DISTRIBUTION OF HEAVY METALS IN THE TOPSOIL OF AGRICULTURAL LAND IN NAM DINH PROVINCE, VIETNAM

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Abstract. Surface soil samples were collected from different land use types of the agricultural land in Nam Dinh province, Vietnam to determine the level of heavy metal contamination and identifying potential sources. The farming areas of rice and cereal show similar heavy metal contents, however, the index shows that the content of heavy metals in the aquacultural area is lower compared to the other types. The mean enrichment factor (EF) values of Cr, Cu, Pb, and Zn are less than 1.5, suggesting that these are not a major concern in the research area; whereas, the mean EF values for Cd is higher than 2 and As varies from 5-20 suggest that the pollution of these heavy metals is present in agricultural soil. The data analysis indicates that Cr mainly originates from a natural source; Cd and As have a significant anthropogenic input; Cd, Pb and Zn have a mixed source.
Keywords: *different land use, paddy, cereal, aquaculture, environment*

Introduction

Soil is widely recognized as a pool of nutrients and pollutants, and plays a critical role in socio-ecological stability and national safety (Wu et al., 2018). Human-induced increase of soil contamination with heavy metal input is noteworthy, including atmospheric deposition, irrigation, application of sewage sludge, organic manures, fertilizers, and other soil amendments (Cheng, 2003; Vodyanitskii, 2013; Hou et al., 2014). When heavy metals enter the agricultural soil, they not only degrade environmental quality but they also influence the health of people and other organisms through the food chain (Nabulo et al., 2010). Therefore, it is of great importance to study the characteristics and sources of heavy metal contamination in agricultural soil to protect the environment and human health (Huang et al., 2018; Li et al., 2018).

Agriculture plays a prominent role in Nam Dinh province, with approximately 67% of the land used for agricultural production. It is usually used for 2 paddy rice crops per year equipped with a developed irrigation system (in total 3% of the province area are covered by rivers and channels (Dao et al., 2005). Traditionally, the biggest industry is textile and garment which has been developed since 1889 with French support. The craft production in Nam Dinh, especially bronze and silver casting, has a long tradition. For example, Tong Xa village has been well known for bronze and iron casting in the Red River delta since 1200, Xuan Tien commune with bronze casting and mechanical engineering since 1535, and Van Chang village with iron, steel and aluminum foundry since 1868. According to the data provided by provincial government, there are a total of 71 villages that are specialized on handicraft (e.g. metalworking, food processing, salt production) up to 2018 in Nam Dinh province (Joern et al., 2013). Such production places are most often based on family enterprises located all over the village; therefore, it can be stated that living and working place are rarely distinguished (Dao and Nguyen, 2000). However, all untreated wastewater from industrial and living usages discharges directly open channels or infiltrate into the soil. Previous research shows that water channels in handicraft villages are loaded with heavy metals (Zn, Pb, Cu, Ni, Cd, Cr, and Fe) and cyanides, exceeding the limits by up to 50 times (Le et al., 2003). In recent years, with the increase in population, the industrial sector has achieved prominence. This has resulted in environmental pollution caused by manufacturing activities in industrial zones. Furthermore, the Red and Day rivers receive pollutants from upstream before running across the province. Agricultural activities in the province utilize approximately 300 tons of insecticides per year (Dao et al., 2005), which causes the water to be polluted, that is then returned to the soil via the irrigation network.

Thus far, there has been very little published information on their contaminant level and sources in Nam Dinh province. To better investigate local soil quality, we have used a combined method of enrichment factor (EF) and multivariate statistical analyses with the objectives of analyzing pollution level, characteristics of spatial distribution and identifying potential sources of heavy metals in agricultural soil.

Materials and methods

Study area

Nam Dinh (19°52’ - 20°30’N, 105°55’ - 106°35’E) is a coastal province located to the south of Red river delta with an area of 1,652.6 km² and population of 1,825,771 people; population density is 1,196 people per km². The administrative unit of this province is composed of 9 districts and one city. Nam Dinh is a tropical area experiencing monsoon with hot and humid rain. The average annual temperature is ca. 23 – 24 °C, and the average annual rainfall is ca. 1,700 - 1,800 mm. On average, up to 250 days a year are sunny, with total sunshine hours from 1650 to 1700 h. The province is affected by storms or tropical depressions 4 to 6 times per year.

The river and estuary systems of the Red river and its tributaries (Dao, Ninh Co, Day rivers) have greatly impacted morphological and hydrological characteristics of the region. The terrain is quite flat, gradually dipping to the sea in Northwest - Southeast direction. The formation of this region was historically associated with and the evolution of the Red River Delta. It can be divided into two zones: (1) the low-lying plains with elevations of 0.2 to 3 m above sea level with some exceptions in the northwest (7-100 m above sea level) (Vu Ban, Y Yen, Nam Truc, Truc Ninh and Xuan Truong districts). This region has a high level of agriculture, textile and manufacturing industries; (2) the lowland coastal region including Giao Thuy, Hai Hau and Nghia Hung districts. Running from north to south, Dao river seperates the two regions. In the northern region of the province (My Loc, Y Yen, Vu Ban districts and Nam Dinh city), the water is pumped directly from stagnant canals which is not well circulated and used for irrigation purposes. In the southern region (Nam Truc, Truc Ninh, Xuan Truong, Hai Hau, Giao Thuy and Nghia Hung districts), irrigation water is taken from rivers, which is well circulated because water from upstream flows into the sea.

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Samples and methods

Samples

A total of 38 surface agricultural soil samples from different land use types were collected in May, 2018 by grid method (using 10 × 10 km grid). They included 20 samples from paddy field, 12 samples from cereals soil, and 6 samples from aquaculture farm (*Fig. 1* and *Table 1*). The samples were taken at depth of 0-20 cm with volume of 0.5 kg soil by using hand steel drill. Per site, two samples were taken. Samples were packed in plastic bags to send to the laboratory. All samples were dried at 40 °C, then desegregated prior to analysis.

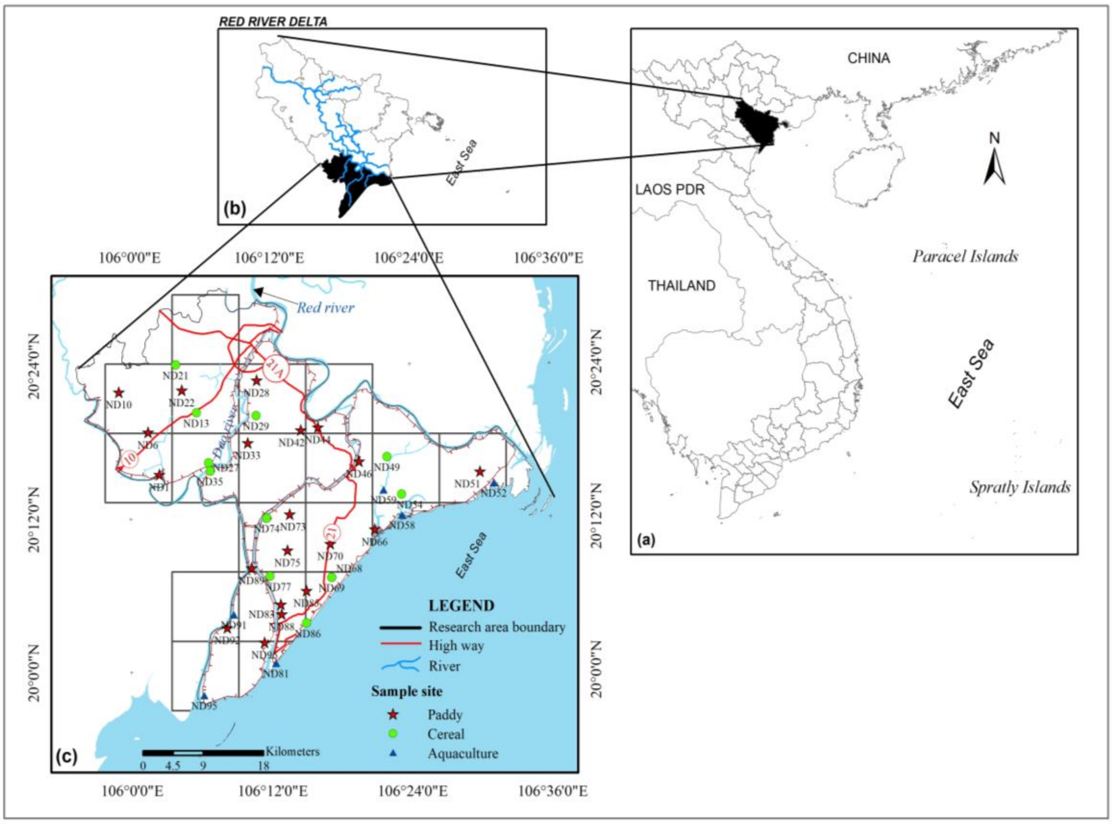

Figure 1. *Map of the study area (a), Red river delta (b), with the sampling sites detailed in (c)*

Methods

For heavy metal analysis, ~ 0.1 g dry soil was weighed into Teflon beakers, in which a mixture of concentrated 2 ml HF – 6 ml HCl – 2 ml HNO_3 were added (Elsorogy et al., 2016), a Teflon watch cover was put in place, and the sample was left at room temperature overnight. On the following day, the sample was digested using a scientific microwave system (Mars 6, USA) with the following heating program: the temperature rises from room temperature to 180 °C in 15 min, keep at 180 °C for decomposition for 30 min, then let solutions cool down to room temperature again. The solution is transferred to the plastic volumetric tube and filled up to the mark by using deionized water. Heavy metals (As, Cd, Cr, Cu, Pb, and Zn) concentration were determined by inductive couple plasma - mass spectrometry (ICP-MS, Agilent 7900). European

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commission community bureau of reference material Estuarine sediment sample identification No0087 was included for quality control. The analytical precision and error of the analysis are within 10%.

Table 1. *The global positioning system coordinates of the sampling points*

CODE	Yho	Ymi	Yse	Ydec	Xho	Xmi	Xse	Xdec	Land use type
ND1	20	15	30	20.25833	106	2	27	106.04083	Paddy
ND6	20	18	39	20.31083	106	1	26	106.02389	Paddy
ND10	20	21	57	20.36583	105	59	1	105.98361	Paddy
ND13	20	20	18	20.3383	106	5	40	106.0944	Cereal
ND21	20	24	3	20.4008	106	3	55	106.0653	Cereal
ND22	20	22	5	20.36806	106	4	22	106.07278	Paddy
ND27	20	16	19	20.2719	106	6	37	106.1103	Cereal
ND28	20	22	49	20.38028	106	10	51	106.18083	Paddy
ND29	20	20	3	20.3342	106	10	48	106.1800	Cereal
ND33	20	17	56	20.29889	106	10	4	106.16778	Paddy
ND35	20	15	49	20.2636	106	6	53	106.1147	Cereal
ND42	20	18	54	20.315	106	14	37	106.24361	Paddy
ND44	20	19	7	20.31861	106	15	66	106.26833	Paddy
ND46	20	16	30	20.275	106	19	30	106.325	Paddy
ND49	20	16	46	20.2794	106	22	1	106.3669	Cereal
ND51	20	15	33	20.25917	106	30	0	106.5	Paddy
ND52	20	14	39	20.2442	106	31	11	106.5197	Aquaculture
ND54	20	13	50	20.2306	106	23	15	106.3875	Cereal
ND58	20	12	11	20.2031	106	23	17	106.3881	Aquaculture
ND59	20	14	10	20.2361	106	21	42	106.3617	Aquaculture
ND66	20	11	6	20.185	106	20	55	106.34861	Paddy
ND68	20	7	21	20.1225	106	17	12	106.2867	Cereal
ND69	20	7	21	20.1225	106	17	12	106.2867	Cereal
ND70	20	10	3	20.1675	106	17	1	106.28361	Paddy
ND73	20	12	12	20.20333	106	13	38	106.22722	Paddy
ND74	20	12	2	20.2006	106	11	39	106.1942	Cereal
ND75	20	9	30	20.15833	106	13	25	106.22361	Paddy
ND77	20	7	29	20.1247	106	11	55	106.1986	Cereal
ND81	20	0	40	20.0111	106	12	23	106.2064	Aquaculture
ND83	20	5	17	20.08806	106	12	49	106.21361	Paddy
ND85	20	6	21	20.10583	106	15	2	106.25056	Paddy
ND86	20	3	48	20.0633	106	14	60	106.2500	Cereal
ND88	20	4	31	20.07528	106	12	52	106.21444	Paddy
ND89	20	8	9	20.13583	106	10	20	106.17222	Paddy
ND91	20	4	29	20.0747	106	8	46	106.1461	Cereal
ND92	20	3	29	20.05806	106	8	12	106.13667	Paddy
ND95	19	57	0	19.9500	106	6	24	106.1067	Aquaculture
ND96	20	2	19	20.03861	106	11	24	106.19	Paddy

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Total organic carbon was determined by titration method using Mohr salt $(NH_4)_2Fe(SO_4)_2.6H_2O$ after digestion of the sample by mixture of $K_2Cr_2O_7$-H_2SO_4, which followed the method of ISO 14235:1998. Grain-size distribution of desalted sediments was determined by wet sieving of sand and gravel and by the pipette technique for silt and clay fractions according to Vietnam Standards: Soil quality – Method for determination of particle size distribution (TCVN 8567:2010).

Enrichment factor (EF) is commonly used to discern metal contamination. EF is calculated as follows (*Eq. 1;* Salomons and Forstner, 1984; Sinex and Wright, 1988):

$$A = \frac{\left(\frac{Me}{Al}\right)_{Sample}}{\left(\frac{Me}{Al}\right)_{Background}} \quad \text{(Eq.1)}$$

where $(Me/Al)_{sample}$ is the metal to aluminum (Al) ratio in the samples; $(Me/Al)_{background}$ is the metal to Al ratio in background. Because Al is one of the most abundant elements on the earth and its concentration is generally not influenced by anthropogenic sources, it is commonly used for normalization purpose (Schropp and Windom, 1988). There is little information about heavy metal background values in the Nam Dinh province. Therefore, we adopted the values of upper continental crust (Taylor and McLennan, 1995) as the background values, which are (in $mg.kg^{-1}$): 80,400 for Al; 0.098 for Cd; 25 for Cu; 20 for Pb, and 71 for Zn. For As and Cr, the updated values of 5.7 $mg.kg^{-1}$ and 73 $mg.kg^{1}$, respectively were used (Hu and Gao, 2008). This approach has been widely used to determine the source heavy metal pollution in soil environment (José et al., 2017; Dragović and Mihailović, 2009; Loska et al., 2004).

Multivariate statistical methods such as cluster analysis (CA), principal component analysis (PCA) provide a classification tool based on the relationship between different metals in different sampling points, which can be used to distinguish between the natural and anthropogenic sources of heavy metal (Wang et al., 2019b; Han et al., 2006; Wu and Zhang, 2010; Nguyen et al., 2016a).

Cluster analysis was performed on the heavy metal concentrations and soil properties using SPSS 20.0 software (IBM, USA) using nearest neighbor linkage method based on correlation coefficients. The distance cluster represents the degree of association between elements, the smaller the value on the distance cluster, the more significant the association (Luo et al., 2007).

Principal component analysis using SPSS 20.0 software (IBM, USA) was used in the data set to determine the relationships and common origins between metals. PCA was performed with Varimax rotation with Kaiser Normalization, which facilitated the interpretation of output by minimizing the number of variables that loaded high loads on each component. In this study, all principal factors extracted from the variables were retained with eigenvalues > 1.0, as suggested by the Kaiser criterion (Kaiser, 1960). According to the results obtained from PCA, possible sources of chemical elements were interpreted (Lu et al., 2012).

In this paper, Inverse Distance Weighted which one of tool on ArcGIS 10.5 software is used for interpolating map of heavy metal content. The reclassify the results following the method of equal values to show the distribution of each heavy metal.

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Results and discussion

Soil properties in different land use types

Soil properties that could influence the accumulation ability of heavy metals include total organic carbon (TOC), pH, soil grain size, and concentration of aluminum (Al). The variation of these properties in the 38 samples is presented in *Table 2*. From *Table 2* we can recognize that TOC concentration varied among the land use types in Nam Dinh province. Highest TOC content occurred in the paddy soil (TOC_{mean} = 2.99%), which might be related to the tradition of applying organic fertilizers in rice production in this area (Nguyen et al., 2018). The second highest TOC content occurred in the cereals soil (TOC_{mean} = 1.09%), and the least in the aquaculture (TOC_{mean} = 0.58%).

The mean pH value in the studied area was 6.08. The pH values of the sampling sites ranged from 3.87 to 8.05, from extremely acidic to moderately alkaline. According to land use type, the mean pH of paddy soil was 5.6 ± 1.06, close to moderately acidic; the mean pH of cereal soil was 6.8 ± 1.08, near neutral; the mean pH of aquaculture soil was 7.82 ± 0.15, close to slightly alkaline.

Soil grain size varies in each land use type, with sand always being dominant and the mean clay percentage in different types of land use decreases in the order of paddy soil > cereal soil > aquaculture soil in the study area.

Table 2. *Soil properties of samples from different land use types*

Land use type	Parameter	pH	TOC (%)	Grain size			Al (mg.kg^{-1})
				Sand (%)	Silt (%)	Clay (%)	
Paddy n = 20	Mean	5.6	2.99	34.76	36.6	28.64	46524.48
	Max	8.05	7.75	92.78	57.8	48.34	118010.8
	Min	3.87	0.22	6.16	2.52	4.12	2463
	SD	1.06	1.37	23.48	13.81	11.34	25161.74
Cereal n = 12	Mean	6.8	1.09	66.78	18.23	14.98	34433.53
	Max	7.83	3.08	98.18	41.5	35.98	77992.67
	Min	4.04	0.12	23.86	0	1.82	5710.1
	SD	1.08	0.71	25.59	14.43	11.64	22384.12
Aquaculture n = 6	Mean	7.82	0.58	72.32	14.19	13.49	49716.46
	Max	8.05	1	93.52	38	22.26	85773.7
	Min	7.59	0.06	41.78	0	6.48	12825
	SD	0.15	0.39	18.87	13.12	6.32	28360.69
All samples n = 38	Mean	6.08	2.34	45.45	30.38	24.17	44181.78
	Max	8.05	7.75	98.18	57.8	48.34	118010.8
	Min	3.87	0.06	6.16	0	1.82	2463
	SD	1.21	1.53	28.18	16.54	12.95	25149.49

Heavy metal concentration in agricultural soil in Nam Dinh province

Heavy metal concentrations in agricultural soil in Nam Dinh province are summarized in *Table 3* and *Figures 2-9*. The mean concentrations of heavy metals in agricultural soil are in decreasing order of Zn > Cr > Cu > Pb > As > Cd. A comparison of the concentrations of heavy metals in the studied soil with the documented data from

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agricultural soil areas in Vietnam show that the contents of As, Cr and Zn are close to previously reported result in the Ba Lat estuary of the Red River (located in Giao Thuy and Xuan Truong districts of Nam Dinh province), while the contents of Cu and Pb are lower 2 to 3 times. In comparison with heavy metal concentration in agricultural soil of Duy Tien district, Ha Nam province, which is also located in Red River delta, we found that the contents of As and Pb in this study are higher 2 and 2.5 times, respectively, while the contents of Cu and Zn are lower. The concentration of As, Cd is higher 5.3 and 1.2 times, respectively while the concentration of Cr, Cu, Pb and Zn is lower in comparison to their counterparts in the upper continental crust.

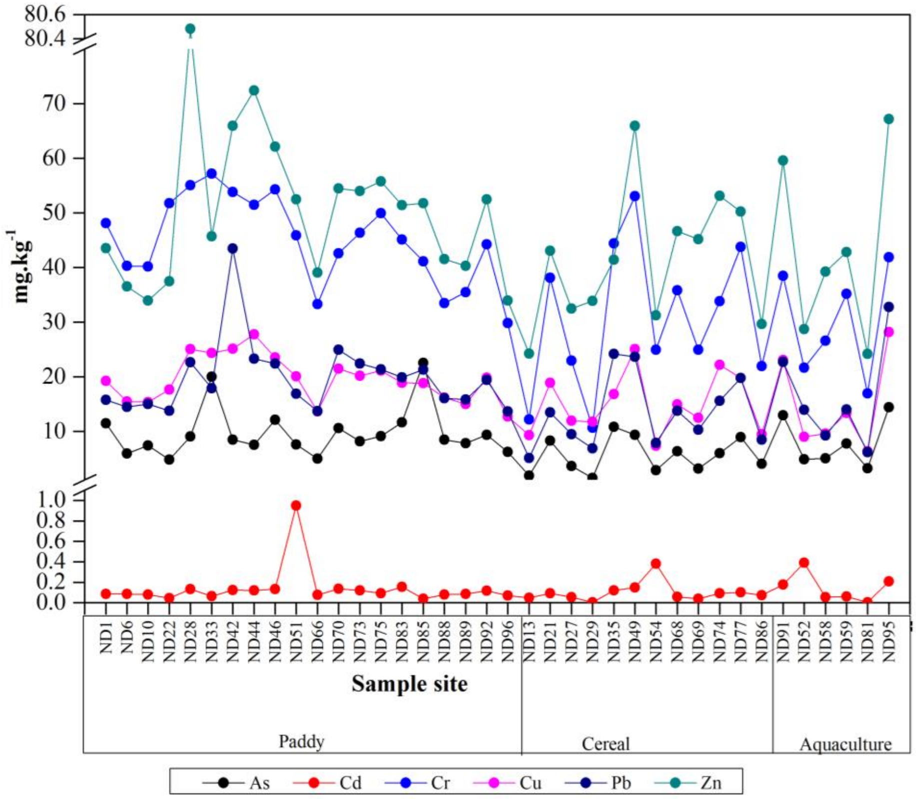

Figure 2. *Spatial variations of heavy metals of the agricultural soil in Nam Dinh province*

Concentrations of metals in soil from different land uses are also presented in *Table 3* and *Figure 3*. In general, paddy soil samples have the highest heavy metal concentration, which was followed by cereal soil samples and aquaculture soil samples. The concentrations of Cd do not exhibit a clear trend. The hotpots of higher Cd contents occurred in Giao Thuy district.

Assessment of heavy metal pollution

The enrichment factor (EF) values can give an insight into differentiating an anthropogenic source from a natural origin. Typically, an EF value of < 1.5 suggests a dominance of natural sources (Zhang and Liu, 2002). Further, EF values can also assist the determination of the degree of metal contamination. Five contamination categories are recognized on the basis of the enrichment factor (Sutherland, 2000; Loska and Wiechula, 2003) (*Table 4*).

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Table 3. *Heavy metal concentrations in the topsoil of the agricultural soil in Nam Dinh province, Vietnam*

	As	Cd	Cr	Cu	Pb	Zn	Mn	Al	Reference
	(mg.kg^{-1})						%		
Nam Dinh									This study
Mean±SD	7.99±4.36	0.12±0.16	37.82±12.33	16.96±5.99	16.78±7.53	45.74±13.49	0.06±0.03	6.01±2.79	
Min-Max	1.47-22.56	0.01-0.95	10.68-57.20	6.37-28.19	5.13-43.51	24.17-80.48	0.01-0.17	1.60-11.80	
Ba Lat									Nguyen et al., 2016b
Mean	14.5				43.4	59.5			
Min-Max	6.9-31.0	0.05-0.43	26.9-63.1	14.9-67.2	24.2-78.3	32.1-92.4			
Duy Tien, Ha Nam									Phan and Tran, 2016
Mean	3.27	0.52		39.48	8.52	93.06			
Min-Max	2.56-5.15	0.28-0.86		27.61-55.28	8.11-8.61	65.81-123.51			
Upper continental crust (UCC)	1.5	0.098	85	25	20	71			Taylor and McLennan, 1995

Table 4. *Contamination categories based on EF values*

EF < 2	Deficiency to minimal enrichment
EF = 2-5	Moderate enrichment
EF = 5-20	Significant enrichment
EF = 20-40	Very high enrichment
EF > 40	Extremely high enrichment

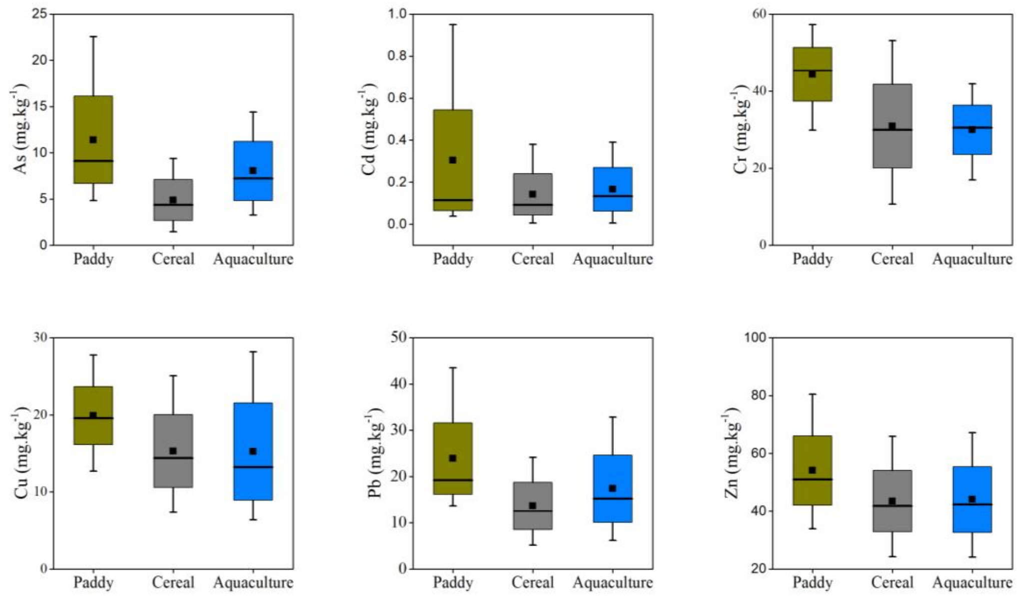

Figure 3. *Box plot of the heavy metal concentrations in soil samples of the three land use types. The black solid line inside the box is the median value, the black rhombus is the mean value, and the black vertical line is individual samples*

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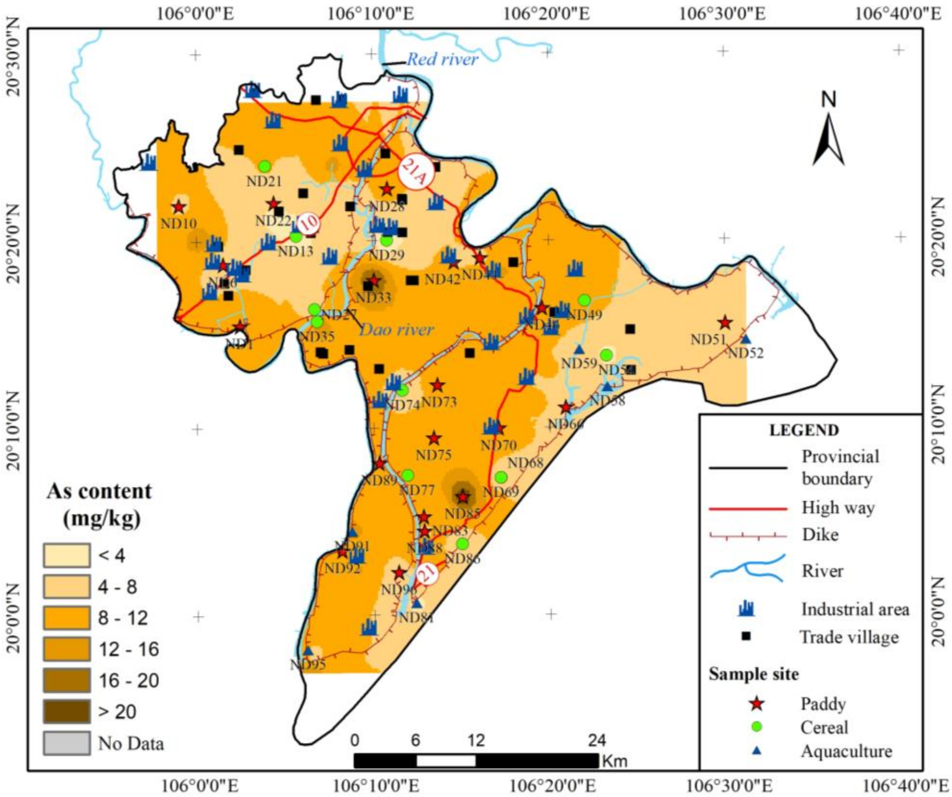

Figure 4. Distribution of As in the topsoil of the agricultural soil in Nam Dinh province

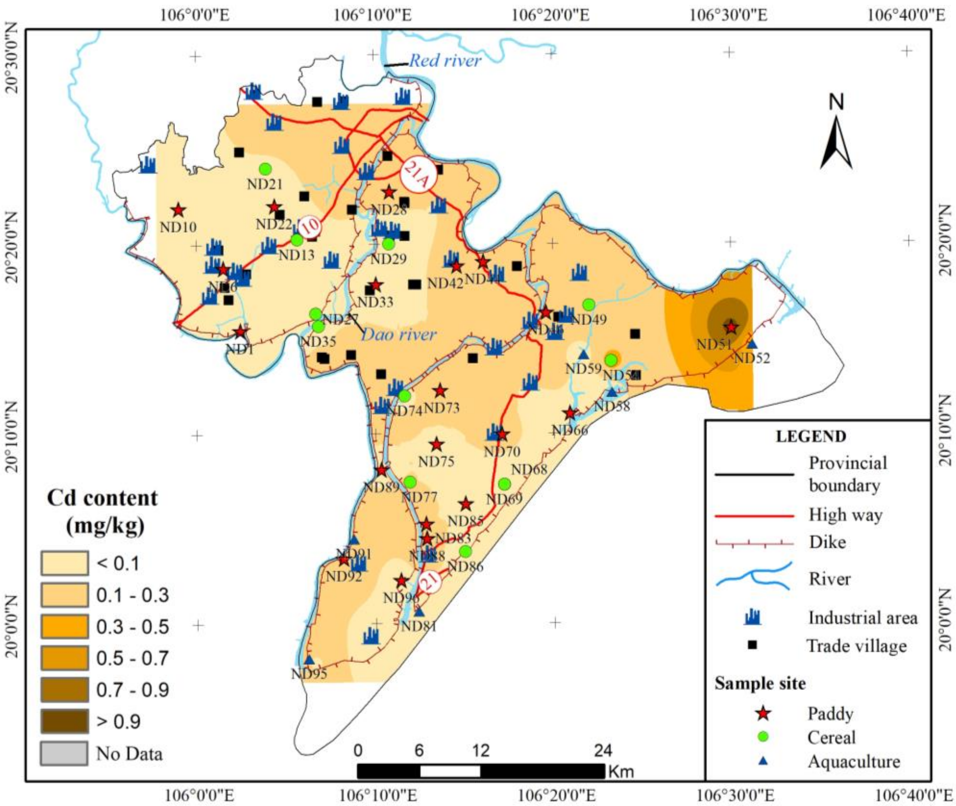

Figure 5. Distribution of Cd in the topsoil of the agricultural soil in Nam Dinh province

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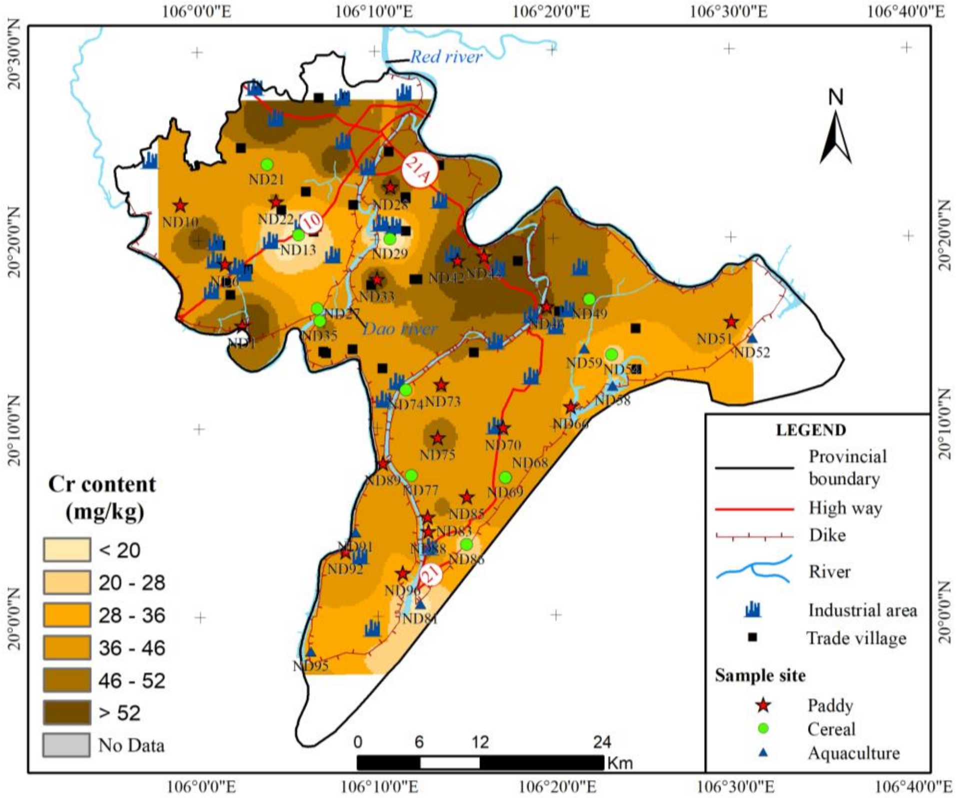

Figure 6. *Distribution of Cr in the topsoil of the agricultural soil in Nam Dinh province*

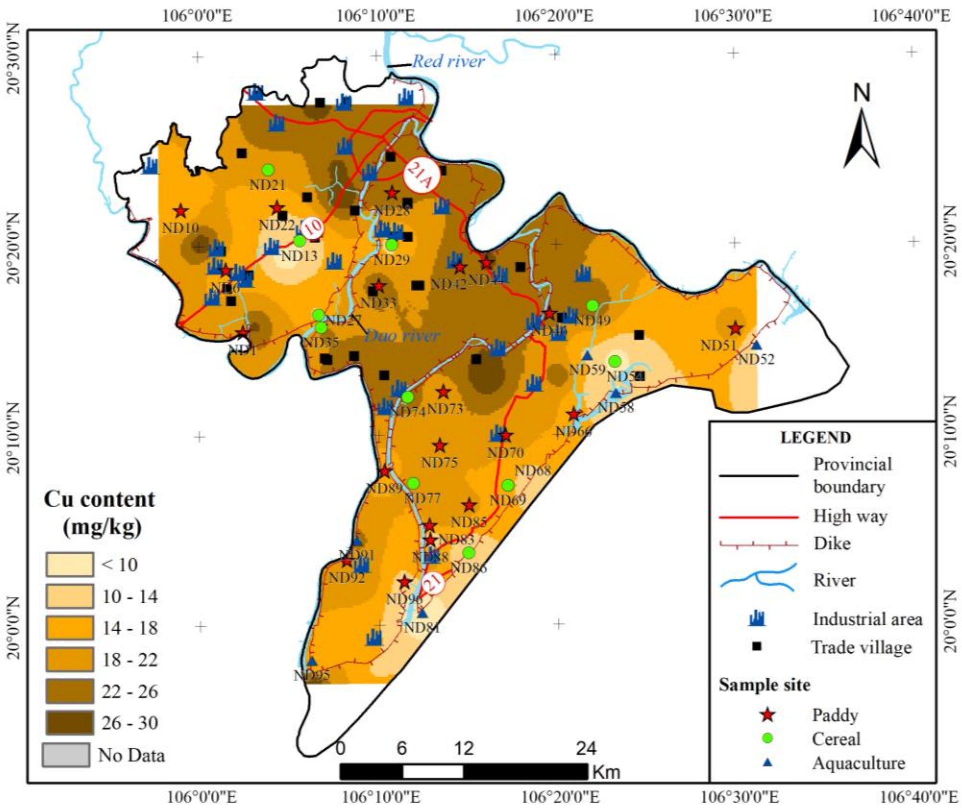

Figure 7. *Distribution of Cu in the topsoil of the agricultural soil in Nam Dinh province*

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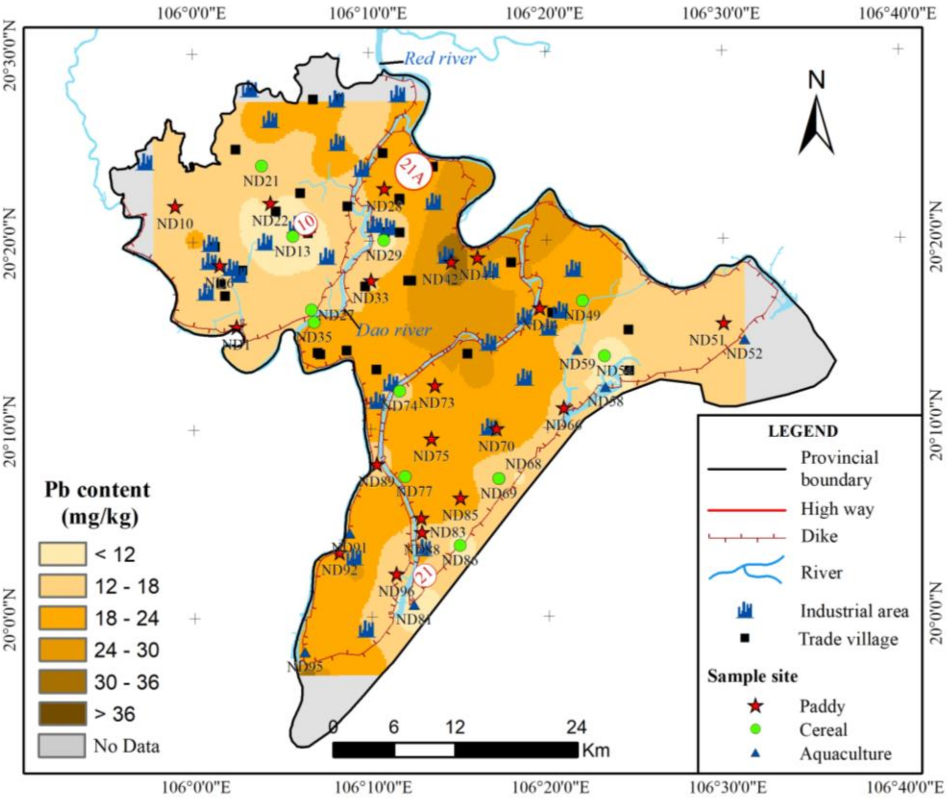

Figure 8. *Distribution of Pb in the topsoil of the agricultural soil in Nam Dinh province*

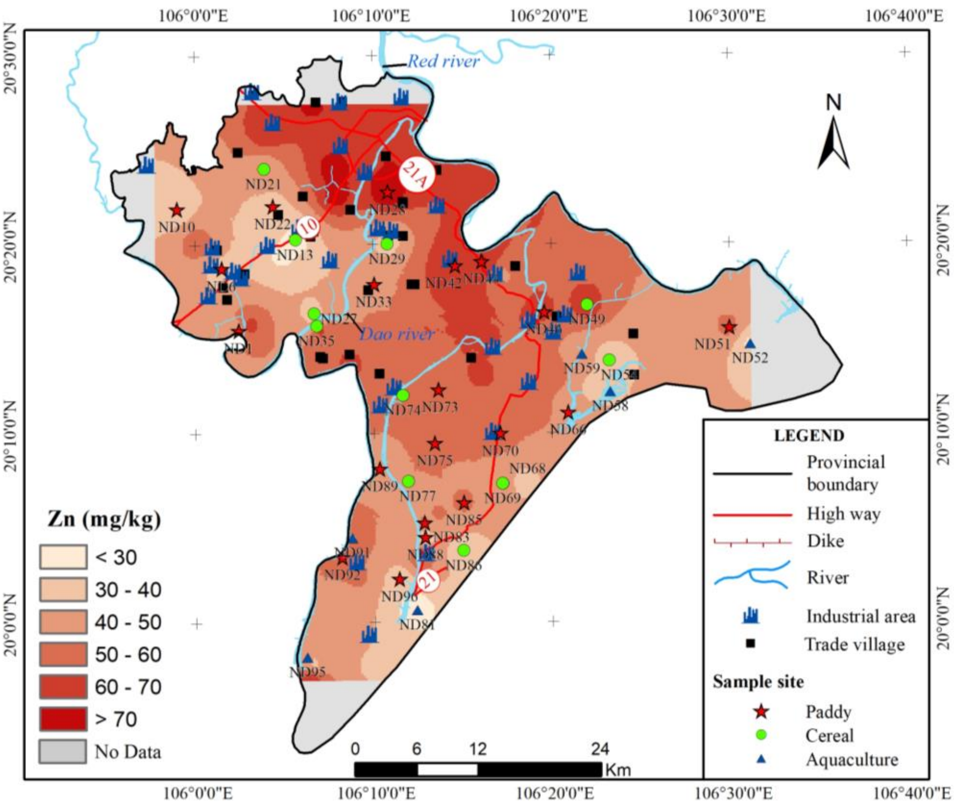

Figure 9. *Distribution of Zn in the topsoil of the agricultural soil in Nam Dinh province*

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The enrichment factors in agricultural soils in Nam Dinh province are shown in *Figure 10* and *Table* 5. It is clear that Cr, Cu, Pb, and Zn have a mean EF less than 1.5, confirming their mainly natural sources except some sites have EF values higher than 1.5 (e.g. ND29, ND35, ND73, ND96). On the other hand, the mean EF values of As and Cd are higher than 2, indicating existence of heavy metal contamination in agricultural soil of Nam Dinh province (Han et al., 2006). In this study, the mean EF values were ranked in the order of As > Cd > Pb > Cu > Zn > Cr. The element Cd has mean EF value between 2 and 5, which was classified as moderately contaminated. The mean EF values of As lie between 5 and 20, which means a significant contamination in this study area.

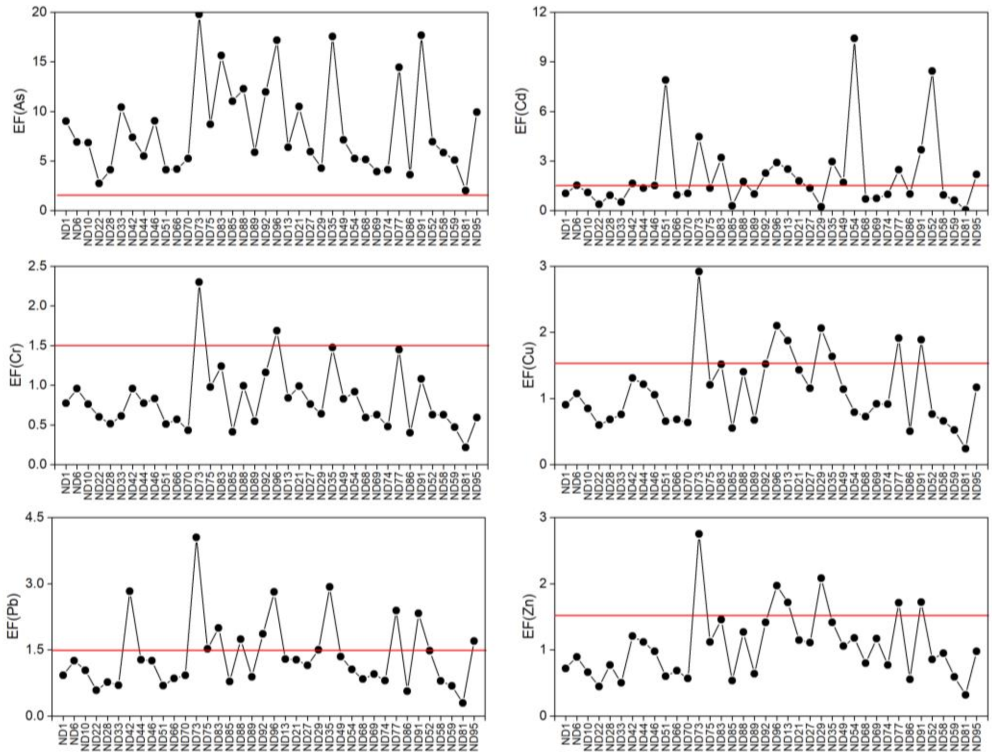

Figure 10. *Spatial variations of EF values of the agricultural soil in Nam Dinh province*

According to land use type and spatial distribution, the smallest mean EF values occurred in aquaculture soil samples, lower 1.4 to 2 times than its in paddy and cereal soil. There is no significant difference in the degree of metal contamination between paddy soil and cereal soil samples. The EF values of As show pronounced higher values in Nghia Hung, Hai Hau, and Nam Truc districts, these sites are localed near industrial zone and traditional handicraft village (e.g. ND88 near to the Thinh Long industrial zone; ND91 and ND92 near to Quy Nhat industrial zone, ND33 near to Dong Quy metal smelting village). The EFs (Cd) show higher in Hai Hau, Nghia Hung and Giao Thuy districts (ND51, ND52, ND54, ND73, ND83, ND92, ND96).

Sources of heavy metal in agricultural soil

Correlation analysis is not only an effective approach to reveal the relationships between heavy metals and soil physicochemical properties, but also an operative way to understand the controlling factors of heavy metals as well as their possible sources

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(Chai et al., 2015). Correlation analysis reveals diverse relationships between particle size, TOC and pH of soil and heavy metal contents (*Table 6*).

Table 5. *Enrichment factor (EF) of heavy metals for agricultural soil in Nam Dinh province*

Land use type	Parameter	EF(As)	EF(Cd)	EF(Cr)	EF(Cu)	EF(Pb)	EF(Zn)
Paddy soil n = 20	Mean	8.89	1.86	0.88	1.12	1.44	1.02
	Max	19.77	7.90	2.30	2.92	4.05	2.75
	Min	2.74	0.28	0.41	0.55	0.58	0.45
	SD	4.65	1.75	0.46	0.59	0.90	0.57
Cereal soil n = 12	Mean	8.15	2.35	0.85	1.30	1.42	1.26
	Max	17.68	10.41	1.47	2.06	2.93	2.08
	Min	3.63	0.22	0.40	0.50	0.56	0.55
	SD	5.17	2.62	0.33	0.53	0.71	0.44
Aquaculture soil n = 6	Mean	5.96	2.45	0.51	0.67	0.99	0.74
	Max	9.93	8.44	0.63	1.17	1.70	0.98
	Min	2.03	0.05	0.22	0.24	0.29	0.32
	SD	2.87	3.44	0.17	0.34	0.58	0.28
All samples n = 38	Mean	8.09	2.03	0.82	1.09	1.34	1.04
	Max	19.77	10.41	2.30	2.92	4.05	2.75
	Min	2.03	0.05	0.22	0.22	0.29	0.32
	SD	4.62	2.24	0.41	0.57	0.80	0.52

Table 6. *Statistical results from principal component analysis (PCA)*

	As	Cd	Cr	Cu	Pb	Zn	Mn	Al	pH	TOC	Sand	Silt	Clay
As	1.00	0.02	**0.64**	**0.65**	**0.59**	**0.52**	-0.02	**0.41**	-0.26	**0.45**	-0.27	0.33	0.17
Cd		1.00	0.14	0.14	0.14	0.16	0.08	0.11	0.15	-0.01	0.25	-0.24	-0.24
Cr			1.00	**0.82**	**0.73**	**0.74**	-0.05	**0.40**	**-0.46**	**0.52**	-0.34	**0.35**	0.30
Cu				1.00	**0.83**	**0.91**	-0.18	**0.34**	**-0.48**	**0.58**	**-0.40**	**0.43**	**0.34**
Pb					1.00	**0.80**	-0.13	0.24	-0.24	**0.46**	**-0.42**	**0.45**	**0.36**
Zn						1.00	-0.01	0.37	-0.32	**0.54**	-0.33	0.35	0.28
Rotated loading matrix (VARIMAX Gamma = 1.000)													
	PC1	***PC2***	***PC3***										
Cu	**0.91**	0.16	-0.19										
Zn	**0.90**	0.12	-0.03										
Cr	**0.87**	0.10	-0.14										
Pb	**0.84**	0.24	0.00										
As	**0.75**	0.06	-0.07										
Al	**0.55**	-0.53	-0.13										
Sand	-0.27	**-0.94**	0.14										
Clay	0.20	**0.93**	-0.11										
Silt	0.31	**0.91**	-0.15										
Cd	0.27	-0.35	**0.28**										
pH	-0.33	-0.09	**0.86**										
Mn	0.06	-0.11	**0.80**										
TOC	**0.57**	0.17	-0.58										
Eigenvalue	*5.64*	*2.64*	*1.48*										
% total variance	*43.40*	*20.33*	*11.34*										
% cumulative	*43.40*	*63.74*	*75.08*										

Bold type indicates significance at $p < 0.05$

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Based on Pearson's correlation coefficients Cr, Cu, Pb, and Zn were found significantly positively correlated with each other ($P < 0.01$). A highly positive correlation ($P < 0.01$) was found between Cu and Zn ($r = 0.91$), Cu and Pb ($r = 0.83$), Cu and Cr ($r = 0.82$), Pb and Zn ($r = 0.80$), Cr and Pb ($r = 0.73$), Cr and Zn ($r = 0.74$), indicating their similar sources. Arsenic has a positive correlation ($P < 0.01$) with Cr, Cu, Pb, and Zn, but these correlation coefficients were relatively weak, i.e., As and Cr ($r = 0.64$), As and Cu ($r = 0.65$), As and Pb ($r = 0.59$), As and Zn ($r = 0.52$). Cadmium does not show correlations with any heavy metals in agricultural soil, suggesting Cd perhaps has different sources or geochemical behaviour.

Soil pH does not show correlations with As, Cd and Pb, however, it shows a negative correlation with Cr, Cu, and Zn (*Table 6*), indicating that neutral soil contains less heavy metals (Chai et al., 2015; Kua et al., 1983; Manta et al., 2002). TOC, Al and silt percentage show a weakly positive correlation with As, Cr, Cu, Pb, and Zn ($p < 0.01$), indicating that these heavy metals are controlled by the contents of organic carbon as well as proportions of finer grain size fractions. Since Cd is not correlated with TOC, Al, and grain size, there exits other factor influencing its contents, which most probably is anthropogenic input.

The results are illustrated in the dendrogram in *Figure 11*, two distinct clusters are identified. The first cluster includes Cu, Zn, Pb, Cr, As and TOC, while Cd cluster into the second group.

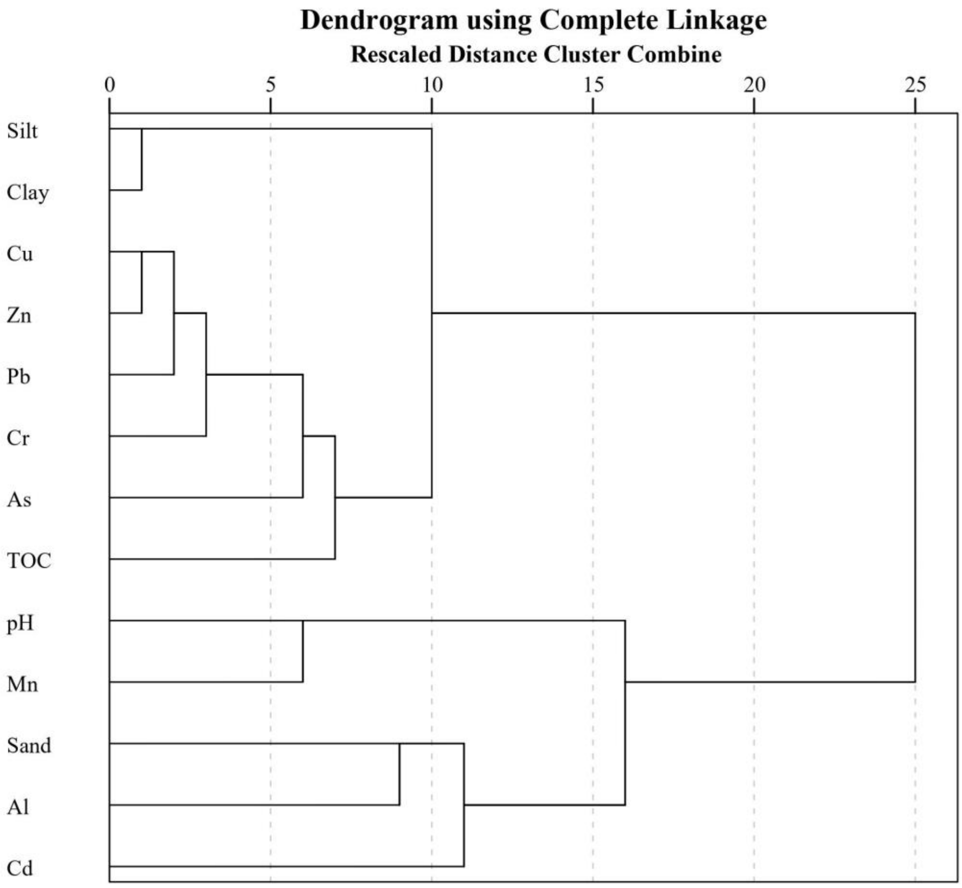

Figure 11. *Hierarchical cluster analysis among particle size and geochemical compositions in topsoil of agricultural soil in Nam Dinh province*

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The results of PCA are presented in *Table 6* and *Figure 12*. The extracted four components with eigen values > 1 explain 75.08% of total variance. The first principal component (PC1) accounts for 43.40% of total variance, showing high positive loadings of Cu (0.91), Zn (0.90), Cr (0.87), Pb (0.85), As (0.75), and medium loading of TOC (0.57) and Al (0.55). The second principal component (PC2) with a variance loading of 20.33% is dominated by the loading clay (0.94) and silt (0.91). The third principal component (PC3) is a less important component, accounting for 11.43 of the total variances, showing positive loading of Mn (0.80), pH (0.86) and Cd (0.28).

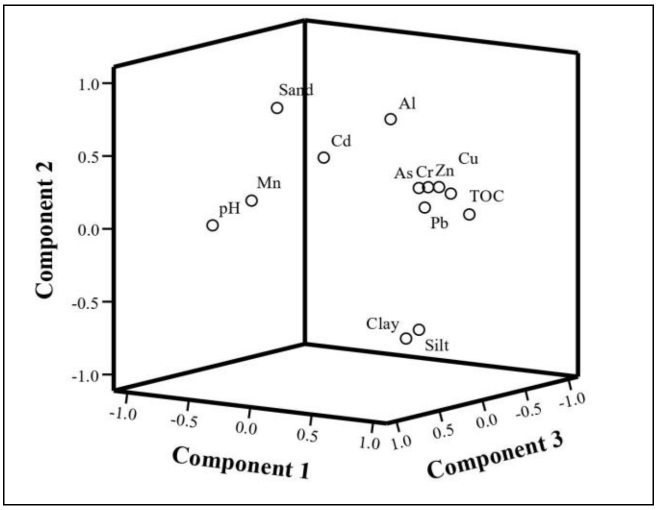

Figure 12. *Principal component analysis loading plots for rotated components of heavy metals and soil properties in Nam Dinh province*

According to the results from cluster and PCA analyses, two groups of elements can be identified: group 1 includes As, Cu, Zn, Pb and Cr, which show affinity with TOC and clay minerals; group 2 include Cd only.

Group 1 can be further subdivided into three sub-clusters. The first one sub-cluster includes Cr element. Since the concentration of Cr in the soil (10.68-57.20 mg/kg) was less than its concentration in UCC (85 mg/kg) and enrichment factor values of Cr were less than 1.5, it can state that Cr originated from natural sources. In addition, a previous study suggested that natural weathering processes are a major factor dominating the amount and distribution of Cr in surface sediments of the Red River, Vietnam, and it has a non-anthropogenic origin in Ba Lat estuary (Nguyen et al., 2016b).

The second sub-cluster includes As. The element As has a weak correlation with other heavy metals in this group, and it has enrichment factor values higher than 2. It indicated that this element has industrial and domestic sources. The main reason for the high enrichment factor values of As could be that the groundwater at these sites contains higher As level, which is commonly used to irrigate agricultural soil. The geology of Red delta shows similarity with the Ganges-Brahmaputra, where high As levels in the groundwater have been reported (Agusa et al., 2005, 2006; Berg et al., 2001, 2007; Chander et al., 2004; Nguyen et al., 2008). The same result was reported in agricultural soils in the Pear River, China (Chai et al., 2004; Huang et al., 2011). Element As was also found in pig and chicken manure, which are often used on the soil as a fertilizer (Zarcinas et al., 2005; Duan et al., 2016; Wang et al., 2019a). In contrast,

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increased industrial activities, such as chemical and fertilizer production as well as manufacturing in traditional handicraft villages (e.g. metal smelting and processing and painting), might have become additional sources of pollution in recent years.

The third sub-cluster includes Cu, Pb and Zn. These heavy metals have mean enrichment factor values less than 1.5 and they have a close correlation with TOC, silt and Al. These factors indicate a natural origin of Cu, Pb and Zn.

The second group indicates for Cd. Element Cd pollution was possibly caused by anthropogenic wastes, including sewage sludge, wastewater and/or fertilizers and pesticides.

As mentioned above, the EF values of Cd show higher values in Nghia Hung and Giao Thuy, these two districts are coastal districts of Nam Dinh province. These sites are located near the dike, high way, ecotourism zone, and industrial zone (e.g. ND95 near to Thinh Long ecotourism zone, ND51, ND52, ND54 near to the dike). Trinh and Shin (2004) also pointed out that, possible sources of Cd in Red River delta were irrigation water contaminated by inflow of improperly disposed wastewater, sewage sludge that was incorporated in the agricultural soil as an amendment, and vehicle tires.

Conclusions

Heavy metal contents are higher in soils of paddy fields and cereal fields, but lower in aquaculture soil.

According to cluster and PCA analyses, heavy metals can be grouped into two groups. Elements Cu, Pb, Cd, As and Zn have similar geochemical behaviours while Cd is different from them.

According to enrichment factor, elements Cr are mainly from natural source, while Cd and As have a significant anthropogenic input. Elements Cu, Pb and Zn have a mixed source.

Hot spots with high levels of As and Cd pollution are normally located next to industrial zones and traditional handicraft villages. These hotspots should be managed properly in terms of human health.

The effect of land use type on heavy metal concentrations will be discussed deeply in future studies.

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