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Heavy Metal Pollution of Soils in the Site of a Retired Paint and Ink Factory

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Abstract

In this paper, concentrations of heavy metals such as arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn) in topsoil (0-30 cm). subsoil (30-60 cm), and basal-soil (60-100 cm) in the site of a retired paint/ink manufactory nearby Hangzhou, Zhejiang Province, China were investigated. For the assessment of heavy metal pollution in soils, both the Index of Geo-accumulation (Igeo) and the Values of maximum allowable limits (MAL) for heavy metals in soil were used. The results indicated that the soils collected in this survey were contaminated by As, Cd, Cu, Hg, Ni, Pb, and Zn, and chromium pollution in the soils was not apparent. Hg, As, and Cd pollution in the soils were extremely serious. Hg, As, and Cd concentrations in some soil samples were excessive to the MAL, and the safe treatments of the soils represented by these samples is needed.

Keywords: Index of Geo-accumulation; mobilization; pollution; retired paint/ink factory

1. Introduction

Contamination of soils with heavy metals is a widespread problem all over the world. Anthropogenic soil pollution by trace metals has been recognized in many countries [1-3]. And the anthropogenic sources of heavy metal contaminants in soils include metalliferous mining and smelting, metallurgical industries, electronic industries, sewage sludge treatment, waste disposal sites and agricultural fertilizers [4-10]. It was estimated that the annual worldwide release of heavy metals reached 22,000 t (metric ton) for cadmium, 939,000 t for copper, 783,000 t for lead and 1,350,000 t for zinc [11]. Heavy metal toxicity can result in

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damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon and repeated long-term contact with some metals or their compounds may even cause cancer [12-15]. Paint/ink manufactory is regarded as one of "hot points" of heavy metal discharge [16]. Monitoring and assessing heavy metal contamination was usually focused on the factories being on active duty and was neglected of those retired.

This study was aimed at evaluating the status of heavy meal pollution of soils in the site of a retired paint/ink manufactory nearby Hangzhou, Zhejiang Province, China. The mobilization of heavy metals in soil profile was also discussed. The data of heavy metal concentrations in soils obtained from this practical survey can be used as the referent evidence for the safe re-use of the lands on which the plant had been located.

2. Materials and methods

A set of 17 samples of each topsoil (1-30 cm), subsoil (30-60 cm), and basal-soil (60-100 cm) in the site of a retired paint/ink factory near suburb of Hangzhou, Zhejiang Province, China (latitudes 30˚15'-20'N and longitudes 120˚6'-10'E), randomly. The soil samples were air-dried, dissagregated and passed though a 0.25mm nylon screen, and than homogenized and stored in polyethylene containers until the analysis was carried out.

For the determinations of the total concentrations of trace metals such as arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn), the homogenized sample (0.5 g) was digested with aqua regia and diluted to 100 mL with 2% HNO_3. Trace metal concentrations in digested solutions were analyzed using an ICP-MS (Inductively Coupled Plasma Mass Spectrometer, Agilent 7500a).

For evaluating the degree of metal contamination in soils, the Index of Geo-accumulation (Igeo) was used. The Igeo of a metal in soil was calculated with the following formula:

$$Igeo = Log_2 Cmetal/1.5Cmetal\ (baseline) \quad (1)$$

Where Cmetal is the concentration of the heavy metal in the enriched sample and Cmetal (baseline) is the concentration of the metal of the geochemical background or in the unpolluted sample. The factor 1.5 is introduced to minimize the effect of the possible variations in the background or control values which may be attributed to lithogenic variations in the soil. [7]

The degree of metal pollution is assessed in terms of seven contamination classes based on the increasing numerical value of the index as follows:

Igeo <0 = means unpolluted
0<=Igeo<1 means unpolluted to moderately polluted
1<=Igeo<2 means moderately polluted
2<=Igeo<3 means moderately to strongly polluted
3<=Igeo<4 means strongly polluted
4<=Igeo<5 means strongly to very strongly polluted
Igeo>=5 means very strongly polluted. [7]

Values of maximum allowable limits (MAL) for heavy metals in soil used in this work were as follows: As-40, Cd-1.0, Cr-300, Cu-400, Hg-1.5, Ni-200, Pb-500, Zn-500 mg kg^{-1} soil [17], and the geochemical background of heavy metals in soils in Hangzhou, Zhejiang Province, China were as follows: As-6.86, Cd-0.110, Cr-79.0, Cu-23.6, Hg-0.0445, Ni-33.3, Pb-26.5, Zn-83.3 mg kg^{-1} soil [18].

3. Results and discussion

3.1. Concentrations of heavy metals in soils

The total concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in topsoil (0-30 cm) collected from the site of a retired paint/ink manufactory nearby Hangzhou are presented in Table 1. The results indicated that the concentrations of total As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in topsoil range 24.8-44.1 mg kg^{-1}, 0.29-1.21 mg kg^{-1}, 20.6-85.4 mg kg^{-1}, 22.3-108.6 mg kg^{-1}, 0.57-11.25 mg kg^{-1}, 23.6-66.2 mg kg^{-1}, 26.6-86.8 mg kg^{-1}, and 64.2-261.5 mg kg^{-1}, respectively.

The total concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in subsoil (30-60 cm) from the same site are presented in Table 2. The results indicated that the concentrations of total As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in topsoil range 20.5-45.7 mg kg^{-1}, 0.25-1.03 mg kg^{-1}, 22.0-80.4 mg kg^{-1}, 16.7-70.9 mg kg^{-1}, 0.68-18.11 mg kg^{-1}, 22.1-58.6 mg kg^{-1}, 24.5-51.7 mg kg^{-1}, and 72.5-215.0 mg kg^{-1}, respectively.

The total concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in subsoil (60-100 cm) from the same site are presented in Table 3. The results indicated that the concentrations of total As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in topsoil range 21.8-44.4 mg kg^{-1}, 0.16-1.75 mg kg^{-1}, 20.7-84.9 mg kg^{-1}, 18.5-86.3 mg kg^{-1}, 0.52-6.73 mg kg^{-1}, 22.7-50.2 mg kg^{-1}, 27.2-53.8 mg kg^{-1}, and 60.7-298.1 mg kg^{-1}, respectively.

With the comparison to the values of maximum allowable limits (MAL) for heavy metals in soil, it could be found that Hg concentrations in nine topsoil samples, twelve subsoil samples, and nine basal-soil samples were higher than the MAL for mercury, As concentrations in two topsoil samples, two subsoil samples, and three basal-soil samples were higher than the MAL for arsenic, and Cd concentrations in

Table 1. Heavy metal concentrations in topsoil (0-30 cm)

Sample number	Heavy metal concentration (mg kg^{-1})							
	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1	26.1	0.36	20.6	108.6	2.82	23.6	46.1	131.3
2	24.8	0.47	23.9	22.3	1.65	28.0	60.4	126.1
3	31.5	0.47	48.9	24.4	1.10	29.1	40.9	95.3
4	44.1	0.46	24.8	23.2	9.18	23.7	44.4	109.4
5	32.0	0.52	31.0	36.2	3.76	28.0	43.8	114.6
6	27.6	0.37	29.6	25.1	3.23	25.2	86.8	135.1
7	28.4	0.32	45.5	46.8	6.47	36.4	47.4	122.5
8	30.8	0.43	82.9	29.6	11.25	66.2	47.0	167.0
9	36.6	0.29	48.9	30.0	5.77	30.7	38.0	128.9
10	31.9	0.34	68.8	48.4	1.05	36.0	48.4	146.2
11	25.2	0.42	28.4	44.8	1.45	36.7	68.2	116.0
12	33.4	0.79	46.9	36.2	0.57	47.4	47.5	240.0
13	32.5	0.80	50.9	41.3	0.44	41.4	62.0	157.9
14	32.0	1.21	53.3	104.0	3.81	51.6	69.6	226.1
15	43.7	0.65	48.4	28.1	0.72	44.1	36.4	261.5
16	34.8	0.39	45.8	33.4	1.05	35.9	52.9	135.4
17	32.9	0.60	85.4	23.5	0.88	61.5	26.6	64.2

one topsoil samples, one subsoil samples, and one basal-soil samples were higher than the MAL for cadmium. The soils represented by these samples should be treated as hazardous substances.

3.2. Heavy metal pollution in soils

The range and average of Igeo of heavy metals in soils calculated were shown in Table 4. According to the terms of contamination classes based on Igeo, the status of heavy metal pollution in topsoil (0-30 cm) were strongly to very strongly polluted for mercury (Hg), moderately to strongly polluted for arsenic (As), unpolluted to strongly polluted for cadmium (Cd), unpolluted to moderately polluted for copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn), and unpolluted for chromium (Cr). The status of heavy metal pollution in subsoil (30-60 cm) were strongly to very strongly polluted for mercury (Hg), unpolluted to strongly polluted for arsenic (As), and cadmium (Cd), unpolluted to moderately polluted for copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn), and unpolluted for chromium (Cr). The status of heavy metal pollution in basal-soil (60-100 cm) were strongly to very strongly polluted for mercury (Hg), moderately to strongly polluted for arsenic (As), unpolluted to strongly polluted for cadmium (Cd), unpolluted to moderately polluted for copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn), and unpolluted for chromium (Cr). It was also found that the order of heavy accumulation in topsoil, subsoil or basal-soil was as Hg>As and Cd>Cu, Ni, Pb, and Zn>Cr. Hg, As, and Cd pollution in the soils in the site of the retired paint/ink manufactory should be paid more attention. As the status of heavy metal contamination in subsoil and basal-soil were similar to that in topsoil, the mobilization of heavy metals in soil profile was noticeable, which probably polluted the groundwater in the site.

Table 2. Heavy metal concentrations in subsoil (30-60 cm)

Sample number	Heavy metal concentration (mg kg^{-1})							
	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1	30.1	0.25	25.4	66.2	2.06	24.4	35.8	101.0
2	20.5	0.31	22.0	19.2	1.73	27.1	45.8	75.6
3	28.8	0.51	35.0	23.0	2.39	25.0	35.9	79.3
4	45.7	0.51	26.6	26.1	5.09	23.5	32.5	129.7
5	21.3	0.31	41.5	29.8	18.11	37.7	42.0	90.3
6	26.4	0.16	30.9	16.7	4.03	23.5	29.5	72.5
7	31.0	0.19	37.4	61.5	10.70	22.1	33.9	134.6
8	40.8	0.41	53.7	23.5	2.58	39.4	36.2	134.5
9	32.1	0.27	39.5	27.4	10.69	23.7	35.9	126.4
10	33.8	0.39	58.4	70.9	2.25	33.3	45.6	146.7
11	35.9	1.03	33.5	49.8	3.14	31.6	50.0	104.1
12	25.0	0.59	39.9	30.9	0.70	43.6	42.5	79.9
13	32.3	0.63	52.0	33.2	0.68	33.7	39.3	147.4
14	34.8	0.69	80.4	56.1	1.50	58.6	46.9	215.0
15	30.7	0.58	49.5	55.2	0.73	48.9	44.0	118.2
16	22.8	0.36	55.4	29.8	0.82	23.2	51.7	154.1
17	33.9	0.57	66.0	18.1	2.21	39.7	24.5	146.0

Table 3. Heavy metal concentrations in basal-soil (60-100 cm)

Sample number	Heavy metal concentration (mg kg^{-1})							
	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1	24.9	0.16	20.7	86.3	2.22	22.7	31.4	60.7
2	23.1	0.67	26.8	18.7	4.00	28.2	36.5	83.8
3	25.7	0.46	30.9	23.3	1.98	50.2	36.1	85.3
4	29.8	0.51	29.2	19.5	4.65	25.2	33.1	88.9
5	23.6	0.34	28.2	28.6	2.78	25.2	34.0	91.4
6	26.6	0.18	41.1	18.5	6.73	30.7	31.9	81.2
7	33.4	0.20	35.3	24.4	4.55	20.3	33.6	94.2
8	34.1	0.33	45.0	20.3	3.03	24.4	32.9	104.2
9	36.1	0.28	49.6	26.7	1.78	25.8	39.5	144.5
10	35.0	0.28	47.8	55.2	0.60	30.0	43.1	122.8
11	44.2	0.99	49.2	59.0	0.70	43.0	53.8	298.1
12	36.2	0.85	44.2	29.5	1.25	40.4	36.9	223.2
13	38.6	0.52	45.4	24.7	1.29	37.4	31.5	151.3
14	42.6	0.73	48.9	36.0	0.64	45.1	48.5	237.7
15	44.4	0.68	45.2	30.5	0.52	47.3	34.3	169.3
16	21.8	0.22	84.9	29.0	0.54	35.3	39.4	138.0
17	39.5	1.75	50.2	21.4	0.85	30.6	27.2	71.3

Table 4. Range and average of Igeo of heavy metals in soils

Heavy metals	Igeo					
	Topsoil (0-30 cm)		Subsoil (30-60 cm)		Basal-soil (60-100 cm)	
	Range	Average±SD	Range	Average±SD	Range	Average±SD
As	1.27-2.10	1.63±0.24	0.99-2.15	1.56±0.31	1.08-2.11	1.64±0.34
Cd	0.81-2.87	1.56±0.54	0.60-2.64	1.31±0.71	-0.04-3.41	1.39±0.96
Cr	-2.52 - -0.47	-1.48±0.61	-2.43 - -0.56	-1.52±0.51	-2.52 - -0.48	-1.55±0.47
Cu	-0.67-1.62	0.05±0.68	-1.08-1.00	-0.07±0.69	-0.94-1.29	-0.28±0.63
Hg	3.09-7.40	4.95±1.44	3.35-8.08	5.23±1.42	2.96-6.66	4.61±1.22
Ni	-1.08-0.41	-0.47±0.46	-1.18-0.23	-0.67±0.43	-1.14-0.01	-0.65±0.40
Pb	-0.58-1.13	0.31±0.40	-0.70-0.38	-0.03±0.29	-0.55-0.44	-0.14±0.24
Zn	-0.96-1.07	0.14±0.50	-0.79-0.78	-0.11±0.44	-1.04-1.25	-0.07±0.65

4. Conclusions

With the investigation, the status of heavy metal pollution in the topsoil, subsoil, and basal-soil in the site of the retired paint/ink manufactory were identified, Hg, As, and Cd pollution in the soils were extremely serious according to the assessment with the terms of contamination classes based on the Index of Geo-accumulation. In addition, Hg, As, and Cd concentrations in several soil samples were excessive

to the MAL, and the soils represented by these samples should be treated safely before the land re-used for settlement or public park.

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