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Nguyen Van Thinh

Graduate School of Integrated Science for Global Society, Kyushu University

Ozaki, Akinori

Institute of Tropical Agriculture, Kyushu University

Xie, Yiping

Graduate School of Social and Cultural Studies, Kyushu University

Anh Nguyen Duc

Soil Science Laboratory, Faculty of Land Management, Vietnam National University of Agriculture

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CONTAMINATION OF AGRICULTURAL SOILS BY TOXIC TRACE METALS IN AN INDUSTRIAL DISTRICT IN VIETNAM

THINH NGUYEN VAN ^{1*}, AKINORI OZAKI ², YIPING XIE ³, ANH NGUYEN DUC ⁴ AND KIYOSHI KUROSAWA ²

¹ Graduate School of Integrated Science for Global Society, Kyushu University, Fukuoka, 819-0395, Japan

² Institute of Tropical Agriculture, Kyushu University, Fukuoka, 812-8581, Japan

³ Graduate School of Social and Cultural Studies, Kyushu University, Fukuoka 819-0395, Japan

⁴ Soil Science Laboratory, Faculty of Land Management, Vietnam National University of Agriculture, Hanoi, Vietnam

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ABSTRACT

Contamination of agricultural soils by toxic trace metals of arsenic (As), lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu) and zinc (Zn) was investigated in an industrial district in Vietnam. In the district, irrigation agriculture is performed through channels, in addition, there are two industrial parks are nearby agricultural land. The purpose of the study is to clarify the magnitude and spatial distribution of the trace metal concentrations, the source of the trace metals, the difference in the concentrations between the two industrial park areas, and usability of soils for agriculture. As a result, the trace metal concentrations were in the order of Cr>Zn>Pb>Cu>As>Cd for the district. No significant differences were observed between the two park areas in concentrations. Cr and Zn concentrations were high near factories in the park areas, and the other concentrations were comparatively high in the areas, showing that the trace metals were supplied from the factories with wastewaters. The correlations observed between Cd, Pb and Zn, between Cr and Zn, and between Cu and As in the concentrations suggested that there were several groups of wastewaters supplying the trace metals. Concentrations of all kinds trace metals exceeded the permissible level for agricultural soils, and the remediation measures to reduce contamination are necessary.

INTRODUCTION

As Contamination of agricultural soils by trace metals caused by irrigation water, which is mixed with industrial wastewater, has been reported frequently since 2000. These reports have been made worldwide, for instance in China, Bangladesh, Egypt, India (Rattan, *et al.*, 2005; Rahman, *et al.*, 2012; Elbana, *et al.*, 2013; Liang, *et al.*, 2015; Mahmoud, *et al.*, 2016). According to these reports, the dominant trace metal contaminating the soils was different depending on the areas, however, the concentration of the trace metals mostly exceeded the permissible level for agricultural soils, indicating that the contamination

is serious. Moreover, the crops grown in the contaminated soils were also contaminated with the trace metals (Li, *et al.*, 2009; Yadav, *et al.*, 2013; Mani, *et al.*, 2014). Contamination of soils by trace metals can be caused by long-term irrigation, even though the irrigation water was not contaminated highly with trace metals (Rattan, *et al.*, 2005; Qureshi, *et al.*, 2016). The trace metal concentrations of the soils were high in soil surface and became lower as the soil depth became deeper (Rajmohan, *et al.*, 2014; Wei, *et al.*, 2016; Shen, *et al.*, 2017).

In Vietnam, soil trace metal contamination in Hanoi City has been reported as follows. Namely, the

agricultural soils in a factory-concentrated area were contaminated with Cd, Cu, Pb and Zn, caused by the irrigation water contaminated with industrial wastes (Huong, *et al.*, 2010; Thuong, *et al.*, 2013). According to (Phuong, *et al.*, 2009), soils of paddy field located in a copper casting village were contaminated with Cu, Pb and Zn.

While in outside near Hanoi, industrial parks have been built since around 2000, and untreated industrial wastewaters have been discharged into nearby rivers. The river water is used for the irrigation of crops in agricultural land near factory areas, and the trace metal contamination is thought to occur in agricultural soils, however, the situation of the contamination has not been clarified yet.

Therefore, in the present study, trace metal contaminations of agricultural soils were investigated in a district of Hung Yen Province locating near Hanoi City, where two industrial parks are located. The foundation year and factory composition are different between these industrial parks. Irrigation for agriculture is performed through channels there. The present study investigated five toxic trace metals that probably contaminated the soils, and intended to clarify the magnitude and spatial distribution of the soil trace metal concentrations and the source of the trace metals; difference of the concentrations between the two industrial park areas; and the usability of soils for agricultural purposes, respectively.

MATERIALS AND METHODS

Study area

The study area is an agricultural area belonging to the districts of Van Lam, Yen My and My Hao of Hung Yen Province, which are neighboring to Hanoi City. In the study area (which is referred to as study district here after), two industrial parks of Pho Noi and Thang Long are located, whose areas are 6 and 2.2 km², respectively. The population of these areas in total is 351,340 in 2013, occupying 30% of the provincial population.

The Pho Noi industrial park was built in 2003. Forty-six percent of the factories are mechanical factories, 13% plastic factories, 5% electronic factories, and the remaining are chemical, textile, food, wood and ceramic factories. While, the Thang Long industrial park was built in 2009. Thirty-eight percent of the factories are mechanical factories, 14% plastic factories, 14% electronic factories, and the remaining are steel, fluorescent lamp, electric conductivity equipment factories. Wastewater from the factories is discharged into drains and then the drain water flows into irrigation canals.

According to the Asian Development Bank (2011), average air temperature in the district is 23°C during summer and 16°C during winter, and average annual humidity is 84%. Total annual rainfall is 1,584 mm, and the total rainfall in the rainy season reaches 80% to 85% of the total annual rainfall. The rainy and dry seasons are May to October and November to April, respectively. Topography of Hung Yen Province is flat without hills and mountains. There are many rivers in the province, and flooding is common in the rainy season.

Soil sampling and chemical analysis

A total of 18 sites (points) were targeted for soil sampling in paddy field of the district, considering the distribution of irrigation canals. The sampling was done in August, 2013. The locations of the sampling are shown in Fig. 1. The soil collection was done at 5 spots for the respective points. At a spot, 1 kg top soil (0-20) cm was collected by using stainless steel drill. The soils were stored in plastic bags. All soils were air dried, and crushed by ceramic mortar and sieved through a 2 mm sieve in order to remove gravels and plant residue. The five topsoil samples were thoroughly mixed to be homogeneous. After then, 500 g soils were taken from the mixture for the chemical analysis.

The soil samples prepared above were digested with HNO₃ and H₂O₂ by using USEPA method 3050B (1996) for analyzing the total concentrations of cadmium (Cd), lead (Pb), chromium (Cr), copper (Cu) and zinc (Zn). These analyses were done by flame atomic absorption spectrometer (ANA82-Tokyo Photo Electric Co., LTD).

While, for determining arsenic (As) concentration, hydride generation atomic absorption spectrometer (280FS AA, Agilent) was used, where the soil samples were digested by HNO₃, HCl, HClO₄, H₂SO₄ and HF (SSSA. Methods of Soil Analysis, 1996).

Data analysis

The one-way repeated measures analysis of variance (ANOVA) was performed to identify the effect of sampling location on the trace metal concentrations, and Welch's t-test was performed to detect the difference in the concentrations between the two industrial park areas. The correlation analysis was performed to detect significant correlation between the trace metal concentrations. All the statistical analyses were done by Microsoft Excel.

Further, the Smirnov-Grubbs' outlier test was performed to detect the extreme value in the trace metal concentrations. The extreme value may occur

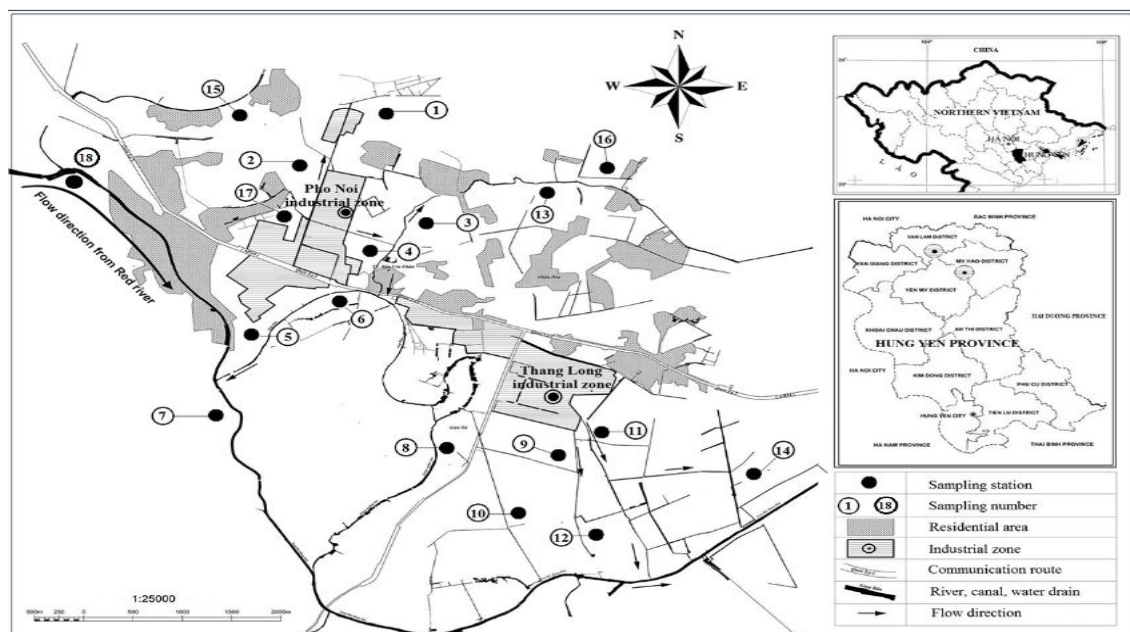


Fig. 1 Study area and soil sample sites in industrial zones in Hung Yen province, northern Vietnam.

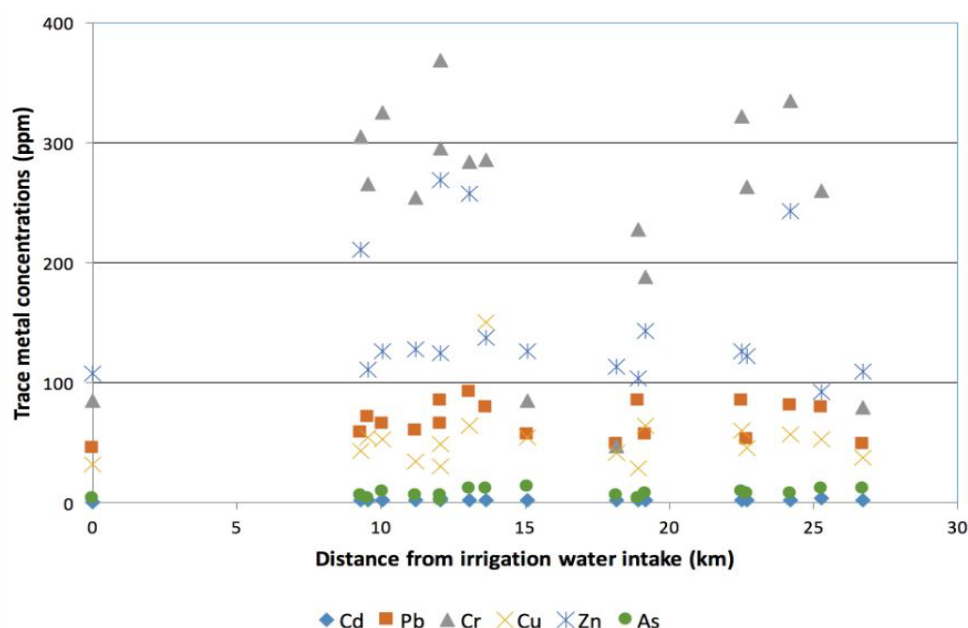


Fig. 2 Trace metal concentrations of Cd, Pb, Cr, Cu, Zn and As in relation to the distance from irrigation water intake.

due to possible errors in sampling, measurement and/or data recording. The extreme values detected were excluded from the subsequent analysis. For performing the test, SPSS software was used.

RESULTS

Fig. 1 shows the location map of the study district. Irrigation canals are located from east to south-east, covering the district. All 18 points for sampling were indicated in Fig. 1. The total target area is 48.5 km².

Fig. 2 shows the trace metal concentrations of Cd, Pb, Cr, Cu, Zn and As at each point. The horizontal axis shows the distance from the irrigation water intake

to each point along the irrigation canal. Canal to reach a point from the irrigation water intake is not limited to one (Fig. 1), however, the canal with the shortest distance was adopted. The points around 9 km to 15 km and 18 km to 27 km in the distance belonged to Pho Noi and Thang Long industrial park areas, respectively. According to Fig. 2, the Cd, As, Cu and Pb concentrations were less than 100 $\mu\text{g}\cdot\text{g}^{-1}$ in all points, while Zn and Cr concentrations mostly exceeded 100 $\mu\text{g}\cdot\text{g}^{-1}$. At point P1, where the distance from the intake was 0, all the concentrations were lower than 111 $\mu\text{g}\cdot\text{g}^{-1}$, and the point P18, where the distance was about 27 km, the concentrations were as low as those in P1. The Cr and Zn concentrations

Table 1. Trace metal concentrations at respective sampling points, their descriptive statistics and some other items

Sampling points, belonging area, descriptive statistics and other items		Trace metal concentrations ($\mu\text{g.g}^{-1}$)					
		Cd	Pb	Cr	Cu	Zn	As
Irrigation water intake	P18	1.3	45.1	85.2	32.4	108.1	4.2
Pho Noi area	P1	3.5	84.7	369.0	31.1	268.3	2.3
	P2	2.8	65.8	325.2	52.8	126.2	9.6
	P3	2.2	57.3	85.2	55.6	126.7	12.7
	P4	2.6	80.0	285.3	151.3	137.6	11.5
	P5	1.9	58.2	305.4	43.0	211.6	6.3
	P6	2.3	93.2	283.7	63.8	258.5	11.8
	P7	2.3	61.4	254.3	34.1	128.3	5.8
	P13	2.0	50.1	46.8	42.6	113.8	6.3
	P15	2.0	71.3	264.8	55.8	110.9	4.8
	P16	2.2	57.6	188.2	63.7	143.3	7.0
Thang Long area	P17	1.6	65.8	296.1	50.2	125.0	5.3
	P8	2.3	84.8	227.7	29.1	104.5	3.5
	P9	2.5	84.3	321.9	60.3	125.8	9.3
	P10	1.7	53.7	264.0	45.4	122.5	7.3
	P11	3.1	81.3	334.7	55.9	242.9	7.6
	P12	3.3	79.6	260.0	52.8	93.4	11.4
	P14	1.8	49.2	79.9	38.5	110.2	11.3
Max		3.5	93.2	369.0	151.3	268.3	12.7
Min		1.3	45.1	46.8	29.1	93.4	2.3
Mean		2.3	68.0	237.6	53.2	147.6	7.7
Coefficient of variation		0.25	0.21	0.40	0.49	0.37	0.40
Permissible level for agricultural soils in Vietnam		2	70	200	50	200	12
Number of sampling points exceeded the permissible level		12	8	13	10	4	1

Table 2. Summary of the one way repeated measures ANOVA for the effect of sampling points on trace metal concentrations

Source of variance	Sum of squares	Df	Mean square	F	p value
Trace metals	743,991	5	148,798		
Sampling points	67,135	17	3,949	1.99	0.02
Trace metals \times sampling points	168,707	85	1,985		
Total	979,833	107			

were high with peaks (peak concentrations were higher than $300 \mu\text{g.g}^{-1}$ and $240 \mu\text{g.g}^{-1}$ for the respective trace metals) at the distance around 12 km and 24 km, respectively.

Table 1 shows the trace metal concentrations at respective points and its belonging area, descriptive statistics for the concentrations and some other items.

According to Table 1, the concentrations of Cd, Pb, Cr, Cu, Zn and As ($\mu\text{g.g}^{-1}$) ranged from 1.3-3.5, 45.1-93.2, 46.8-369.0, 29.1-151.3, 93.4-268.3, and 2.3-12.7, respectively. According to the means, the magnitude of the concentrations was in the order of $\text{Cr} > \text{Zn} > \text{Pb} > \text{Cu} > \text{Cd} > \text{As}$.

In Table 1, the permissible level for agricultural soils, based on Vietnamese standard (MONRE, 2008), was shown. The number of the sampling points that the permissible level was shown in Table 1 for each trace

metal. In Table 1, every kind of trace metal exceeded the permissible level. In more detail, arsenic (As) concentration exceeded the level at one point, and Cd, Cr and Cu concentrations exceeded at 10 to 13 points out of 18 points. The maximum exceeding rate in the concentrations in all cases was a little higher than 3 times the permissible level occurred in Cu concentration.

Table 2 shows the summary of the one way repeated measures ANOVA for the effect of sampling points (sampling locations) on the trace metal concentrations. The p value in Table 2 ($p < 0.05$) shows that the effect of sampling locations was significant, i.e. the trace metal concentrations were different between the sampling locations.

According to Table 1, the concentrations were high in the points 1 and 6, more precisely, Cd, Cr, and Zn concentrations was the highest in P1, and Pb the

highest, and Cu, Zn and As the 2nd highest in P6 in the concentrations. While, the concentrations were generally low in P18. More precisely, Cd and Pb was the lowest, and Cr, Cu, Zn and As was the 3rd lowest in the concentrations in P18.

The Smirnov-Grubbs' outlier test was performed separately. As a result, the extreme value (extremely high value) was detected in Zn concentration at P1, P5, P6 and P11 and in Cu concentration at P4. The extreme value was not detected in Cd, Pb, Cr and As concentrations at any point.

Table 3 shows the results of Welch's t-test for the concentrations between the two industrial park areas. According to Table 3, p-values ($p > 0.05$) did not show significant differences between the two industrial park areas for the respective concentrations. This result shows that the concentrations were not different between the two park areas.

Table 3. Results of Welch's t-test for Cd, Pb, Cr, Cu, Zn and As concentrations between the two industrial parks

Trace metals	Industrial Park	t	d.f.	p value
Cd	Pho Noi	0.52	8.3	0.61
	Thang Long			
Pb	Pho Noi	0.56	8.74	0.59
	Thang Long			
Cr	Pho Noi	0.05	11.21	0.96
	Thang Long			
Cu	Pho Noi	1.06	13.74	0.31
	Thang Long			
Zn	Pho Noi	0.91	10.93	0.38
	Thang Long			
As	Pho Noi	0.51	11.56	0.62
	Thang Long			

Table 4 shows the correlation coefficients between the concentrations of Cd, Pb, Cr, Cu, Zn and As. According to Table 4, significant correlations were found between Pb, Cd, and Cr at 1% significant level, and between Cr and Zn, and between Cu and As at 5% significant level, respectively.

Table 4. Correlation coefficients between the trace metal concentrations of Cd, Pb, Cr, Cu, Zn and As.

	Pb	Cr	Cu	Zn	As
Cd	0.69**	0.55*	0.16	0.40	0.15
Pb		0.70**	0.29	0.47	0.09
Cr			0.19	0.51*	-0.14
Cu				0.01	0.51*
Zn					-0.09

Note: * and **: significant at 0.05 and 0.01 levels.

DISCUSSION

Source of the trace metals

Most of the trace metal concentrations were higher

in the central part of the industrial park areas than in the irrigation water intake Table 1 (Fig. 2). The high concentrations were observed in particular in the points 1, 2, 4, 9, 11, 12 in the central part Table 1. These points were located near factories (Fig. 1), therefore, the high concentrations were thought to be caused by the entry of the factory-discharged wastewater into the paddy field. As mentioned previously, the district is a flood-prone district, and all of waste water from the industrial zone were directly discharged to the irrigation system. Therefore, the entry of heavy metal in soils in these points was probably caused by the flooding of wastewater and irrigation water mixture and long-term application this mixture as the irrigation water source. The concentration was low, where the points were away from factories (Fig. 1), indicating that the soil contamination was restricted to near factory areas.

The extremely high Zn concentration was observed at points 1, 5, 6 and 11 according to the outlier test, indicating that the factories discharging Zn-containing wastewater that contains Zn were located near around the points. The extremely high Cu concentration was observed at point 4 by the test, indicating that the factories discharging Cu-containing wastewater were located near around the point.

According to the correlation coefficients Table 4, there are three groups of the trace metals, i.e. group of Cd, Pb and Cr, group of Cr and Zn, and group of Cu and As, based on the significant correlations. The classification of the groups shows that there were several groups of wastewater containing trace metals. In particular, the high concentrations of Cr and Zn with the significant correlation show that the trace metals may be supplied from the same kind of wastewater. Cr and Zn are considered to be discharged from metal plating processes in a factory. The factory perhaps belongs to the category of mechanical factory mentioned in study area, and which is present in both industrial parks.

Difference in the trace metal concentrations between the two industrial park areas

The trace metal concentrations were in the order of $Cr > Zn > Pb > Cu > As > Cd$ for the respective industrial park areas, based on the average concentrations of the respective areas (that was separately calculated from Table 2). Further, no significant differences were observed in the respective concentrations between the two industrial park areas Table 3.

On these characteristics, factory composition and foundation year probably did not affect. Here, the absence of the effect of factory composition may be

caused by that the concentrations become similar with each other after the mixing of wastewaters in irrigation channels in the respective industrial park areas. The absence of the effect of foundation year (the passage of time), where there are 6 years difference in foundation, may be caused by the absorption of trace metals by crops and/or loss of trace metals by soil washing due to the flooding. These could decrease the concentrations to be similar between the two areas. Usually, the soil trace metal concentrations are considered to increase with the increased passage of time, which was mentioned previously as the long-term effect of irrigation on the trace metal contamination.

Usability of the soils for agricultural purposes

The Cd, Cu, Pb, Zn and As concentrations exceeded the permissible levels for agricultural soils of Vietnam at 1 to 13 points out of 18 points Table 1. Even though the concentrations did not exceed the levels, many concentrations were close to the levels based on Table 1. Though there is no permissible level for soil Cr concentration of Vietnam, Cr concentrations exceeded $200 \mu\text{g.g}^{-1}$ that was the highest permissible range determined by (SSSA. Methods of Soil Analysis, 1996; MONRE, 2008; Kabata-Pendias, 2011) at many points. The soils in this district, contaminated by all trace metals, are therefore inadequate for agricultural soils, and some measures such as soil decontamination are necessary.

CONCLUSIONS

Wastewater The following conclusions were drawn from the study.

The magnitude of the trace metal concentrations of the soils was in the order of $\text{Cr} > \text{Zn} > \text{Pb} > \text{Cu} > \text{As} > \text{Cd}$ for the study district. The concentrations were high in the center of the industrial park areas, where there were many factories, compared to those in the irrigation water intake, indicating that the trace metals were supplied from factories of the industrial parks with the wastewater. Even inside the district, the concentrations were low where the points were away from factories, indicating that the contamination was restricted to near factory areas.

No significant differences were observed between the two industrial park areas in the concentrations, despite there were differences in foundation year and factory composition between the two industrial park areas.

The trace metal concentrations of the soils exceeded or close to the permissible level for agricultural purposes, thus the soils were not adequate for the

usage of agriculture and some remediation measures are necessary.

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