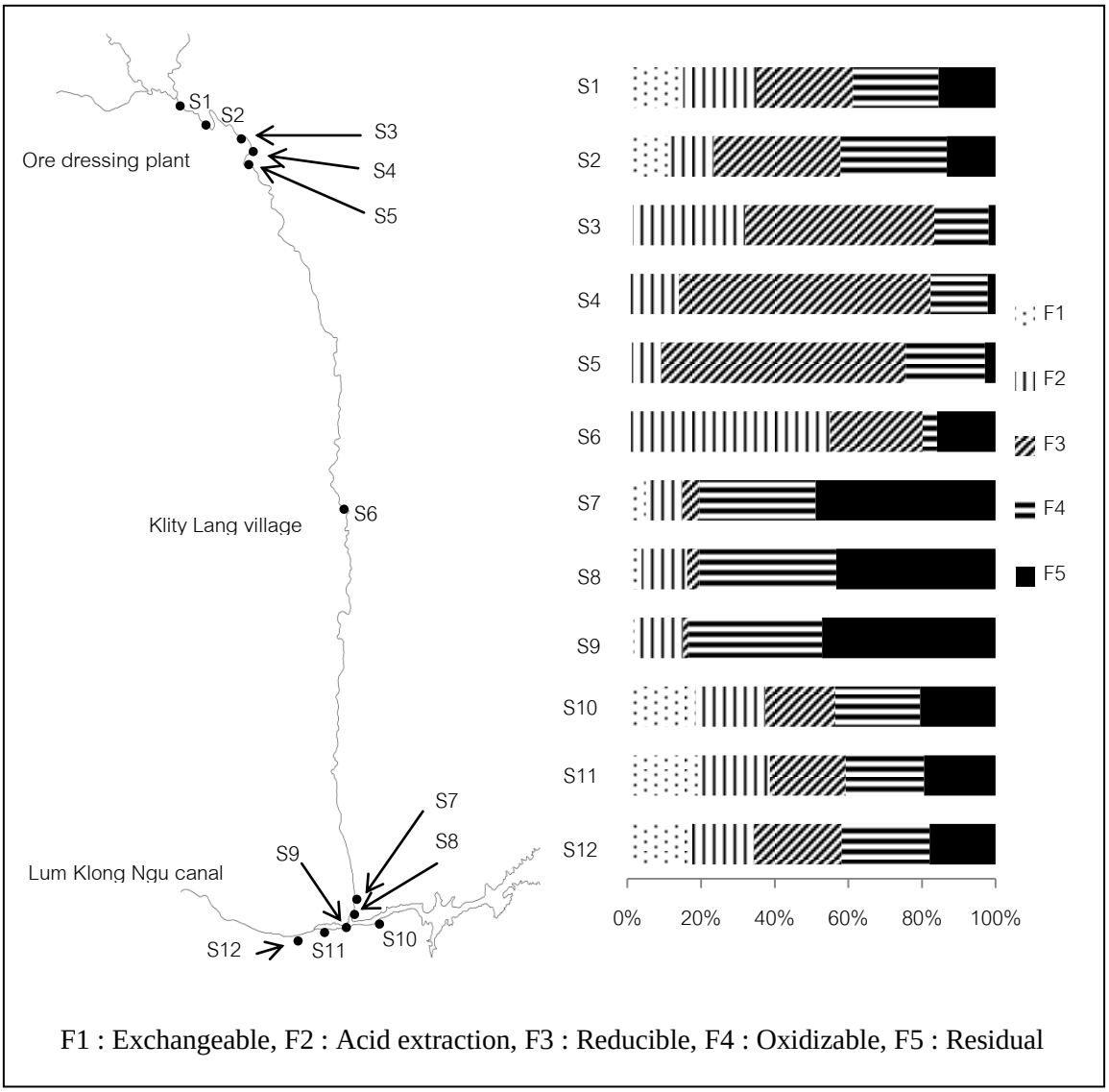

Figure 3 Distribution of lead fractions in Klity Creek sediment samples

2.5) Residual Fraction

The residual phases of metals are generally much less toxic to living organisms in the aquatic environment. In Klity Creek sediments the proportion of residual fraction varied from 1.9 to 48.9%; the percentage in the non-polluted area was higher than in the polluted area (Figure 3). High values were detected downstream of the creek, ranging from 43.1–48.9%; this might indicate that the residual was transported by streamflow and accumulated at downstream locations.

Table 3 Lead fractionation results of the Klity Creek sediments

Site	Exchangeable (F1)		Acid extraction (F2)		Reducible (F3)		Oxidizable (F4)		Residual (F5)		Total
	mg kg^{-1}	%	mg kg^{-1}	%	mg kg^{-1}	%	mg kg^{-1}	%	mg kg^{-1}	%	mg kg^{-1}
S1	58.33	15.22	76.25	19.89	100.4	26.20	88.88	23.18	59.46	15.51	383.4
S2	57.21	11.35	60.77	12.06	174.1	34.54	145.5	28.87	66.42	13.28	503.9
S3	121.3	1.48	2506	30.52	4220	51.38	1206	14.68	159.5	1.94	8213
S4	94.68	0.85	1459	13.12	7616	68.44	1719	15.45	237.7	2.14	11,127
S5	103.8	1.18	703.7	8.00	5846	66.49	1885	21.44	253.9	2.89	8,792
S6	580.0	0.98	31864	54.05	14825	25.15	2303	3.91	9378	15.91	58,952
S7	64.02	5.13	121.8	9.75	59.98	4.80	392.5	31.43	610.5	48.89	1,248
S8	71.10	3.88	230.6	12.58	61.12	3.32	679.5	37.07	790.7	43.14	1,833
S9	8.25	2.00	54.57	13.24	6.05	1.47	149.3	36.23	193.9	47.06	412.1
S10	60.87	18.61	62.00	18.96	61.67	18.85	75.48	23.08	67.05	20.50	327.1
S11	57.88	19.35	58.05	19.41	61.70	20.63	63.55	21.25	57.94	19.37	299.1
S12	59.59	17.28	59.10	17.14	81.99	23.78	82.42	23.90	61.71	17.90	344.8

3) Mobility and risk of lead in sediments

The mobility of lead in river sediments may be assessed by a comparison of the weakly bound fractions with the total metal content. Exchangeable and acid extractable fractions are considered as easily available [12]. Mobility Factor values as reported in Table 4 demonstrate lead mobility in polluted sediment (average 23.6%) were slightly lower than non-polluted sediments (average 29.1%). Although high mobility of lead was found in non-polluted sediments (upstream before the discharge point, Srinakarin Reservoir and Lum Klong Ngu canal samples), these samples contained low lead concentrations. The distribution into the sediment fractions indicates that the lead was rather mobile in sediment being largely in the acid extractable fraction.

In this study, the risk assessment code (RAC) established by Perin et al (1985) [25] was used to evaluate the risk of lead in sediments. RAC was determined based on the percentage of exchangeable and acid extraction fractions compared with the sum of all fractions, as a means of assessing the total availability of metals in sediments. RAC uses the following classification: lower than 1% sediment = No risk; 1–10% = Low risk; 11–30% = Medium risk; 31–50% = High risk; and over 50% = Very high risk (associated with forms of lead that easily enter the food chain). Table 4 shows the result of RAC classification of sediment levels. Most samples exhibited values categorized as medium risk, with RAC values over 14%. Only one sample (S5) was categorized as low risk (9.2%) and one very high risk sample (55.0%) at Tidadoy waterfall located in Lower Klity village.

Table 4 Comparison of total lead concentration, mobility factors and RAC classification in studied sediments

Site	Total Lead (mg kg^{-1})	Mobility Factor (%)	RAC Classification
S1	383.4	35.1	High risk
S2	503.9	23.4	Medium risk
S3	8,213	32.0	High risk
S4	11,127	14.0	Medium risk
S5	8,792	9.2	Low risk
S6	58,952	55.0	Very high risk
S7	1,248	14.9	Medium risk
S8	1,833	16.5	Medium risk
S9	412.1	15.2	Medium risk
S10	327.1	37.6	High risk
S11	299.1	28.7	Medium risk
S12	344.8	34.4	High risk

Conclusions

The findings from this work demonstrate that major fractions of lead contamination from the ore dressing plant in the sediment of Klity Creek were similar to the natural forms of lead in the area. Analysis proved that most of the lead in the sediments throughout the creek was in the form of reducible and oxidezable fractions. These compounds are typically stable and could not be easily taken up by living organisms. However, they could be converted to a more readily bioaccumulation form, such as the acid extraction fraction when presented in a location such as Thidadoy waterfall, where bioconversion of organic residues to some form of organic acids might occur. Major lead fractions in Srinakarin Reservoir were presented as residual and oxidizable fractions. These differ from those found in the creek which suggested that these leads might not have originated from the same source as that found in the Klity village.

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