Health risk assessment of soil Contaminated by As-containing CWAs from JACW

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Abstract. The environmental investigation, sampling analysis and health risk assessment were carried out on the soil contaminated by As-containing chemical warfare agents (CWAs) from Japanese abandoned chemical weapons (JACW) in Northeast China, referring to “Technical Guidelines for Risk Assessment of Soil Contamination of Land for Construction”. The results indicated that the arsenic content in the contaminated sites exceeded the risk screening value. The health risks resulting from oral exposure were higher than those of other exposure pathways, and exceeded the acceptable level of human body. Therefore, the contaminated land must be carried out the soil remediation to reduce the risk to the acceptable level of human health before site development.

1. Introduction

During the war of aggression against China, Japan used and stored a large number of chemical weapons in China. In order to cover up their crimes when they were defeated and surrendered, these chemical weapons were secretly buried and discarded in China, with a wide distribution. At present, many JACW in China have not been found [1, 2]. The types of toxicants loaded in JACW included mustard gas, Louis agent, hydrocyanic acid, phosgene, diphenylcyanarsenide, diphenylchloroarsenide and chloroacetophenone, and so on. Among them, mustard gas, Louis agent and diphenylcyanarsine were the most, accounting for more than 95% of the total, and their common feature was that they all contained arsenic.

During the long burial process, these As-containing CWAs of JACW leaked and spread to the environment due to the corrosion of shells, accidental excavation, or other reasons. Then the surrounding environment was contaminated and the animals, plants were poisoned. So far, more than 2000 people have been injured or died. Most of the toxicants leaked into the soil are degraded, and the degradation products are also highly toxic [3]. Therefore, As-containing CWAs and their degradation products pose a significant practical and potential security threat to the surrounding environment and personnel.

Up to now, very few researchers have carried out the risk assessment of soil contaminated by As-containing CWAs from JACW. Therefore, on the basis of a comprehensive investigation of the contaminated land by As-containing CWAs from JACW, the health risk assessment of contaminated land was carried out according to the model and parameters recommended by “Technical guidelines for risk assessment of soil contamination of land for construction (HJ 25.3-2019)” [4] (hereinafter referred
to as “the GUIDELINES”). In this study, the recommended target value of soil remediation based on risk was proposed, which can provide basis for making remediation plan and later management of arsenic contaminated sites, and has great significance for the reuse and environmental management of similar contaminated areas.

2. Methodology

2.1. Study Area Description
In this study, the area contaminated by As-containing CWAs from JACW is located in the eastern mountainous area of Jilin Province, with latitude of 43.59° to 43.62°, longitude of 128.60° to 128.62° and altitude of more than 350m. It is a southeast northwest piedmont, sunny slope and valley below. The terrain is generally higher in Northeast and lower in southwest. It belongs to the cold wet alpine climate zone. The dark brown soil mainly formed by weathering and slope deposit of granite and basalt is weakly acidic [5].

2.2. Investigation on Soil Contamination
Since JACW were discovered in this area in 2004, Zhou Ting, et al conducted an environmental investigation in 2005 and 2006 [3, 6], covering an area of 26.19hm². It was confirmed that the arsenic contamination in this area came from the leakage of JACW. The general scope and degree of arsenic contamination were identified, and the specific forms of arsenic were analyzed [7]. However, due to the particularity of the destruction method and the long-term migration of arsenic in the soil, as well as the artificial disturbance of farming, digging up and recycling JACW [8], the distribution of arsenic content in this area was different from that caused by natural arsenic soil, arsenic-bearing slag or pollution from industry.

![Figure 1. The area of environmental investigation and soil sampling.](image)

In September 2020, we also conducted an environmental investigation in this area. Figure 1 showed the study area in this paper. In Figure 1, arsenic content in the soil which was in the zone of red star and black grid was the highest [9]. By field investigation, it was found that the site seriously contaminated by As-containing CWAs were isolated by wire meshes, and the weeds were overgrown inside the isolation area, which had been abandoned for many years. Outside the isolation area, there were farmland planted with soybeans and vegetables, bee breeding facilities, and several rural houses.

2.3. Sample Collection and Analysis
According to the distribution characteristics of arsenic in this area, samples were taken inside the barbed wire isolation area along the roadside. The soil samples were dig from 5 points randomly selected in the area of 1 m × 1 m on the sampling sites and fully mixed. The size of each sampling point kept 5 cm (long) × 5 cm (wide) × 20 cm (depth). Then the soil samples were held in the sealed plastic bag and stored in dark place under -20 °C. The total arsenic in soil samples was determined by the method specified in reference 10.
3. Hazard identification

3.1. Land-use Types
By data analysis and field investigation, the land-use types of the surrounding areas of the land contaminated by As-containing CWAs were mainly farmland, woodland and rural residence. At present, the contaminated land is in the state of unused land, and its future land-use types should be consistent with the surrounding areas.

According to Ministry of Ecological Environment on “Reply to the question of how to select the evaluation standard about the soil of forest land and unused land.” [11]: “Unused land can select corresponding evaluation standards by the future use type and protection target”. In this paper, health risk assessment is carried out by reference to the GUIDELINES. Thus, the future land-use type of unused land can be defined as the first type of land, residential land (rural housing).

3.2. Contaminant of Concern
Obviously, the contaminants of concern in the areas contaminated by As-containing CWAs were arsenic. By the analysis of soil samples, the results showed that the concentration of arsenic ranged from 6.163 to 44.502 mg/kg. Five of the ten samples were in the heavily contaminated area, and the average value of these five samples was 35.993 mg/kg, which exceeded the risk screening value (20 mg/kg) for soil contamination of the first type of land [12]. There may be risks to human health, so further risk assessment should be carried out to determine the risk level.

4. Exposure assessment

4.1. Exposure Scenarios Analysis
Under the first type of land use, children and adults may be exposed to land contamination for a long time and cause health hazards. For carcinogenic effects, considering the lifetime exposure of the population, the lifetime carcinogenic risk of arsenic contaminants was evaluated according to the exposure of children and adults; for non-carcinogenic effects, children with lighter weight and higher exposure were evaluated according to their childhood exposure.

4.2. Determination of Exposure Pathways
Exposure pathway refers to the way that contaminants in soil migrate to and are exposed to human body. Because the residents in this area do not use groundwater as drinking water source, and arsenic is not volatile, the following three exposure pathways are mainly considered:
(a) Mouth-intake-soil: people are directly exposed to soil contaminated areas, and inadvertently ingest contaminated soil by mouth, such as eating food adhered with soil.
(b) Skin-contact-with-soil: the contaminated surface soil can be directly contacted through skin.
(c) Inhalation of soil particles: contaminants in soil contaminated areas enter the atmosphere through adsorption / absorption of inhalable particles, and are exposed to people by breathing.

4.3. Exposure Dose Calculation
For the carcinogenic and non-carcinogenic effects of contaminants, the exposure dose of sensitive people to contaminants in soil was calculated under each exposure pathway. The recommended model and values of each parameter referred to the GUIDELINES. The calculation results were shown in Table 1.

|          | Mouth-intake-soil | Skin-contact-with-soil | Inhalation of soil particles |
|----------|-------------------|------------------------|-----------------------------|
| Carcinogenic | 1.28×10<sup>-6</sup> | 1.23×10<sup>-7</sup>  | 6.51×10<sup>-9</sup>       |
| Non-carcinogenic | 9.99×10<sup>-6</sup> | 8.53×10<sup>-7</sup>  | 2.42×10<sup>-8</sup>       |
5. Toxicity assessment
Toxicity assessment is to analyze the hazard effect of contaminants on human health, that is, the relationship between contaminants concentration level and health response, including carcinogenic effect and non-carcinogenic effect, and determine the toxic parameters related to arsenic-containing pollutants, including reference dose, reference concentration, carcinogenic slope factor and unit carcinogenic factor, and so on. The calculation results were shown in Table 2 with reference to the recommended model and parameters in the GUIDELINES.

Table 2. Toxicity parameters of arsenic contaminants.

| Cancer Slope Factor of Oral Ingestion (mg·kg⁻¹·d⁻¹⁻¹) | Unit Carcinogenic Factor of Respiratory Inhalation (mg·m⁻³⁻¹) | Reference Dose of Oral Ingestion (mg·kg⁻¹·d⁻¹) | Reference Concentration of Respiratory Inhalation (mg·m⁻³) | Absorption Efficiency Factor of Digestive Tract (Dimensionless) | Skin Absorption Factor (Dimensionless) |
|------------------------------------------------------|---------------------------------------------------------------|-----------------------------------------------|-------------------------------------------------------------|------------------------------------------------------------|-------------------------------------|
| 1.5                                                  | 0.15                                                          | 0.0003                                        | 0.00015                                                     | 1                                                         | 0.03                                |

6. Risk assessment

6.1. Contamination Risk Calculation
Arsenic has both carcinogenic and non-carcinogenic hazards. It is necessary to calculate the carcinogenic risk and non-carcinogenic risk simultaneously. Referring to the model recommended by the GUIDELINES, the risk value of arsenic contaminant was calculated as shown in Table 3. The carcinogenic risk of arsenic was greater than 10⁻⁶, and the two exposure pathways of mouth-intake-soil and skin-contact-with-soil had the greater risk. The non-carcinogenic hazard quotient of arsenic was higher than 1, which had health risk to human body. And the contaminated land was designated as the area with unacceptable risk. Therefore, it is necessary to carry out soil remediation before the contaminated land is reused.

Table 3. Risk value of arsenic contaminants.

|                        | Mouth-intake-soil | Skin-contact-with-soil | Inhalation of Soil Particles | Total         |
|------------------------|-------------------|------------------------|------------------------------|---------------|
| Carcinogenic Risk      | 6.90×10⁻⁵         | 6.62×10⁻⁶             | 1.50×10⁻⁷                    | 7.58×10⁻⁵     |
| Non-carcinogenic Risk  | 2.40              | 0.205                  | 0.496                        | 3.101         |

6.2. Risk Contribution Rate Analysis
Figure 2 showed the contribution rates of carcinogenic and non-carcinogenic risks of As-containing contaminants with health risks through different exposure pathways. It can be seen from Figure 2 that among the carcinogenic risk of the contaminated site, the risk contribution rate of mouth-intake-soil was 91.07%, which was the most important exposure pathway. The next exposure pathway was skin-contact-with-soil, with a risk contribution rate of 8.74%; the risk contribution rate of inhalation of soil particles was only 0.20%, which can be ignored. Among the non-carcinogenic risks, mouth-intake-soil was also the main exposure pathway, with the risk contribution rate of 77.38%, followed by skin-contact-with-soil and inhalation of soil particles, with the risk contribution rates of 16.01% and 6.61%, respectively. Therefore, in the process of soil remediation, it is necessary to pay special attention to reducing the harm to human health by the exposure pathway of mouth-intake-soil, so as to reduce the arsenic content of soil particles below the risk level.
7. Determination of risk control value

The model recommended by the GUIDELINES was used to calculate the soil risk control values of comprehensive carcinogenic and non-carcinogenic effects of various exposure pathways. The results were 0.475 mg/kg and 11.6 mg/kg, respectively. The smaller value, namely 0.475 mg/kg, was selected as the risk control value of the contaminated site. According to the GUIDELINES, the risk control value calculated based on the risk assessment model should be taken as the main reference value when determining the target value of contaminated soil remediation, and the recommended target value of arsenic in soil remediation was 0.475 mg/kg. To achieve this target value, a more feasible approach of soil remediation is phytoremediation. Planting plants that can quickly and efficiently enrich arsenic, such as Pteris vittata [13, 14], should be harvested, transplanted and managed regularly by special persons to improve the efficiency of soil remediation.

8. Conclusion

The distribution of arsenic content in the area contaminated by As-containing CWAs from JACW was different from that caused by natural arsenic soil, arsenic-bearing slag or pollution from industry. The area with serious arsenic contamination had been isolated and no one had paid attention to it for many years. And its future land-use type can be defined as the first type of land, residential land (rural housing). The carcinogenic risk of arsenic in the contaminated area was greater than 10^-6, and the non-carcinogenic hazard quotient was higher than 1, which was unacceptable risk area. For carcinogenic risk and non-carcinogenic risk, mouth-intake-soil was the main exposure pathway, and the risk contribution rates were 91.07% and 77.38%, respectively. The soil risk control value of arsenic and the recommended target value of soil remediation were 0.475mg/kg. It was recommended to plant highly arsenic-enriched plants for soil remediation, to reduce the risk to the acceptable level of human health and realize the safe reuse of contaminated land.

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