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Assessment of soil contamination with Cd, Pb and Zn and source identification in the area around the Huludao Zinc Plant

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ABSTRACT

The distribution characteristics of heavy metals (cadmium (Cd), lead (Pb) and zinc (Zn)) in the natural soil profiles around the Huludao Zinc Plant (HZP), an old industrial base in Northeast China, were analyzed. The pollutant source was identified using ^{210}Pb isotope technique to evaluate the geochemical characteristics of Pb and the historical production records of HZP. The results indicated: dust precipitation from HZP was the primary source of the pollutants. The average deposition rates of Cd, Pb and Zn were 0.33, 1.75, and 30.97 g/m^2 year, respectively at 1 km away after HZP, and 0.0048, 0.035, and 0.20 g/m^2 year, respectively at 10 km away after HZP. There is a risk of secondary pollution to the environment as well as the food chain in seriously polluted areas used for cultivation.

1. Introduction

The accumulation of heavy metals in agricultural soils is of increasing concern due to food safety issues, potential health risks, and the detrimental effects on soil ecosystems [2,7,11]. Air pollution associated with metal smeltery has been increasing in China. The soil surrounding the Zhuzhou Smeltery had a high Cd pollution index, and the nearby paddy fields were primarily polluted with Pb [12]; most lands around the Shenyang Smeltery in Northeast China were found to be heavily polluted with Cd, Pb and Zn, which led to the shut down of Shenyang Smeltery in 2002 [1]. Hrsak et al. [6] evaluated the surroundings of a lead smeltery contamination with Pb, Zn and Cu. However, few studies have demonstrated when the pollution occurred and where it came from.

The excess ^{210}Pb (^{210}Pbex) isotope technique can be used to identify the sources and pathways of soil pollutants, as well as to distinguish the pollution intensities of natural and anthropogenic activity. This method can also be used to quantitatively evaluate the relative contribution and effect of pollutants released by anthropogenic activity on environmental quality [3,5,14,17]. A Pb isotope study was conducted on soil profiles in the Swiss National Park and was found that the deposition intensity was approximately 2.2 g/m^2 in polluted soils [4].

The Huludao Zinc Plant (HZP), which is the largest Zn smeltery in Asia, was constructed in 1937. The smelter recovery rate of non-ferrous metals was maintained at 92.30–95.26% from 1980 to 2005, and the atmospheric recovery rate was less than 27.46% in 1985. A few atmospheric recovery devices were put into use in the 1990s, but the atmospheric recovery rate did not change (Internal Information of the Archives Office of HZP). The major goals of this study were (1) to assess the extent of soil pollution and crop pollution in the surroundings of HZP; (2) to determine the atmospheric deposition rate of Cd, Pb and Zn associated with HZP, and (3) to identify the date of soil pollution and the source of pollutants using the ^{210}Pbex isotopic technique.

2. Materials and methods

2.1. Site description

Huludao Zinc Plant (HZP) is a state enterprise of non-ferrous metal smelter and is the largest Zn smeltery in Asia. It was constructed in 1937 and is located at E120°56′18.2″, N40°43′.8″ (Fig. 1). The annual production capacity of non-ferrous metals was 430,000 tons in 2006, including 330,000 tons of zinc, 600 tons of cadmium, etc. It has 13 smoke stacks higher than 60 m and 6 smoke stacks higher than 100 m. Smoke and dust discharged from HZP contains Cd, Pb and other heavy metals. The discharged particles are eventually deposited in the surrounding soil. According to the statistic data of Environmental Protection Bureau of Liaoning Province (2003),

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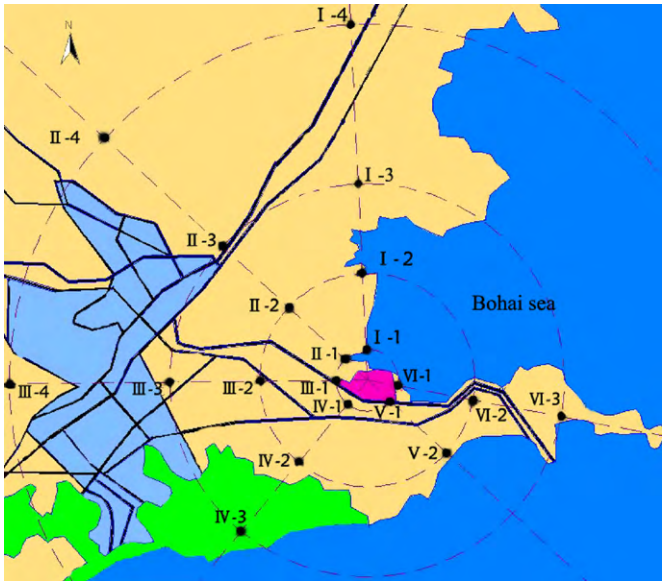

Fig. 1. Sketch map of the HZP and sampling sites.

97.3% Cd and 89.6% Pb discharged in waste gas of Liaoning Province were from HZP, respectively [8].

Huludao City is land-locked and located in an area with a monsoon climate. Its prevailing wind direction is from north-west in winter and south-east in summer [18]. Local farming is rain-fed and not irrigated.

2.2. Sampling and analysis

To evaluate the degree of soil contamination in the area surrounding HZP, soil and maize samples were collected in October 2005 and October 2006. Sampling sites (SS) were approximately 1, 3, 6 and 10 km away from HZP. Since some sampling sites were located in the buildings or the sea, only 18 soil samples and 8 maize samples were collected in 6 sampling strips along different wind trajectories (Table 1). The study area is characterized by brown soil with soil organic matter, total N, Olsen-P, and available K levels of 15.36 g/kg, 0.92 g/kg, 19.36 mg/kg and 73.0 mg/kg, respectively, and pH value of 6.5–7.8 [20]. Along the primary wind trajectory (north-west) of the Huludao City, 2 natural soil profiles were selected. These profiles were denoted HLD-II-1 and HLD-II-4 and were located at 1 km and 10 km north-east of HZP, respectively. Soil samples of 2 natural profiles were collected from 0 to 2, 2 to 4, 4 to 6, 6 to 8, 8 to 10, 10 to 12, 12 to 14, 14 to 16, 16 to 18, 18 to 20, 20 to 25, 25 to 30, 30 to 40 and 40 to 60 cm. Surface soil samples were collected 5 individual samples from the top 0 to 20 cm within the scope of 20 m, then mixed and homogenized. Soil and maize samples were air-dried to a constant weight, grounded and sieved through a 0.2 and 0.5 mm mesh, respectively.

Soil samples were digested with HF-HNO_3–$HClO_4$ and plant samples were digested with H_2O_2–$HClO_4$, after which all samples were analyzed for heavy metals by Flame-Graphite Furnace AAS (Varian SpectrAA 220 FS/Z). Two soil or plant standard samples were analyzed after every 10 soil or plant samples to ensure the accuracy of the analyses.

2.3. Evaluation of the degree of soil contamination

The Muller index [12] was utilized to evaluate the contamination degree of soil heavy metals. The Muller index is a geo-accumulation index (Igeo) to quantitatively evaluate the intensity of the historical heavy metal pollution, which is described as:

$$\text{Igeo} = \log_2[Cn/(1.5Bn)]$$

where Cn is the soil concentration of a given heavy metal and Bn is the background value of soil heavy metal elements in Huludao City.

The Cd, Pb and Zn concentration, their Muller index and pollution intensity of surface soil around HZP are shown in Table 2. The background values of soil Cd, Pb and Zn concentration in Huludao City (Table 2) were obtained from the China Eco-environmental Geo-chemistry Atlas (scale 1:200 thousand) [9]. The upper background value was used to calculate the Muller geo-accumulation indexes.

Table 1
Brief description of sampling sites around HZP*.

Sampling stripes	SN	Soil layers (cm)	Land use pattern	Latitude	Longitude
I	HLD-I-1	0–20	Upland	40°44′03.2″	120°54′21.4″
	HLD-I-2	0–20	Upland	40°45′12.6″	120°54′24.6″
	HLD-I-3	0–20	Uncultivated land	40°46′52.3″	120°56′3.4″
	HLD-I-4	0–20	Upland	40°49′3.9″	120°56′38.5″
II	HLD-II-1	0–60	Uncultivated land	40°43′31.2″	120°55′16.4″
	HLD-II-2	0–20	Upland	40°45′0.8″	120°53′53.8″
	HLD-II-3	0–20	Uncultivated land	40°46′29.7″	120°52′9.7″
	HLD-II-4	0–60	Uncultivated land	40°48′06.0″	120°49′16.4″
III	HLD-III-2	0–20	Upland	40°43′43.8″	120°53′28.6″
	HLD-III-3	0–20	Orchards	40°43′58.4″	120°51′50.5″
	HLD-III-4	0–20	Uncultivated land	40°42′58.5″	120°47′59.3″
IV	HLD-IV-1	0–20	Uncultivated land	40°43′26.2″	120°54′54.0″
	HLD-IV-2	0–20	Uncultivated land	40°42′53.8″	120°53′58.3″
V	HLD-V-1	0–20	Uncultivated land	40°43′19.6″	120°55′53.3″
	HLD-V-2	0–20	Uncultivated land	40°42′45.4″	120°57′2.5″
VI	HLD-VI-1	0–20	Upland	40°43′19.0″	120°56′18.2″
	HLD-VI-2	0–20	Uncultivated land	40°43′22.6″	120°57′27.2″
	HLD-VI-3	0–20	Uncultivated land	40°43′11.5″	120°58′29.7″

SS-2: sampling sites about 3 km away from HZP, including HLD-I-2, HLD-II-2, HLD-III-2, HLD-IV-2, HLD-V-2 and HLD-VI-2.
SS-3: sampling sites about 6 km away from HZP, including HLD-I-3, HLD-II-3, HLD-III-3 and HLD-VI-6.
SS-4: sampling sites about 10 km away from HZP, including HLD-I-4, HLD-II-4 and HLD-III-4.
* SS-1: sampling sites about 1 km away from HZP, including HLD-I-1, HLD-II-1, HLD-IV-1, HLD-V-1 and HLD-VI-1.

Table 2
The Cd, Pb and Zn concentration and their Muller index of surface soil around HZP.

Sample sites	Items	Concentration (μg/g)			Geo-accumulation index (Igeo)		
		Cd	Pb	Zn	Igeo-Cd	Igeo-Pb	Igeo-Zn
Background value		014–0.19	21.84–26.50	59.01–67.09			
SS-1	Average	242.1	1159.2	12054.9	9.7(VSP)	4.9(SP-VSP)	6.9(VSP)
	Min	53.9	96.0	696.9	7.6(VSP)	1.3(MP)	2.8(MP-SP)
	Max	352.5	2953.1	20690.3	10.3(VSP)	6.2(VSP)	7.7(VSP)
SS-2	Average	25.6	69.7	1737.6	6.5(VSP)	0.8(UP-MP)	4.1(SP-VSP)
	Min	6.8	20.6	180.8	4.6(SP-VSP)	−0.9(UP)	0.8(UP-MP)
	Max	55.0	112.5	7429.2	7.6(VSP)	1.5(MP)	6.2(VSP)
SS-3	Average	15.6	63.9	427.6	5.8(VSP)	0.7(UP-MP)	2.1(MP-SP)
	Min	0.8	15.2	89.1	1.5(MP)	−1.4(UP)	−0.2(UP)
	Max	46.0	141.4	750.0	7.3(VSP)	1.8(MP)	2.9(MP-SP)
SS-4	Average	5.9	27.6	182.9	4.4(SP-VSP)	−0.5(UP)	0.9(UP-MP)
	Min	1.5	13.3	96.1	2.4(MP-SP)	−1.6(UP)	−0.1(UP)
	Max	12.8	40.9	317.8	5.5(VSP)	0.0(UP)	1.7(MP)

Notes: (1) SS-1, SS-2, SS-3 and SS-4 were sampling sites at about 1, 3, 6 and 10 km away from HZP, respectively.
(2) Geo-accumulation index (Igeo) value >5, 4–5, 3–4, 2–3, 1–2, 0–1 and <0, respectively represent very strongly polluted (VSP), strongly to very strongly polluted (SP-VSP), strongly polluted (SP), moderately to strongly polluted (MP-SP), moderately polluted (MP), unpolluted to moderately polluted (UP-MP) and unpolluted (UP).

2.4. Analysis of the specific activity of environmental ^{210}Pbex

The activity of ^{210}Pb was determined using a multi-channel gamma spectrometer in conjunction with a GR2519 detector (American Canberra Corporation) at a relative efficiency of 25% and a resolution of 1.9 keV at 1.33 MeV. This technique is a common method of dating and source identification of external pollutants in sediments [16,19]. Briefly, the soil samples were air dried, grounded and sieved through a 0.2 mm mesh, after which 300 g aliquots were put into a sample survey box that was sealed for 21 days. The samples were then measured at 46.5 keV characteristic peak area with measuring error controls in ≤10%. The balance between ^{226}Ra and its daughter nuclides of ^{222}Rn and ^{214}Pb was then used to determine the activity of ^{226}Ra at 351.9 keV. Specifically, the activity of soil sample ^{210}Pbex was considered to be the difference between the grass activity of ^{210}Pb and ^{226}Ra. The specific activity of ^{210}Pbex expressed in Bq/kg was its activity divided by soil sample weight.

3. Results and discussion

3.1. Surface soil Cd, Pb and Zn pollution in the area surrounding HZP

The Cd, Pb and Zn concentration of surface soil decreased as the distance from HZP increased. As shown in Table 2, the average Cd, Pb and Zn concentration of surface soil at 1 km away from HZP was 242.1, 1159.2 and 12054.9 μg/g, respectively, while they were only 5.9, 27.6 and 182.9 μg/g, respectively at 10 km away from HZP.

The Cd Muller indexes of surface soil of 4 samples at SS-1 (SS-1: sampling sites at about 1 km away from HZP) were greater than 7.6 and the average value for Cd was 9.7, which was very strongly polluted. The average Cd Muller indexes of surface soil at SS-2 (SS-2: sampling sites at about 3 km away from HZP), SS-3 (SS-3: sampling sites at about 6 km away from HZP) and SS-4 (SS-4: sampling sites at about 10 km away from HZP) were 6.5, 5.8 and 4.4, respectively, which were very strongly to strongly polluted (Table 2). Table 2 also shows similar surface soil Pb and Zn pollution at SS-1, SS-2, SS-3 and SS-4. The pollution grade of heavy metals in surface soil surrounding HZP occurred in the order of Cd > Zn > Pb [10].

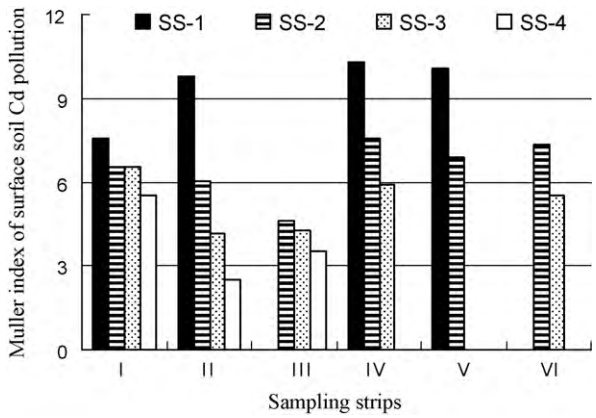

Fig. 2. Soil Cd Muller index of the surface layers in 6 sampling strips. *Notes*: SS-1, SS-2, SS-3 and SS-4 were sampling sites at about 1, 3, 6 and 10 km away from HZP, respectively.

3.2. The effect of land use patters on surface soil Cd, Pb and Zn pollution

Farther away from HZP, surface soil Cd Muller's index of the 6 sampling strips along different wind trajectories decreased. However, surface soil Cd Muller's index along wind trajectories of sampling strips I and III decreased less than that of sampling strips II, IV, V and VI (Fig. 2). This phenomenon was likely due to the difference of land use patterns between sampling strips I and III and sampling strips II, IV, V and VI. To facilitate this analysis, surface soil Cd pollution in the surroundings of HZP was selected.

The land use pattern of sampling strips II, IV, V and VI was mainly uncultivated land, and deposited Cd was not removed. More Cd was deposited into surface soil closer to HZP than into surface soil farther from HZP (Fig. 2).

The land use pattern of sampling strips I and III were farming land. The annual harvested maize straw and grain in 2005 and 2006 removed about 161.3 g Cd/hm^2 from SS-1, while they only removed about 25.3 g Cd/hm^2 from SS-4 (Table 3). Even if more Cd was deposited into surface soil of SS-1 than that of SS-2, SS-3 and SS-4, more Cd was removed from surface soil in SS-1 than SS-2, SS-3 and SS-4 (Fig. 2).

3.3. Serious secondary Cd and Pb contamination of maize grain and straw

The Cd concentration of maize seed collected from SS-1 and SS-2 were 0.30 and 0.46 μg/g, respectively, which are higher than the food limit in China (GB2762-2005, Cd_{max} < 0.2 μg/g) (Table 3).

Table 3
Annual removal of Cd by maize seed and straw.

Items	SS-1	SS-2	SS-3	SS-4
Maize yield (kg/hm^2)	5880	6915	7740	7860
Maize straw (kg/hm^2)	6468	6886.9	7894.8	8123.2
Amount removed by maize seed and straw (g/hm^2 year)				
Cd	161.3	72.2	20.7	25.3
Pb	446.1	292.2	131.8	132.8
Zn	5324.2	2718.3	1859.9	1402.5

Notes: SS-1, SS-2, SS-3 and SS-4 were sampling sites at about 1, 3, 6 and 10 km away from HZP, respectively.

The Pb concentration of maize seed from SS-1 and SS-2 were 7.4–25.2 times higher than China's food limit (GB2762-2005, Pb_{max} < 0.2 μg/g) (Table 3). Maize is the primary food consumed by local farmers, and local human health may be at serious risk.

The health limits of Cd and Pb in chicken and pig fodder in China are 0.5 and 13 μg/g, respectively (GB13078-2001). The Cd contents of maize straw ranged from 2.56 to 24.66 μg/g, which was 6.1–49.3 times the national fodder limit, while the Pb contents of maize straw ranged from 14.73 to 65.93 μg/g which was 1.13–5.07 times the national fodder limit (Table 3). Since maize straw in Huludao city is usually harvested as a winter livestock fodder, it may lead to serious secondary pollution of local livestock. Indeed, we made an investigation in 2005 and found that sheep could not be raised in the study area, and local farmers believed that the sheep had eaten contaminated forages.

3.4. Atmospheric deposition intensity and deposition rate of Cd, Pb and Zn

For profile HLD-II-1 and HLD-II-4, the Cd, Pb and Zn concentration in 0–60 cm soil profiles all gradually decreased as the soil depth increased, eventually reaching a relatively stable value at 30–60 cm (Figs. 3 and 4). It is assumed that the soil Cd, Pb and Zn concentration at 30–60 cm depth was representative of Cd, Pb and Zn concentration of local soil parent material, and the difference between Cd, Pb and Zn concentration of the 0–30 cm soil profile and of the 30–60 cm soil profile was the amount contributed by external atmospheric deposition [4].

Based on the soil bulk density and the soil Cd, Pb and Zn concentration of the profile HLD-II-1 and HDL-II-4 soil layers, the Cd, Pb and Zn deposition intensities of profile HLD-II-1 were 20.71, 110.19 and 1951.24 g/m^2, respectively, and the average annual deposition rates of Cd, Pb and Zn were 0.32, 1.72 and 30.49 g/m^2 year, respectively from 1942 to 2005. From 1942 to 2005, the Cd, Pb and

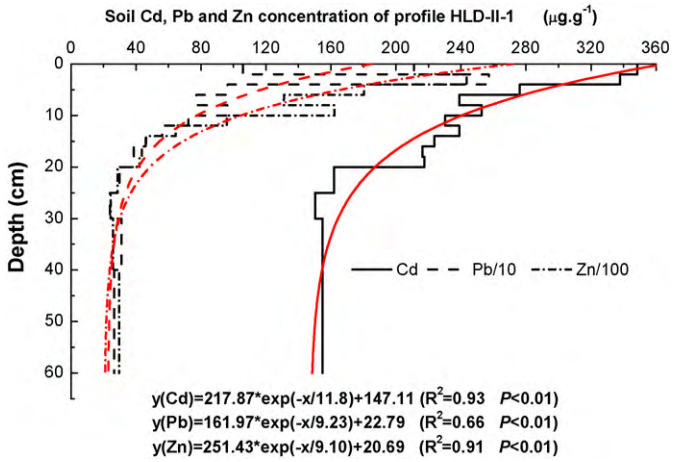

Fig. 3. Soil Cd, Pb and Zn concentration of profile HLD-II-1.

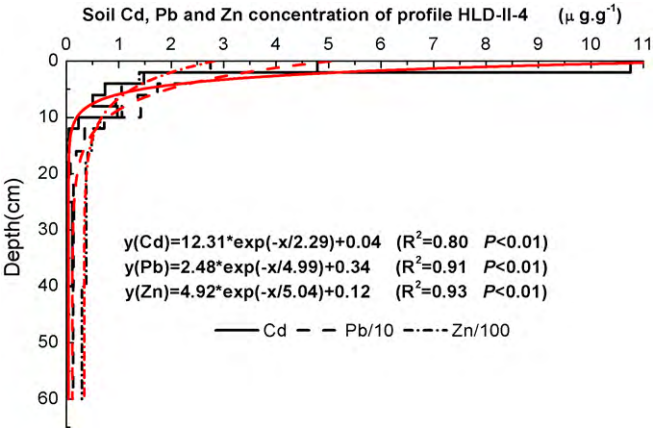

Fig. 4. Soil Cd, Pb and Zn concentration of profile HLD-II-4.

Zn deposition intensities of profile HLD-II-4 were 0.30, 2.18 and 12.62 g/m^2, respectively, while the average annual deposition rates of Cd, Pb and Zn were 0.005, 0.034 and 0.197 g/m^2 year, respectively (Table 4).

The high atmospheric deposition rate in the area surrounding HZP is caused by long-term shortage of the recovery system of waste gas. The survey revealed that HZP did not implement waste gas recovery until 1985, and the atmosphere recovery rate in 1985 was lower than 27.46%. A few waste gas recovery systems were used in 1990, but the atmospheric recovery rate did not change (Internal Data of the Archives Office of HZP). The smoke dust emitted from HZP contains a high level of Cd, Pb and Zn oxides or salts, which has led to serious soil contamination with Cd, Pb and Zn in the area around HZP [13].

3.5. The source identification of soil heavy-metal contamination

The specific activity of ^{210}Pbex in the 0–2 cm surface soil layer at profiles HLD-II-1 and HLD-II-4 were 119.12 and 128.71 Bq/kg, respectively. It indicates that the specific activity of ^{210}Pbex mainly deposited in 2005, which was the year that the samples were collected. The vertical distribution of ^{210}Pbex specific activity in 2 profiles showed an obvious peak, which indicated that the profile had undergone exterior disturbance, including external pollution. The highest deposition occurred in the 0–8 cm soil layer of profile HLD-II-1 and in the 0–12 cm soil layer of profile HLD-II-4, below which a low deposit formation existed (Figs. 5 and 6). The specific activity of ^{210}Pbex in profile HLD-II-1 and HLD-II-4 had 2 inflection points that appeared in the 6–8 and 10–12 cm layers, respectively. This difference indicated that the soil profiles had undergone many disturbances from internal and external sources. It is difficult to identify exactly when perturbation of the deposition in the profiles occurred using the natural decay law of ^{210}Pbex. This article used the average specific activity of ^{210}Pbex at 0–2 cm surface soil layers of two profiles to develop a time table of ^{210}Pbex decay (Fig. 7). According to the specific activity of ^{210}Pbex at the special peak in vertical distribution, the deposition time of 6–8 cm soil layer of pro-

Table 4
Atmospheric deposition intensity and deposition rate of Cd, Pb and Zn.

Soil profiles	Cd	Pb	Zn
HLD-II-1 deposition intensity (g/m^2)	20.71	110.19	1951.24
HLD-II-1 deposition rate (g/m^2 year)	0.32	1.72	30.49
HLD-II-4 deposition intensity (g/m^2)	0.30	2.18	12.62
HLD-II-4 deposition rate (g/m^2 year^1)	0.005	0.034	0.197

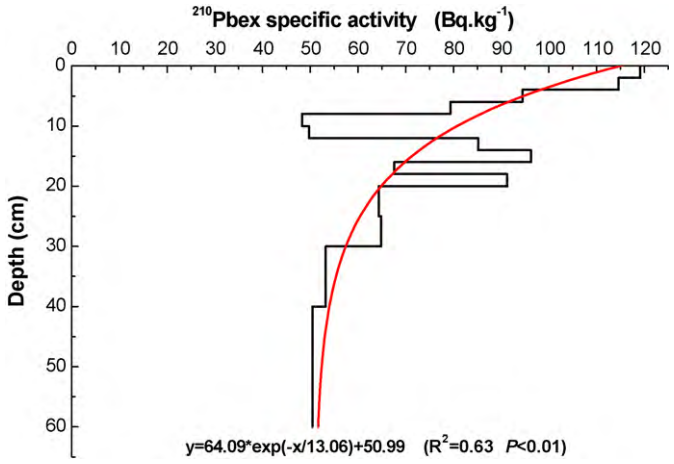

Fig. 5. ^{210}Pbex distribution of profile HLD-II-1.

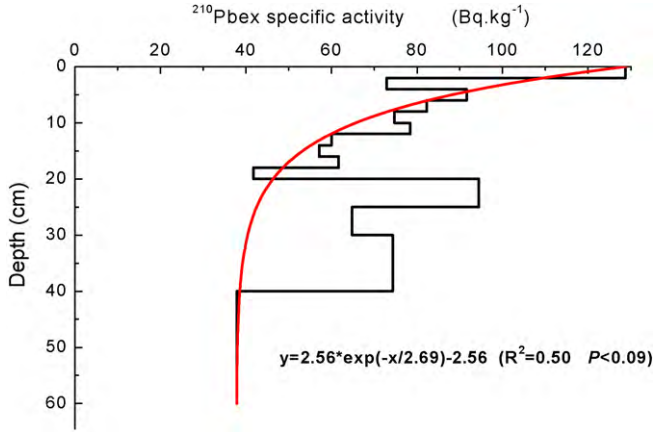

Fig. 6. ^{210}Pbex distribution of profile HLD-II-4.

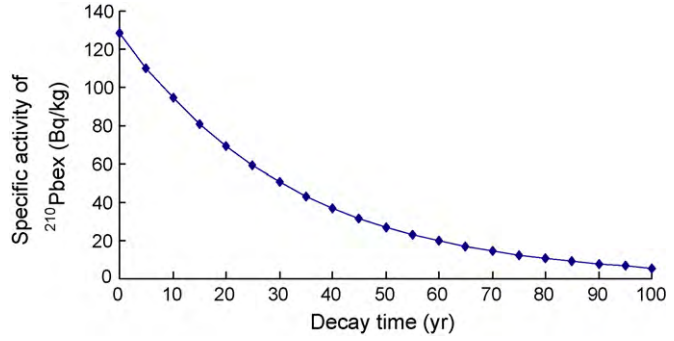

Fig. 7. Time table of the ^{210}Pbex decay curve.

file HLD-II-1 and of 10–12 cm soil layer of profile HLD-II-4 was 1989. Therefore, the ^{210}Pbex deposition in 2 profiles occurred in 2 periods from 1942 to 1989 and from 1989 to 2005 [15].

When determining methods of controlling pollutants, it is important to know when the pollution occurred as well as where the pollution occurred. It is known that HZP was established in 1937 and there were yield records from 1942 to the sampling time (2005). Fig. 8 indicates that the zinc yield of HZP had two obvious stages identified with a low yield occurring from 1942 to 1989, and a high yield occurring from 1989 to 2005 (Fig. 8, Internal Information of the Archives Office of HZP). These findings confirmed the results of the dating analysis conducted in this study.

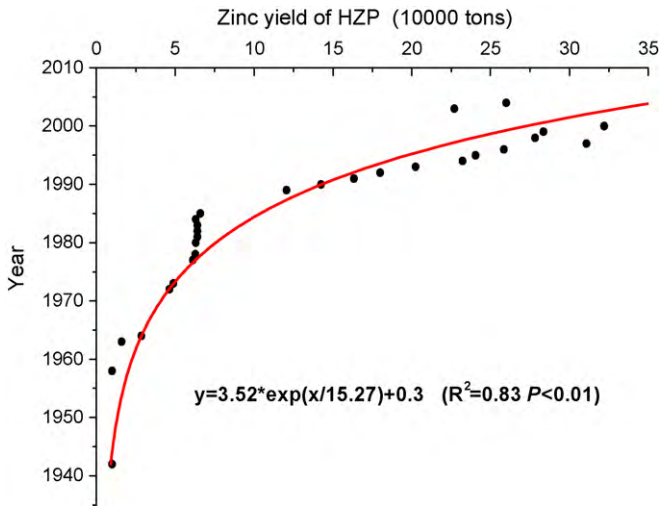

Fig. 8. Historical record of HZP Zinc yield.

4. Conclusions

The average concentration of Cd, Pb and Zn in surface soil (0–20 cm) at 1 km away from HZP was very strongly polluted. The maize grain and straw was contaminated with Cd and Pb at levels high enough to pose a serious risk to human health and livestock. Dust precipitation from the Zinc Plant was the primary source of heavy metals pollution. The average deposition rates of Cd, Pb and Zn at 1 km from the Zinc Plant were 0.33, 1.75 and 30.97 g/m^2 year, respectively, while at 10 km from the Zinc Plant were 0.0048, 0.035 and 0.20 g/m^2 year, respectively. Contamination of the soil surrounding HZP with Cd, Pb and Zn occurred at the beginning of 1940s. However, this contamination occurred at different intensities during two periods, 1942–1989 and 1989–2005.

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