Heavy metal pollution characteristics and risk assessment of the soil of Lotus Pool influenced by JACW

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Abstract. During quite a long time, the Japanese Abandoned Chemical Weapons (JACW) has been a constant threat to the public safety and the environment. Because of the environmental corrosion, the chemical agents leaked from the JACW pollute the soil and water severely, especially the heavy metal chemicals. This paper demonstrated the analytical result of heavy metal pollution caused by JACW in the soil of Lotus Pool, where located in the Northeast of China. 10 typical soil samples were taken, in which 7 heavy metal elements were quantified by ICP-MS. By calculating the Nemerow Index and the ecological potential risk index, the pollution degrees and risk assessment of most sites were evaluated.

1. Introduction
During the World War II, the Japanese army widely used the chemical weapons in the battle field [1, 2]. Especially in the Northeast of China, the Japanese army developed and produced a large amount of chemical agents and weapons, which were abandoned locally when defeated [3]. After the past 70 years, the shell of most weapons was corroded seriously, leading to the leak of chemical agents, which threatened the water source and soil quality [3]. Although, most leaking chemical agents degraded in the ambient circumstances, 80% of the chemical agents composed of arsenic or other heavy metal elements [4], such as lewisite, diphenyl nitrile arsenic, diphenyl chloroarsine, arsenic trichloride and so on [5, 6], posed a constantly severe risk to the environment and public safety, because the heavy metal compounds might be enriched by plant and eventually harm the health of human beings [7].

Lotus Pool is a small town locating in the Northeast China, which has a beautiful name and once had a wonderful sight also. However, this area was heavily polluted by JACW since the Japanese invasion. Ten years ago, this town had been chosen as one of the testing points to examine the restoring effect of Pteris vittata by the Institute of Chemical Defense. This plant can enrich the arsenic compound from the soil specifically [8]. In this work, the concentration and distribution of the heavy metals in the soil of Lotus Pool were investigated, aiming to evaluate the remediation efficiencies and assess the potential ecological risk.
2. Experiment

2.1. Sampling

Sampling sites were chosen along the road started from the testing greenhouses that we set to restore the As pollution by Pteris vittata (shown as Figure 1). The geography parameters of the sampling sites were surveyed by GPS and listed in the Table 1 as well as other characters such as color, humidity, plant cover, gravel amount and so on. The soil samples were dig from 5 points randomly selected in the area of 1 m × 1 m on the sampling sites and mixed together. The size of each sampling point kept 5 cm (long) × 5 cm (wide) × 20 cm (depth). The soil samples were held in the sealed plastic bag and stored in dark place under -20 °C.

| Table 1. The information of soil samples |
|-----------------------------------------|
| Geography Parameter | Longitude/E | Color | Humidity | Plant | Gravel | Other |
|----------------------|-------------|-------|----------|-------|--------|-------|
| 01 43°36′26.146″ N   | 128°36′35.796″ E | Dark  | Damp     | Lot   | Few    | Greenhouse inside |
| 02 43°36′25.874″ N   | 128°36′36.110″ E | Dark  | Damp     | Lot   | Few    | Greenhouse outside |
| 03 43°36′26.151″ N   | 128°36′37.331″ E | Dark  | Damp     | Lot   | Few    | Farmland |
| 04 43°36′25.489″ N   | 128°36′38.973″ E | Dark  | Damp     | Lot   | Few    | Farmland |
| 05 43°36′24.339″ N   | 128°36′41.100″ E | Dark  | Damp     | Lot   | Few    | Farmland |
| 06 43°36′22.677″ N   | 128°36′42.663″ E | Dark  | Damp     | Lot   | Lot    | Farmland |
| 07 43°36′20.725″ N   | 128°36′43.685″ E | Dark  | Damp     | Lot   | Few    | Farmland |
| 08 43°36′18.253″ N   | 128°36′46.298″ E | Dark  | Dry      | Few   | Lot    | Farmland |
| 09 43°36′16.077″ N   | 128°36′48.877″ E | Dark  | Damp     | Lot   | Few    | Farmland |
| 10 43°36′14.524″ N   | 128°36′51.823″ E | Dark  | Damp     | Lot   | Few    | Farmland |

2.2. Determination of the Metal Contents in Soil

The fine soil samples were digested according to Method 3051A (USEPA 2007) with minor modification. The mixture of HNO3 and HCl (3:1, v/v) was employed to extract heavy metals from soil samples using microwave digestion. The digestion solutions were filtered through 0.45-μm cellulose acetate membrane filters and then made up to 50 mL by ultrapure deionized water (18.2 MΩ cm−1). The concentrations of heavy metals were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). The method detection limits were 195, 7, 10, 52, 74, 56, and 108 μg/kg for As, Cd, Cr, Cu, Mn, Pb, and Zn, respectively. A method blank was performed throughout the entire pretreatment procedure for each batch of sample preparation. The digestion efficiency was verified using certified reference material (CRM) soil GBW07444 (urban dust) obtained from CRM/RM Information Center (Beijing, China). The recoveries for all investigated metals were in the range of 85–105 %.
3. Results and discussions

3.1. Heavy metal Concentrations

The contents of seven elements including As, Mn, Cu, Zn, Pb, Cd and Cr in the soil from the 10 sampling sites in Lotus Pool were presented in Table 2. As shown in Figure 1, Site 01 and Site 02 were both contaminated by JACW. Site 01 was treated by the Pteris vittata inside the green house while Site 02 was outside the green house without remediation. Comparing the As contents in Site 01 and 02, the value in Site 01 declined by 31%, confirming that the hyperaccumulator applied inside the green house was effective. In contrast, the contents of other metals in these two sites were quite similar, suggesting that the enrich capacity of the Pteris vittata was specific to As. Furthermore, the As contents in Sites 03~10 decreased with the distances away from Site 02 in general, except for Site 09, so there was a strong possibility that the pollution of As in the investigated area was mainly originated from Site 02, which was strongly influenced by JACW.

The pollution caused by other toxic elements in this area were also unignorable. The mean value for Mn (1213 mg/kg), Cu (31.26 mg/kg), Zn (101.1 mg/kg), Pb (130.5 mg/kg), Cd (0.14 mg/kg) and Cr (151.4 mg/kg) were 0.3, 0.6, 0.5, 4.4, 0.8 and 1.6 times higher than the background values, indicating the existing heavy metal pollutions especially for Pb and Cr. As shown in Table 3, Cu, Pb, Cd and Cr were found significantly positively correlated (P < 0.01). On the other side, As was not significantly correlated with any other elements. The results here suggested that the contaminations of Cu, Pb, Cd and Cr in Lotus Pool were likely derived from local geological activity, while As pollution was probably derived from JACW.

Table 2. The results of quantitative analysis of 7 metal elements in the soil samples (mg/kg)

|      | 01  | 02  | 03  | 04  | 05  | 06  | 07  | 08  | 09  | 10  | Background values |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|------------------|
| As   | 30.37 ±2.13 | 44.50 ±3.56 | 40.44 ±2.02 | 36.66 ±2.20 | 27.97 ±2.80 | 6.91 ±0.41 | 8.73 ±0.52 | 6.16 ±0.31 | 12.14 ±0.85 | 6.88 ±0.62 | 6.3 |
| Mn   | 1372 ±137 | 1292 ±155 | 1260 ±176 | 1049 ±157 | 887 ±108 | 1134 ±193 | 1291 ±132 | 1200 ±182 | 1402 ±173 | 963 |
| Cu   | 38.51 ±3.08 | 39.11 ±3.52 | 37.41 ±2.62 | 33.98 ±2.08 | 18.06 ±2.79 | 29.51 ±1.63 | 31.03 ±2.43 | 34.70 ±2.25 | 32.19 |
| Zn   | 104.4 ±8.4 | 92.3 ±6.4 | 106.8 ±10.7 | 102.8 ±8.3 | 71.9 ±4.6 | 91.1 ±8.7 | 96.9 ±9.0 | 128.1 ±7.3 | 112.1 ±6.7 | 104.2 |
| Pb   | 174.8 ±12.2 | 166.6 ±10.7 | 159.9 ±7.2 | 125.1 ±4.3 | 81.4 ±4.6 | 138.8 ±8.7 | 131.1 ±9.0 | 120.7 ±7.3 | 133.5 |
| Cd   | 220.1 ±15.4 | 207.8 ±12.0 | 194.5 ±13.7 | 151.8 ±6.5 | 80.2 ±11.8 | 131.7 ±12.5 | 135.7 ±6.6 | 54.7 ±6.0 | 145.5 |
| Cr   | 6.3 |

Table 3. Pearson’s correlation matrix for heavy metal concentrations

|     | As    | Mn    | Cu    | Zn    | Pb    | Cd    | Cr    |
|-----|-------|-------|-------|-------|-------|-------|-------|
| As  | 1.0000| 0.7355| 0.1820| 0.3996| 0.1808| 0.0512| 0.1298|
| Mn  | 0.1000| 0.0436*| 0.0874| 0.0868| 0.8418*| 0.0401*| 0.0000**|
| Cu  | 0.0100| 0.8235| 0.0001**| 0.0216*| 0.0000**| 0.0000**| 0.9636|
| Zn  | 0.0100| 0.8427| 0.0578| 0.0057*| 0.0003**| 0.0004**| 0.1000|
| Pb  | 0.0100| 0.0057*| 0.0003**| 0.0004**| 0.0000**| 0.0000**| 0.1000|
| Cd  | 0.0100| 0.0057*| 0.0003**| 0.0004**| 0.0000**| 0.0000**| 0.1000|
| Cr  | 0.0100| 0.0057*| 0.0003**| 0.0004**| 0.0000**| 0.0000**| 0.1000|

* Correlation was significant at the 0.05 level (two-tailed)
** Correlation was significant at the 0.01 level (two-tailed)
3.2. Risk Assessment

Considering the existing heavy metal pollution described above, risk assessment for the soil in Lotus Pool was quite necessary. The Nemerow comprehensive index was demonstrated in Figure 2(a). The Ps values of the sampling sites ranged from 2.43 to 5.61. Referring to the Ps category, the pollution degrees of Sites 01, 02 and 03 were seriously contaminated (Ps > 5). Moreover, the pollution degrees of Sites 04, 05, 06, 07, 09 and 10 were strongly contaminated (3 < Ps < 5). Only Site 08 was moderately contaminated (2 < Ps < 3).

The potential ecological risk was illustrated in Figure 2(b). The ecological risks were mainly resulted by As, Cd and Pb, and the RI ranged from 95 to 156. According to the category of RI, the heavy metals posed an overall considerable potential ecological risk in the investigated region.

![Figure 2](image)

**Figure 2.** Risk assessment for heavy metals in soil of Lotus Pool: (a) Nemerow Index; (b) ecological potential risk index.

4. Conclusion

The pollution degree and spatial distribution of heavy metals in the soil of Lotus Pool were investigated in this study. The concentration of As, Mn, Cu, Zn, Pb, Cd and Cr were determined by ICP-MS method. The restoration by the Pteris vittata was proved to be effective. However, the remained As content in the treated site was still much higher than the background value, and this plant could not deal with the pollutions of Pb, Cd and Cr. The pollution degrees of most sites were seriously contaminated, and the potential ecological risk in the region was considerable in general. Thus a comprehensive restore strategy was necessary for the JACW influenced regions.

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References

[1] Hanaoka, S., K. Nomura, and T. Wada, Determination of mustard and lewisite related compounds in abandoned chemical weapons (Yellow shells) from sources in China and Japan. Journal of Chromatography A, 2006. 1101(1-2): p. 268-277.

[2] Hanaoka, S., K. Nomura, and S. Kudo, Identification and quantitative determination of diphenylarsenic compounds in abandoned toxic smoke canisters. Journal of Chromatography A, 2005. 1085(2): p. 213-223.

[3] Zhou, T., et al., Conversion and Species Distribution Characteristics of Arsenical Chemical Agent in the Soil Contaminated by Chemical Weapons Abandoned by Japan. Advanced Materials Research, 2014. 955-959: p. 1194-1203.

[4] Xin-Ling, C., G. Ying-Qiang, and M.A. Guo-Hua, Discussion on management of hazardous
chemicals in on-site laboratory for JACW. Chemical Engineer, 2012.

[5] Yang, J.X., et al., The research of total arsenic analysis for JACW samples by microwave digestion and GFAAS. Chinese Journal of Analysis Laboratory, 2018.

[6] Niemikoski, H., et al., Identification of novel degradation products of sea-dumped chemical warfare agent-related phenylarsenic chemicals in marine sediment. Analytical Chemistry, 2020.

[7] Lin, F., H. Chen, and J. Bai, In Soil Environment Heavy Metal Pollution Harm Research. Environmental Science & Management, 2007.

[8] Xiao-Gang, G.U., et al., Non-polluting Ecological Centipede Grass on Arsenic Absorption and Transformation. Guangzhou Chemical Industry, 2016.