Characteristics of heavy metal pollution in soils of a typical copper smelting site in China

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Abstract. During copper smelting, discharge of waste gas, waste water and waste residue has resulted in heavy metals pollution in soils. In a typical copper smelting site in China, arsenic pollution was the most serious, which could be found in soils within 6 m. All the measured heavy metals including Cu, Pb, As, Cd, Zn, Hg, Ni, Cr exceeded background concentrations in the study area. Key contamination areas of the site distributed nearby the uncontrolled emission source and under the leakage area of waste water and waste residue. This study is of great significance to the soil management and control of copper smelting industry.

1. Introduction

Heavy metal pollution in soil is the hot topic in the international community. Heavy metals can be accumulated over a long period. They destroy the soil ecological environment resulting in the loss of soil quality and migrate to the surrounding surface water and groundwater because of the precipitation eluviation effecting water environment quality. More worryingly, heavy metal pollution in soil has brought a serious threat to human health through bioaccumulation [1]. It is well known that smelting non-ferrous metal activity is one of the important sources of heavy metal pollution. In the process of smelting, heavy metals in waste gas, waste water and waste residue are discharged to the environment. Ore mining and processing are responsible for 13% of global mercury emissions [2]. In China, they are 24.39% and 26.36% of lead and zinc respectively [3]. And numerous investigations have shown that the soil around the non-ferrous smelter is contaminated with heavy metals [4-8]. Heavy metals emitted during production deposite from the atmosphere on to the soil surface or seep into the soil along with wastewater. But the majority of previous research has focused on the soil around the plant. Very little attention has been paid to the characteristics and causes of contamination inside the site.

The present study was carried out inside a typical copper smelting site in China. The smelter has been in operation for 13 years and is now disused. The objective of this investigation was to identify characteristic pollutants, key pollution areas and key pollution sources.

2. Materials and methods

2.1. Study area

The copper smelting site in the study covers about 288km² and can be divided into office region, production region and living region (shown in Figure 1). The smelter was built in 2006 and shut down in 2019. Its designed annual capacity was 125,000 tons of cathode copper, 547,000 tons of sulfuric acid and 330,000 tons of copper smelting slag recycling.
During the 13 years of operation, it has emitted a large amount of organized and unorganized soot containing heavy metals. The organized pollution sources included soot from materials transfer, exhaust gas from acid production and soot of slag crushing. The unorganized emission sources come from raw material preparation, copper smelting, and solid waste dumps. The wastewater was treated by the sewage treatment station and returned to production. And all solid waste was safely disposed of. In the site there was a permanent storage yard for sewage neutralizing residue.

2.2. Soil sampling and analysis
A total of 445 soil samples were collected from 198 sites in the bare area of the factory and 4 sites in the workshop region of the factory during September 2019 to April 2020 when the smelter was shut down (shown in Figure 1). Soil samples each of approximately 1.0 kg were taken from different depths (0-0.5m, 0.5-1.5m, 1.5-3.0m, 3.0-6.0m). Then they were air dried, sieved and stored in plastic bags for analysis.

Soil samples were digested with aquaregia by microwave digestion instrument. And then the soil digests were analyzed for Cu, Zn, Ni, Pb, Cd, Cr using inductively coupled plasma-mass spectrometry (ICP-MS) and for Hg and As using atomic fluorescence spectrophotometer [9-10].

2.3. Data analysis
Contaminations of heavy metals in soil samples were analyzed by the enrichment factor (EF) and the pollution index (PI).

$$EF = \frac{\text{Measured concentration in soil}}{\text{Background concentration in soil}}$$

$$PI = \frac{\text{Measured concentration in soil}}{\text{Standard concentration in soil}}$$

Where background concentration in soil references “The element background values in Chinese soils” [11], standard concentration in soil references “Soil environmental quality Risk control standard for soil contamination of development land (GB36600-2018)” [12].
3. Results and discussion

Total concentrations of 8 trace elements in soil samples in the study area are shown in Table 1. The As, Hg, Ni, Pb, Cd, Cu, Zn, and Cr concentrations in the soils were ranging from 2.75 mg·kg⁻¹ to 1210 mg·kg⁻¹, 0.006 mg·kg⁻¹ to 0.905 mg·kg⁻¹, 14.6 to 940 mg·kg⁻¹, 7.48 to 2108 mg·kg⁻¹, <0.07 to 15.1 mg·kg⁻¹, 12.2 to 23498 mg·kg⁻¹, 24.4 to 1567 mg·kg⁻¹, and <2 to 346 mg·kg⁻¹. According to the table 1, the concentrations of all the measured elements in the surface soil samples at 0-0.5m depth were the highest. They decreased with increasing depth. As, Ni, Pb and Cu exceed risk screening standard values and risk intervention standard values of residential land. The results of pollution evaluation are shown in Table 2. The max risk screening pollution indices (PI) of As, Ni, Pb and Cu were 60.5, 6.27, 5.27, and 11.75. The exceeding standard rates were 48.37%, 19.19%, 7.60% and 6.40%. As was the typical pollutant factor in the copper smelter. Excessive amounts of arsenic were found in both surface soils and subsurface soils, even at 3-6m depth. Compared to background concentrations in the control area, all eight elements in the study were elevated. The maximum enrichment factor of Cu was 3507, much higher than those of others elements. The degree of enrichment decreased as follows: Cu>Pb>As>Cd>Zn>Hg>Ni>Cr.

Table 1. Measured concentrations, standard concentration and background concentration.

| Element | As (Max) | Hg (Min) | Ni (Median) | Pb (Median) | Cd (Min) | Cu (Median) | Zn (Median) | Cr (Max) |
|---------|----------|----------|-------------|-------------|----------|-------------|-------------|---------|
| 0-0.5m  | 1210     | 0.905    | 940         | 2108        | 15.1     | 23498       | 1567        | 346     |
| 0.5-1.5m| 4.83     | 0.006    | 9.2         | 8.94        | <0.07    | 14.6        | 24.4        | 27.4    |
| 1.5-3m  | 96.45    | 0.15     | 171.28      | 117.13      | 2.09     | 638.52      | 139.16      | 138.55   |
| 3-6m    | 447      | 0.022    | 697         | 749         | 4.79     | 4292        | 470         | 288     |

All values are in mg·kg⁻¹.
Table 2. The largest PI of As, Ni, Pb, Cu in different function divisions of the soil.

| Function Division                          | Risk Screening PI | Risk Intervention PI |
|-------------------------------------------|-------------------|----------------------|
|                                           | As    | Ni   | Pb    | Cu    | As    | Ni   | Pb    | Cu    |
| Office and living quarter                 | 2.15  | <1   | <1    | <1    | <1    | <1   | <1    | <1    |
| Equipment maintenance area (east side of laboratory) | 42.8  | 6.27 | 1.87  | 1.11  | 7.13  | 1.57 | <1    | <1    |
| Meltshop                                  | 17.3  | <1   | 2.75  | 2.15  | 2.88  | <1   | <1    | <1    |
| Acid plant                                | 60.5  | <1   | 5.27  | 12.75 | 9.58  | <1   | 2.64  | 2.94  |
| Raw materials storage area                | 48.85 | <1   | 2.52  | 2.90  | 8.14  | <1   | <1    | <1    |
| Acid tank field                           | 8.16  | 4.74 | 1.27  | <1    | 1.36  | 1.19 | <1    | <1    |
| Water-quenched slag yard                  | 12.1  | 5.28 | <1    | <1    | 2.02  | 1.32 | <1    | <1    |
| Flux crushing station                     | 19.35 | <1   | 1.58  | 3.27  | 3.23  | <1   | <1    | <1    |
| Slag beneficiation plant                   | 9.85  | 4.96 | <1    | 1.10  | 1.64  | 1.24 | <1    | <1    |
| Hazardous wastes yard                     | 2.27  | 3.31 | <1    | <1    | <1    | 0.08 | <1    | <1    |
| Below the sewage disposal                  | 15.70 | /    | /     | /     | 1.78  | /    | /     | /     |
| Below the meltshop                        | 0.28  | <1   | /     | /     | <1    | <1   | /     | /     |
| Below the raw materials storage area      | 2.68  | <1   | /     | /     | <1    | <1   | /     | /     |
| Below the sewage tank of acid plant       | 59.5  | /    | /     | /     | 9.08  | /    | /     | /     |

From the perspective of horizontal space distribution (shown in Figure 2), arsenic contamination was ubiquitous. And the pollution areas in the copper smelter are relatively aggregated distribution. Heavily polluted areas were acid plant, raw materials storage area, equipment maintenance area and meltshop. Flux crushing station was polluted area because of the leeward of raw materials storage area. By analyzing the soil below the cement ground in key areas such as the sewage treatment station, meltshop, the material stock yard, and the acid plant, it can be found that the arsenic in the soil below the cement ground in key areas exceeded risk screening standard values of residential land. Moreover, the arsenic in the soil below the cement ground in the sewage treatment station and the acid plant also exceeded risk intervention standard values.

The field soil contamination was associated with the discharge of exhaust gas, wastewater and solid waste on the ground [13-15].

(i) Uncontrolled emission of soot containing heavy metals on site might contaminate the soil in the green belt of the smelting workshop, the material stock yard, and both sides of material transportation roads, etc. by atmospheric deposition. According to the survey result, the content of heavy metal was less in the surrounding area of the hazardous wastes yard covered with dust screens. Evidently, the controls of ground hardening and uncontrolled waste gas are essential for reducing soil contamination on site.

(ii) Wastewater on site might contaminate the soil under the wastewater treatment station, the sewage tank and the waste acid transportation pipeline of the acid plant. Damaged impermeable membrane of the wastewater collection tank is a major cause for contaminating deep soil. Hence, enterprises should strengthen management to prevent wastewater from leaking and venting.

(iii) Solid waste piles on site might contaminate the soil in the bare ground of the equipment maintenance area and the water-quenched slag yard through leaching after precipitation by means of vertical infiltration. Based on the survey findings, no significant soil contamination is found in the hazardous wastes yard that is strictly anti-seepage. Apparently, solid wastes containing heavy metals must be stored and treated according to certain standards.
4. Conclusion
Arsenic, nickel, lead, and copper were specific pollutants of the soil in copper smelter, of which, arsenic contamination could be found in the most areas. After collecting the soil survey statistics of other copper smelting sites in the north, we found that arsenic contamination was common in the soil of copper smelting sites. Other heavy metals might not exceed risk screening standard values and risk intervention standard values although they are higher than the background values.

Key contamination areas of the site involve the material preparation area, the material stock yard, the smelting area, wastewater collection and treatment, both sides of the material transportation road, the maintenance area, the acid-making area, and pipe area, which are primarily caused by uncontrolled discharges of heavy metals, vertical infiltration of wastewater, and leaching of solid waste.

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Figure 2. The As concentration distribution at different depths.
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