Level and Risk Assessment of Arsenic in Muti-Media near Mining Area in Yunnan by Using Inductively Coupled Plasma Mass Spectrometry

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Abstract Arsenic (As) pollution not only affects soil fertility and crops growth, but also exposes to humans through air, soil, water and food, posing a major threat to human health. Mineral exploitation is one of the most important sources of As environmental problems. In this study, the nine villages (S_1—S_9) in the vicinity of a Pb-Zn mining area in Yunnan province were chosen as study area, and the county town 20 km away from mining was selected as reference area (S_{10}). The samples including 76 cultivated soils, 306 crop/vegetables and 86 human hairs were collected. Microwave digestion was used to pretreat these samples by controlling the three variables of acid dosage, temperature and duration to get the optimal solution of muti-media. The Inductively Coupled Plasma Mass Spectrometry (ICP-MS) were used to determine the contents of As in order to investigate the As pollution level and human health risk in muti-media. The results will provide a reference for policy decision on the prevention and treatment of As pollution caused by mining. Results showed that: (1) after these samples were pretreated by microwave digestion, As detection limits for soil, crops and human hair ranged from 0.01 to 0.12 $\mu g \cdot L^{-1}$, and accepted recoveries ranges were 92.43%～112.23% (soil), 97.88%～114.72% (crop/vegetable) and 91.44%～109.65% (hair), respectively, and relative standard deviation was less than 5% with satisfactory results. (2) The mean content of As in soil was 70.66 $mg \cdot kg^{-1}$, which was 3.84 times higher than that of the background value in Yunnan province. According to GB 15618—1995 of "soil environmental quality standard" (Grade Ⅱ) and the single-factor pollution index (P_i), cultivated soil was severely polluted by As. Furthermore, the highest As content was detected in S_1, which might be closely related to the mining, smelting and transportation for many years. In crop/vegetables samples, the mean As content of tuber-vegetables was 1.75 $mg \cdot kg^{-1}$, followed by leafy-vegetables (0.77 $mg \cdot kg^{-1}$), which was higher than the maize (0.52 $mg \cdot kg^{-1}$) and root-vegetables (0.51 $mg \cdot kg^{-1}$). Based on the maximum permissible standard set by China, the excessive rate of As content in crops was 80.64%. (3) The potential health risk assessments of As exposed to multiple pathways among local residents were evaluated by the hazard index (*HI*), the total carcinogenic risk (*TCR*), the target hazard quotient (*THQ*) and carcinogenic risk (*CR*), respectively. The total non-carcinogenic risk of As for adult and child were 1.13～1.20, which was unacceptable risk. The carcinogenic risk was as high as 10^{-3}, exceeding the general risk acceptable level (10^{-4})

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recommended by the United States Environmental Protection Agency (USEPA). Besides, diet was the dominant exposure pathway. The *THQs* (>1) and *CRs* ($>10^{-4}$) of As in vegetables showed that a potential risk did exist, and the *TCR* of As for child was higher than that for adult. In view of high As risk of vegetables grown in local area, so we suggested that the nonlocal foods were input to avoid health risks of As pollution and those crops whose edible parts are not easy to accumulate As should be largely planted. (4) The contents of As in hair samples in mining area were 0.97 $\mu g \cdot g^{-1}$, which was 4.41 times higher than that in $S_{20\ km}$ (0.22 $\mu g \cdot g^{-1}$) ($p<0.05$) and beyond the recommended standard of the Ministry of Health (0.6 $\mu g \cdot g^{-1}$). The contents of As from male were higher than that from female, and the Group Ⅱ (19～40 years) were higher than Group Ⅲ (≥41 years). It meant that the males in 19～40 years who acted as the major participant in mining and smelting activities were more vulnerable to exposure to As than others. (5) This study provided a powerful basis for the As pollution level in muti-media of the mining area, but also for the assessment of As exposure risk to local human health.

Keywords　Arsenic; Risk assessments; Mining area; Inductively coupled plasma mass spectrometry

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Introduction

Arsenic (As) is either consumed passively by humans or incorporated into fodder for poultry and livestock[1]. Excessive As in agricultural soil can reduce soil productivity, lower the quality of crops, and pose a threat to human health via food consumption[2]. Long term As consumption gave rise to several human diseases which included reproductive, neurological, cardiovascular, and diabetic effects in human[3]. As has been documented to cause skin, bladder, and lung cancer[4], the World Health Organization (WHO) and International Agency for Research on Cancer (IARC) have recognized As as a carcinogen. Numerous epidemic-like health accidents linked to As contamination have happened in recent years[1], and hundreds of thousands of people in the world already have been affected by the As contamination[5].

In this study, the US EPA model by calculating the hazard index (*HI*) and the total carcinogenic risk (*TCR*) for As in soil and the target hazard quotient (*THQ*) and the total carcinogenic risk (*CR*) for As in crop/vegetables [6] was employed to estimate the human health risk in human hair samples and was used to assess exposure level because human hair can provide a more permanent record on chemical elements associated with normal and abnormal metabolism from a long-term period [7], thus it is a useful biomonitoring tool to assess the extent of chemical element exposure to residents[8]. Literature (Baker et al[9], Huang et al[10], Trojanowski et al[7]) reported that the contents of As in hair are affected by age and gender and decrease with age in the high As exposure population.

The production and output value of Pb, Zn, Cu, Sn minerals from Yunnan Province leap into the front ranks of China, and Pb-Zn smelting industries is classified as key prevention and control industry, and As is mostly associated with Pb-Zn mines in nature, and the process of non-ferrous metal mining causes the removal of arsenide, leading to As pollution[8], thus the As are listed as one of the focuses of pollutants prevention and control. Although the groundwater contamination by As is already considered as a serious and severe global environmental problem, but little is known about diet as an additional source of arsenic exposure near mining area in Yunnan. Therefore, the identifications of As contaminated level in soil and crop/vegetables, daily dietary intake of As and associated health risk assessment are urgent for local residents around the mining area.

1　Experimental

1.1　Apparatus and Reagents

Agilent 7700 inductively coupled plasma mass spectrometer (Agilent Technologies, USA), the operating parameters were listed in Table 1; Milli-Q laboratory water purification system (Millipore, USA); MDS-10 high throughput microwave digestion instrument (Shanghai Sineo Microwave Chemistry Technologies, China).

1 000 $mg \cdot L^{-1}$ As standard solution (IERM, China); Multi-element mixed solution of internal standard (Agilent, USA); 65% HNO_3, 29%～32% H_2O_2, 40% HF (Sinopharm Chemical Reagent Beijing Co., Ltd, China); GBW 07403 (soil), GBW 07602 (vegetable) and GBW 0901 (hair) (National Standard Sample Study Center, China).

Table 1 Operating parameters of ICP-MS

Parameters	Numerical Value
RF power/W	1 550
Nebulizer gas flow/($L \cdot min^{-1}$)	0.9 (0.6～1.0)
Auxiliary gas flow/($L \cdot min^{-1}$)	0.25 (0.3～1.0)
Sampling depth/mm	8 (7～10)
Peristaltic pump speed/rps	0.1 (0.1～0.3)
Sample cone/mm	1.0
Skimmer cone/mm	0.7

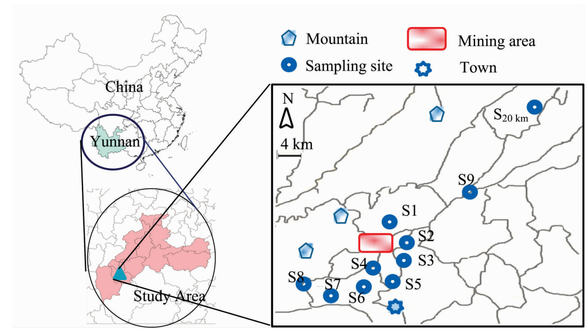

Fig. 1 Sampling sites of the study area

1.2 Samples Collection

In this study, the nine villages (S_1—S_9) around a Pb-Zn mining area in Yunnan province were determined as study area, and the county town 20 km away from mining was selected as reference area (S_{10}). The samples including 76 cultivated soils, 306 crop/vegetable and 86 human hairs were collected, respectively (Fig. 1). The crops/vegetables samples included 51 maize (crop, as a staple crop) and ten kinds of vegetables, which were leafy vegetables (24 Chinese cabbages, 16 pak-choi, 22 scallions, 17 garlic, 14 lettuces, 9 parsley, 17 tine peas and 16 spinach), tuber vegetables (96 potatoes) and root vegetables (24 radishes), respectively. The soil samples (0～10 cm depth) below the crop/vegetables were also collected. To characterize the exposure levels, 60 no colored or treated hair samples from local inhabitants and 26 hair samples from $S_{20\ km}$ area were collected.

1.3 Samples Pretreatment

Hair samples were washed according to the procedure recommended by the IAEA Advisory Group (acetone, three times water, acetone) to remove surface dirt and grease. The collected crop/vegetables were dried in oven for 24 h at 70～80 ℃, and the soil samples were air-dried at room temperature and the washed hair samples were dried at about 50 ℃ to constant weight. The samples (0.1 g) of dried and ground soil, vegetable and the hair which were cut into pieces less than 1 cm long and were digested according to the conditions of Table 2, and the As contents were measured by using inductively coupled plasma mass (ICP-MS) spectrometry (Agilent Technologies, USA).

Table 2 Microwave digestion conditions of samples

Sample type	HNO_3/mL	H_2O_2/mL	HF/mL	Programming Temperature/Heating time
Soil	6	1	2	120 ℃/6 min, 160 ℃/5 min, 200 ℃/5 min, 240 ℃/5 min
Crop/vegetable	7	1	0	120 ℃/5 min, 150 ℃/5 min, 175 ℃/5 min, 240 ℃/5 min
Hair	7	1	0	100 ℃/6 min, 130 ℃/5 min, 170 ℃/5 min, 200 ℃/5 min

1.4 Risk Assessment Methods

Contents of As in the soil and crops were assessed by single-factor pollution index (SFPI, $Pi=\frac{C_i}{S_i}$), and definition and calculation were referred to Ref. [11].

The human health risk models including non-carcinogenic hazard and carcinogenic risk assessment for all the elements through ingestion (CDI_{ing}), inhalation(CDI_{inh}), diet (EDI), and dermal contact (CDI_{der}) raised by USEPA, which were expressed as the hazard index (*HI*) and total cancer risk (*TCR*) for individual elements in soil while the target hazard quotient (*THQ*) and the carcinogenic risk (*CR*), respectively. The definitions of symbols and parameters were referred to Ref. [12]

2 Results and Discussion

2.1 Quality Control and Quality Assurance

Quality assurance and quality control were assessed using the analysis of duplicate samples, method blanks and standard reference materials. Precision and accuracy for As analysis in different samples were verified using the standard reference materials [GBW 07403 (soil, China), GBW 07602 (vegetable, China) and GBW 0901 (hair, China)]. Accepted recoveries ranges were from 92.43% ～ 112.23%, 97.88% ～ 114.72%, and 91.44%～109.65% for soil, crop/vegetable and hair samples, respectively. The difference of ≤5% between the determined and certified values of As contents were considered acceptable.

2.2 The Pollution Levels of As in the Multiple Media

2.2.1 The pollution levels of As in the soil and vegetables

In this study, the contents of total As ($mg \cdot kg^{-1}$ dw) in the different samples were shown in Fig. 2. The highest As content of soil was detected in S_1 sampling site (100.53 $mg \cdot kg^{-1}$), because the S_1 was the nearest sampling site from mining area, and the mean content of As in the soil samples was 3.84 times higher than that of the background value in Yunnan province (18.4 mg • kg^{-1}). The single-factor pollution index (P_i) of As in soil varied from 2.22 to 3.26, which reached heavy pollution. The possible reason was that As was associated with Pb-Zn mines in nature, and the long-term Pb-Zn mining smelting caused the removal of arsenide, leading to As pollution and irrational use of pesticides and chemical fertilizers led to As pollution in the soil.

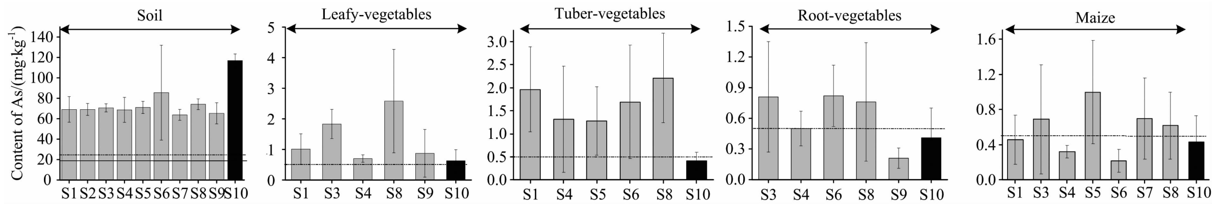

Fig. 2 Statistical comparison of As contents (mg • kg^{-1}, mean±SD), their respective Chinese National Quality Value (dotted line) and the background values of Yunnan province (solid line) in soil, leafy-vegetables, tuber-vegetables, root-vegetables and maize at different localities

As shown in Fig. 2, the As contents varied from different vegetables ($p<0.05$), and the As contents in tuber-vegetables and leafy-vegetables were higher than that in others, and the mean were 1.75 and 0.77 mg • kg^{-1}, respectively, followed by maize (mean value=0.52 mg • kg^{-1}) and root-vegetables (mean value=0.51 mg • kg^{-1}). The variation of As contents in all sorts of vegetables might be due to variable capabilities of absorption and accumulation of As, variations in growth period and growth rates. It was very interesting that As contents in tuber-vegetables were much higher than that in others, indicating that this vegetable (potato) had the potential bioaccumulation for As. The contents of As in crops were similar to that in $S_{20\ km}$. Compared with the threshold values issued by the Chinese Ministry of Health and WHO/FAO (2007), the As contents in agricultural crops were beyond the limits of food safety and the exceeding standard rate was 80.64%, which suggested a potential risk in view of product quality and human health. In this study, As levels in the agricultural food crops was high because the soil was rich in As, coinciding with the result that the soil was seriously polluted by As mentioned above.

2.2.2 The exposure level of As in hair samples

The contents of As in different gender and age hair samples were detected for local and $S_{20\ km}$. (Fig. 3). The Kolmogorov-Smirnov test showed that the contents of As ($p<0.05$) in local area samples appeared to a normal distribution and varied from 0.01 to 9.10 mg • kg^{-1}, with the mean value approximately 4.41 times higher than that in $S_{20\ km}$. Therefore, the high As levels in hair showed that the people living in the exposure area might be at high risk of toxic chemical element exposure.

Results found that at local area, hair As contents were observed comparatively higher in the male populations (2.71 mg • kg^{-1}) than the females (0.89 mg • kg^{-1}), which was consistent with the study of Baker[8]. Variabilities among individuals were based on their susceptibilities in As accumulation and genetic differences. The possible reason is that their occupational exposure in mining, smelting and welding activities where the As is irreversibly adsorbed on human hair.

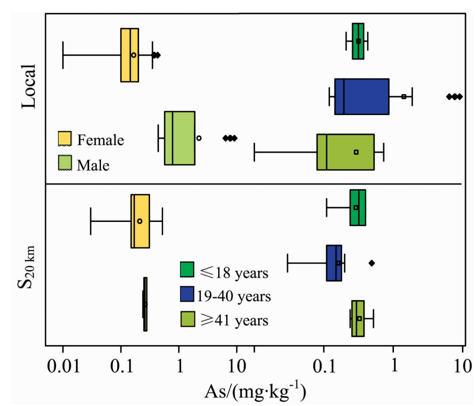

Fig. 3 Box-plot diagram of As for the subjects by gender and ages

Male ($n=36$), Female ($n=24$), ≤18 years ($n=18$), 19～40 years ($n=28$), ≥41 years ($n=14$). Middle band, box and whiskers represented the median, 25th and 75th percentile, and 5th and 95th percentile, respectively. Circles represented the mean value, whereas "*" represented extreme values

In this study, based on the frequency and intensity of outdoor life and work for study population, the participants were divided into three groups (Fig. 3): Group Ⅰ (≤18 years, $n=18$), Group Ⅱ (19～40 years, $n=28$) and Group Ⅲ (≥41 years, $n=14$). In local area, the As contents in hair observed that Group Ⅱ were higher than other groups, indicating that this group people were the main participants in mining and metallurgy activities, having more opportunity to accumulate As by inhalation and dermal contact. On the contrary, Group Ⅱ was the lowest contents in reference area ($S_{20\ km}$) due to the difference of work types. Notably, the mean content of As in the hair samples of different age groups in the local area was higher than that of the corresponding age group in the $S_{20\ km}$ area, revealing that As was an important element to endanger the health for the residents.

2.3 Human Health Risk Assessment of As

Human exposure to As near the study mining area occurred directly through ingestion, dermal contact and inhalation in soil or consumption of locally grown vegetables and crops, and the health risks to residents through above pathways were assessed by estimating target hazard quotients (*THQ*) and cancer risk (*CR*). Table 5 summarized the results of the actual exposure assessment for adult and child exposed to As through four exposure pathways around mining area. When the *THQ* value was greater than 1, it indicated that a potential health risk might exist. The *THQs* of As in vegetables through diet (>1) were the highest among all pathways, indicating that a potential non-carcinogenic risk might exist. The *THQs* of As from consumption vegetables was in the order of Chinese cabbages>spinach>scallions>radishes>pakchoi>lettuces garlic>potatoes>tine peas >parsley>maize. However, we found that the non-carcinogenic risks from soil by three pathways were relatively lower than diet through consumption of agricultural crops. The *HI* values of As (the sum of all *THQs*) through four main pathways for adult and child were 4.67 and 4.23, respectively.

Table 5 Non-carcinogenic and carcinogenic risk assessments for adult and child exposed to As through four exposure pathways around the mining area

Media	Pathways	CDI/EDI ($mg \cdot kg^{-1}$ bw $\cdot$ day^{-1})		HQ/THQ		Total HQ/THQ		CR		TCR	
		Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child
Soil	Ingestion	4.13×10^{-5}	8.48×10^{-5}	4.13×10^{-2}	8.48×10^{-2}	0.041	0.085	7.78×10^{-5}	3.03×10^{-4}	1.12×10^{-4}	3.37×10^{-4}
	Dermal contact	1.69×10^{-7}	4.40×10^{-7}	1.69×10^{-4}	4.40×10^{-4}			7.56×10^{-7}	4.14×10^{-7}		
	Inhalation	1.73×10^{-8}	1.73×10^{-8}	1.73×10^{-5}	1.73×10^{-5}			3.34×10^{-5}	3.34×10^{-5}		
Leafy-vegetables	Diet	1.41×10^{-3}	1.02×10^{-3}	1.41	1.02	1.16	1.04	2.01×10^{-3}	1.96×10^{-3}	1.66×10^{-3}	2.00×10^{-3}
Root vegetables		5.82×10^{-4}	5.67×10^{-4}	5.82×10^{-1}	5.67×10^{-1}			1.12×10^{-3}	1.09×10^{-3}		
Tuber vegetables		2.00×10^{-3}	1.94×10^{-3}	2.00	1.94			3.85×10^{-3}	3.75×10^{-3}		
Maize		6.39×10^{-4}	6.22×10^{-4}	6.39×10^{-1}	6.22×10^{-1}			1.23×10^{-3}	1.20×10^{-3}		

Concerning carcinogenic risk (*CR*) of As, the *CR* of vegetables and soil varied from 1.12×10^{-4} to 8.30×10^{-3} ($>10^{-4}$), indicating that the potential risk was not negligible both for adult and for child. Similar to non- carcinogenic risk, vegetables consumption played key role in As exposure and risk, and the order of *CR* value from vegetables was the same as *THQ* as well. Notably, the *TCR* of As (the sum of all *CRs*) for child was higher than that for adult, concluding that concern has particularly focused on child, because As could harm brain and nervous system development in childhood.

In soil and agricultural crops, the relative contribution of human health risk for As was compared between adult and child (Fig.4). The intake of tuber-vegetables was the major source of As exposure, accounting for 42.77%～46.24% of the estimated total risks in the study area. Interestingly, for cancer risk of As, soil ingestion, dermal contact and inhalation for child were a relatively important factor. The possible reason was that their hand to mouth activities and playing time increases the chance of exposure to contaminated soil. Among all the main exposure pathways, the most important exposure pathway for As appeared to be the diet of locally grown vegetables, with about several times as much as that through soil and maize.

These results indicated that the high As contents in vegetables were mainly due to enrichment from the soil, and the adult and child living around the mining area might experience adverse health effects based on the contribution of vegetables to the intake of As. The reducing the source of As to relieve soil pollution and controlling the intake of contaminated vegetables were the reliable ways to control the human health risk.

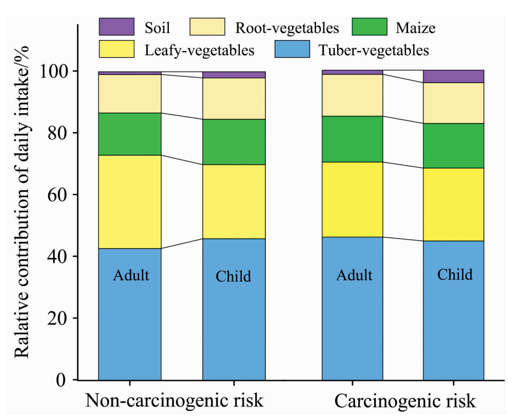

Fig. 4 Relative contribution profile of human (adult and child) health risk, including non-carcinogenic and carcinogenic risks. Relative contribution was derived by dividing the risk estimate from a given source by the total risk from all sources under investigation

3 Conclusions

In this study, the soil samples showed severe As pollution and the As contents in all agricultural food crops were beyond the food safety limits. Diet from vegetables was the main contributor to the *THQs* and *CRs* of As among all pathways, and a potential non-carcinogenic and carcinogenic risk might exist both for adult and for child. Particularly, the *TCR* of As for child was higher than that for adult. We recommend that local people should not consume a large number of these vegetables and avoid the accumulations of As in the body. Furthermore, males were more vulnerable to exposure to As than females. Thus, an urgent and systematic study of As in soils growing vegetables and an assessment of pollution source apportionment were recommended so that it could significantly decrease the intake of As, and thus contribute to the improved human health of the local residents.

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电感耦合等离子体质谱法研究云南某矿区周边不同样品中砷污染水平和风险评价

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摘　要　砷(As)污染不仅会影响土壤肥力和作物生长，而且还会通过空气、土壤、水和食物等途径暴露于人类，对人体健康产生重大威胁。矿产开采是 As 环境问题产生的重要来源之一。本文选择云南省某开采历史悠久的铅锌矿区周边 9 个村落(S_1—S_9)为研究区域，以 20 km 外的县城(S_{10})为对照区域，采集了 76 份土壤、306 份农作物和 86 份人发，利用微波消解对样品进行前处理，通过控制酸用量、温度和持续时间三个变量得到不同样品的最佳消解方案，并采用电感耦合等离子体质谱法(ICP-MS)测定各样品中 As 含量，以探究多介质中 As 污染水平并对人体暴露和健康风险进行评估，对当地矿产资源开采引起的 As 污染提出防治或改善建议。结果表明：(1) 经微波消解前处理后获得的土壤、农作物和人发样的 As 检出限为 0.01～0.12 $\mu g \cdot L^{-1}$，回收率分别为 92.43%～112.23%，97.88%～114.72%和 91.44%～109.65%，相对偏差小于 5%，结果令人满意。(2) 土壤中 As 的平均含量为 70.66 $mg \cdot kg^{-1}$，是云南土壤背景值 3.84 倍。参照 GB 15618—1995《土壤环境质量标准》二级标准和单因子污染指数结果，农田土壤受 As 污染为中度污染；在 S_1 采样点 As 含量最高，这可能与矿区多年开采、冶炼和运输密切相关。农作物样品中，块茎类蔬菜的 As 平均含量为 1.75 $mg \cdot kg^{-1}$，其次叶菜类为 0.77 $mg \cdot kg^{-1}$，玉米和根茎类蔬菜分别为 0.52 和 0.51 $mg \cdot kg^{-1}$。参照我国《食品中污染物限量》标准，研究区域的农作物样品中 As 含量超标率为 80.64%。(3) 采用风险评价指数(HI)、总致癌风险(TCR)、目标危害商数(THQ)和致癌风险(CR)对研究区域 As 通过多暴露途径对暴露人群产生的致癌风险和非致癌风险进行评价和分析。结果表明，土壤和农作物中 As 对成人和儿童的非致癌风险总和分别为 1.13～1.20，为不可接受风险，而致癌风险均在 10^{-3} 水平，大于美国环保局(USEPA)推荐的最高接受水平 10^{-4}，研究区居民有较大的致癌风险。饮食摄入是 As 主要暴露途径，研究区人群食用蔬菜的致癌风险均超过 10^{-4}，且儿童的总致癌风险高于成人。鉴于矿区周边蔬菜受 As 污染的高风险，我们

建议当地居民可以通过外地食物的输入来规避当地 As 污染带来的健康风险，也可以考虑在污染的耕地上种植食用部位不易积累 As 的农作物来替代原有作物以减小 As 污染带来的危害。(4) 矿区人发中 As 含量均显著高于县城($S_{20\ km}$，$p<0.05$)。其中矿区居民头发 As 平均含量（0.97 $\mu g \cdot g^{-1}$）是县城发 As 含量（0.22 $\mu g \cdot g^{-1}$）的 4.41 倍，超出卫生部推荐发 As 标准值(0.6 $\mu g \cdot g^{-1}$)。矿区男性发样 As 含量高于女性，随着年龄增长，矿区人发样中 As 含量水平呈现第二年龄组(Group Ⅱ，19～40 岁)高于第三年龄组(Group Ⅲ，≥41 岁)的趋势。这是因为处于 19～40 岁的男性是采矿冶炼等活动的主要参与者，是 As 的易感人群，具有较高的 As 暴露风险。(5) 本文为矿区多介质的 As 污染研究和居民人体健康风险暴露和评估提供有力的依据。

关键词 砷；风险评价；矿区；电感耦合等离子体质谱法

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