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Risk assessment and management of arsenic in source water in China

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1. Introduction

Source water quality is deteriorating rapidly for water pollution and human activities throughout the world as more and more domestic and industrial wastewater are discharged into source water [1–3], and it is therefore very difficult to keep drinking water sources safe enough to ensure the health of human being [4]. So much work has been done to find effective ways and means to keep high quality of source water. For example, it is clearly stated in the amendments of Safe Drinking Water Act in USA that each state is required to develop a Source Water Assessment and Protection Program (SWAP) in 1996 to protect public water systems from being contaminated by identifying and analyzing potential contaminant sources [5]. Sound policies were formulated in British Columbia, Canada to identify, document, and reduce watershed risks and to sustain clean and safe drinking water sources [6]. As the results of risk assessment, stakeholders and governments have worked out effective protection plans and management strategies.

The quality of drinking water sources in China is also deteriorating fast, and has caused some problems. All the governments at different levels are trying very hard to take various measures to control water pollution and protect drinking water sources in recent years. They adopted the Water Pollution Prevention and Control Law, delineated source water protection areas, worked out national environmental protection plan, implemented water pollution control programs etc. The concept of risk assessment and management

ABSTRACT

As part of our efforts to identify effective ways and means to keep source water safe, the concept of risk assessment and management is introduced in this paper to address the issue of risk assessment and management of arsenic in source water in China. Carcinogenic and non-carcinogenic risk are calculated for different concentrations of arsenic in source water using the corrective equation between potential health risk and concentration of arsenic in source water with purification process taken into consideration. It is justified through analyses that risk assessment and management is suitable for China to control pollution of source water. The permissible content of arsenic in source water should be set at 0.01 mg/L at present in China, and necessary risk management measures include control contaminated sources and improvement of purification efficiency.

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has been gradually introduced into the source water protection system of China.

According to the source water quality monitoring data published by Ministry of Environmental Protection (MEP) of China, arsenic has a very high detectable rate in source water. It has been proved through extensive research that arsenic is a toxic substance with adverse effects on human health [7]. In new *Water Quality Standards for Drinking Water* (GB5749-2006), the Ministry of Healthy in China lowered the permissible content of arsenic from 0.05 mg/L to 0.01 mg/L for centralized water supply.

The potential health risk caused by arsenic in China has been evaluated in this paper on the basis of background data of arsenic in source water and the arsenic removal efficiency of traditional purification processes, and then, the risk management measures has been suggested as the results of risk assessment and cost-effectiveness analysis.

2. Human health risk assessment method for pollutants in source water

The method developed by USEPA was used in this study to estimate the lifetime health risk of pollutants through oral ingestion [8]. The following are the basic equations used for lifetime cancer risk assessment and hazard index (*HI*) of pollutant *i* in drinking water:

$$cancer risk_i = CDI_i \times SF_i \tag{1}$$

$$HI_i = \frac{CDI_i}{RfD_i} \tag{2}$$

where cancer $risk_i$ is the carcinogenic risk of pollutant *i* in drinking water (unitless); HI_i is the hazard index of pollutant *i* in drinking

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Fig. 1. Frequency distribution of annual average arsenic content in surface water sources measured at 428 centralized drinking water sources in 2006 in China (ND: not detected).

water (unitless); SF_i is the slope factor for pollutant i (kg d/mg); RfD_i is the reference dose for pollutant i (mg/kg d); CDI_i is the chronic daily intake (mg/kg d) for pollutant i.

The equation for *CDI_i* is:

$$CDI_{i} = \frac{C_{i} \times L \times EF \times ED}{BW \times AT}$$
(3)

where C_i is the concentration of pollutant *i* in drinking water (mg/L); *L* is the daily water ingestion rate (L/day), taken as 2L/day; *EF* is the exposure frequency (days/year), taken as 365days/year; *ED* is the exposure duration (year), taken as 30 years for non-carcinogens and 70 years for carcinogens; *BW* is the body weight (kg), taken as 70 kg; *AT* is the average exposure time (in day), 30 years \times 365 days/year for non-carcinogens and 70 years \times 365 days/year for carcinogens. Source water can be drunk as drinking water only after being

purified. If the removal efficiency for pollutant *i* is R (%), the relationship between the concentration of pollutant *i* in source water (C_{i0}) and C_i can be expressed as:

$$C_{i0} \times (1-R) = C_i \tag{4}$$

Therefore, the relationship between the concentration of pollutant i in source water and the lifetime health risk by drinking water containing pollutant i can be established using the following



Fig. 2. Frequency distribution of annual average arsenic content in ground water sources measured at 297 centralized drinking water sources in 2006 in China (ND: not detected).

expressions:

cancer risk_i =
$$\frac{C_{i0} \times (1 - R) \times L \times EF \times ED}{BW \times AT} \times SF_i$$
 (5)

$$HI_{i} = \frac{C_{i0} \times (1 - R) \times L \times EF \times ED}{BW \times AT \times RfD_{i}}$$
(6)

If there are several pollutants in source water, the equations for total risk are established as shown below:

cancer risk_T =
$$\sum_{i=1}^{m} \left(\frac{C_{i0} \times (1-R) \times L \times EF \times ED}{BW \times AT} \times SF_i \right)$$
(7)

$$HI_{T} = \sum_{i=1}^{m} \left(\frac{C_{i0} \times (1-R) \times L \times EF \times ED}{BW \times AT \times RfD_{i}} \right)$$
(8)

where cancer risk_T is the total lifetime cancer risk of pollutants in drinking water (unitless); HI_{T0} is the total hazard index of pollutants in drinking water (unitless); *m* is the number of pollutants (unitless).

It is generally accepted that HI below 1 is considered to mean no significant risk of non-carcinogenic effects, and if the value of cancer risk is between 10^{-4} and 10^{-6} , it is believed that the carcinogenic risk is acceptable [9,10].

3. Current concentration of arsenic in source water

3.1. Centralized drinking water sources

MEP of China investigated the current concentration of total arsenic in 725 centralized drinking water sources in 19 provinces in 2006, including 428 surface water sources and 297 ground water sources. Figs. 1 and 2 show the frequency distribution of annual average arsenic content in investigated water sources. It can be seen from Fig. 1 that no arsenic is detected at 28 surface water sources and concentrations of arsenic less than 0.002 mg/L (including 0.002 mg/L) are detected at 152 surface water sources, and their accumulated percentage is 42.1%. Totally, the concentrations of arsenic are less than 0.01 mg/L (including 0.01 mg/L) at 96.3% of surface water sources. There is only one surface water source that has a concentration of arsenic of greater than 0.05 mg/L.

It can be seen from Fig. 2 that there are 33 ground water sources where no arsenic was detected and concentrations of arsenic of less than 0.002 mg/L (including 0.002 mg/L) were detected at 104 ground water sources, and their accumulated percentage of them is 46.1%. The concentration of arsenic at 98.3% of ground water sources is less than 0.01 mg/L (including 0.01 mg L). Only one ground water source has a concentration of arsenic of more than 0.05 mg/L.

3.2. Distributed drinking water sources

China has a rural population of about 900 millions, which approximately accounts for 70% of the national population, and about 63.5% of rural population is consuming distributed drinking water sources. Many distributed drinking water sources are wells and the water from wells is used for drinking without purification. The concentrations of arsenic in 208,820 wells were investigated by Chinese Center for Disease Control and Prevention and relative departments of 11 provinces in 2002–2004. Their findings indicate that the arsenic concentration in 182,044 wells satisfy the requirement of GB5749-2006, which account for 87.1%, and that the concentration of arsenic in 5474 wells exceeds 0.05 mg/L, which account for 2.6%.

Table 1

Technologies available for arsenic(V) removal and their efficiencies. Preoxidation may be required to convert As(III) to As(V).

Technology available	Maximum removal efficiency (%)
Ion exchange (sulfate 50 mg/L)	95
Activated alumina	95
Reverse osmosis	>95
Modified coagulation/filtration	95
Modified lime softening (pH > 10.5)	90
Electrodialysis reversal	85
Oxidation/filtration (iron:arsenic=20:1)	80

4. Technologies available for the removal of arsenic from water

4.1. Arsenic removal efficiency of available technologies

The removal of arsenic from water has attracted much attention from the research community in recent years. A variety of treatment processes has been developed including coagulation (precipitation), adsorption, ion exchange, membrane filtration, electrocoagulation, biological process, oxidation process and so on [11–13]. Coagulation and adsorption processes are most promising for the removal of arsenic from high-arsenic water because of its low cost and high efficiency, and are widely used in the developing world. However, they have not got the ability to bring the concentration of arsenic below 0.01 mg/L. According to Bissen and Frimmel's [14] and Wang et al.'s [15] research, membrane filtration process and ion exchange process can be used to bring the arsenic concentration from 0.048–0.087 mg/L to 0.005 mg/L. Table 1 shows seven technologies identified by USEPA as the best available technologies (BATs) [16].

4.2. Arsenic removal efficiency of simulated purification process

For economic reasons, almost all water treatment plants in China employ the traditional purification process including coagulation–sedimentation, sand filtration and disinfection. Advanced treatment processes, such as ion exchange, reverse osmosis, electrodialysis reversal, and membrane filtration, are still at the trial stage.

In order to investigate the removal efficiency of arsenic by traditional purification process in water treatment plants in China, the traditional purification process was simulated in lab and the arsenic removal efficiency was investigated under simulated condition using source water containing arsenic.

Two kinds of source water were used for simulation, one collected from Miyun Reservoir which supplies source water for Beijing, and called SW-A, and the other collected from Yuqiao Reservoir, and called SW-B. Water quality parameters of these two kinds of source water were tabulated in Table 2. The concentrations of arsenic in the two source water were kept at 0.03 mg/L, 0.04 mg/L, 0.05 mg/L and 0.06 mg/L by adding high-arsenic solution.

The simulation process consists of three steps: (1) coagulation–sedimentation; (2) filtration; (3) disinfection. A series of coagulation–sedimentation experiments were conducted with polyaluminium chloride (PAC) and ferric chloride (FeCl₃), which are widely used in water treatment plants in China.

Tuble 2	
Water quality	parameters of SW-A and SW-B.

Table 2

	TOC $(mg L^{-1})$	COD_{Mn} (mg L ⁻¹)	Turbidity (NTU)	UV254	рН
SW-A	1.786	2.25	4–6	0.03–0.05	8.3–8.5
SW-B	3.234	4.574	70–80	0.18–0.21	8.0–8.5



Fig. 3. Comparison of arsenic removal efficiency in simulated water treatment process: (a) SW-A, 1.0 mg/L PAC by coagulation; (b) SW-B, 10 mg/L PAC by coagulation; (c) SW-A, 10 mg/L FeCl₃ by coagulation; (d) SW-B, 140 mg/L FeCl₃ by coagulation.

The upper water after coagulation–sedimentation was filtrated through a millipore membrane (3 μ m aperture), and the filtrate was disinfected using NaClO as disinfectant. The dosage of NaClO is just right when the concentration of residual chlorine (as Cl₂) is 0.5 mg/L in 30 min from the addition of disinfectant.

The arsenic concentrations of samples collected through three steps were measured using an atomic fluorescence spectrometer, and the measurement results were shown in Fig. 3.

It can be seen from Fig. 3 that the arsenic removal efficiency obtained through coagulation–sedimentation with FeCl₃ used as coagulate is much higher than that obtained using PAC as coagulate. This means FeCl₃ is much more effective for the removal of arsenic by comparing Fig. 3(c) with (d), it can also be seen that when FeCl₃ is used as coagulate, the arsenic removal efficiency obtained in SWB through coagulation–sedimentation can be 77–80%, but only 15–17% in SWA. The results indicate that the removal of arsenic from water through coagulation–sedimentation not only depends on the properties of coagulates, but also the quality of water and the initial arsenic concentration in water.

According to the simulation results, the arsenic removal efficiency can be made more than 80% by optimizing the operational conditions including the selection of the right type of coagulates, increasing the dosage of coagulates, pH, retention time and

Table 3

so on. Actually, the management efficiency in water treatment plants makes obviouse difference. In order to keep safety margin, the arsenic removal efficiency obtained by traditional purification is taken as zero, which is full in line with the monitoring results of the State Urban Water Supply Management Center of China.

5. Health risk assessment of arsenic in source water in China

In the USEPA cancer classifications, arsenic belongs to Group A, and is an assured human carcinogen. The *RfD* and carcinogenic *SF* for arsenic through oral ingestion are 3×10^{-4} mg/kg d and 1.5(mg/kg d)⁻¹ respectively, as provided in the integrated risk information system (IRIS) at the web site of USEPA [17]. It is clearly stated in Section 4.2 that the removal efficiency of arsenic obtained through traditional purification is zero, i.e. *R* is 0. Therefore, the cancer risk and hazard index of arsenic by consumption at different concentrations of arsenic in source water can be calculated using the following equations:

$$cancerrisk_{As} = \frac{C_0}{35} \times 1.5$$
(9)

Lifetime	hazard	index a	and can	cer risk	r of	arsenic a	t different	concentration	in	source	water
LITETITUE	IIdZdIU	much a	inu can	Cel Hsi	01	discinc d	it unierent	concentration	III 3	source	water.

C ₀ (mg/L)	0.001	0.002	0.01	0.02	0.03	0.04	0.05
HI	0.10	0.19	0.95	1.90	2.86	3.81	4.76
Cancer risk	4.29E-05	8.57E-05	4.29E-04	8.57E-04	1.29E-03	1.71E-03	2.14E-03

Table 4

Cancer risk and risk management measures to attain permissible content of arsenic in source waters.

Permissible content of arsenic in source water (mg/L)	Cancer risk	Measures to attain permissible content of arsenic
0.002	<10 ⁻⁴	 (1) More than 50% of centralized drinking water sources and 20% of distributed drinking water sources must be managed for contamination control. (2) More than 50% of centralized drinking water sources must be purified by ion exchange or membrane filtration. (3) Alternative source waters should be selected or necessary purification equipment should be used for more than 20% of distributed drinking water sources.
0.01	4.92×10^{-4}	 (1) 2.9% of centralized drinking water sources and 12.9% of distributed drinking water sources must be managed for contamination control. (2) The arsenic removal efficiency must be improved by optimizing operational parameters for 2.9% of centralized drinking water sources. (3) Alternative source waters should be selected or necessary purification equipment should be used for 12.9% of distributed drinking water sources.
0.05	2.14×10^{-4}	 (1) 0.3% of centralized drinking water sources and 2.6% of distributed drinking water sources must be managed for contamination control. (2) The arsenic removal efficiency must be improved by optimizing operational parameters for 0.3% of centralized drinking water sources. (3) Alternative source waters should be selected or necessary purification equipment should be used for 2.6% of distributed drinking water sources.

$$HI_{As} = \frac{C_0}{35 \times 3 \times 10^{-4}}$$
(10)

According to the results shown in Table 3, arsenic is so harmful that serious health problems have been related to arsenic consumption even when arsenic is at a low concentration, and the adverse effect on health increases as the concentration of arsenic increases. When the concentration of arsenic is 0.002 mg/L, the *HI* value is less than 1 and the cancer risk is already close to the upper limit of the acceptable risk level of 10^{-4} . When the concentration of arsenic is 0.01 mg/L, the *HI* value is close to 1 and the cancer risk is 4.3 times higher than the 10^{-4} , which means there is a significant potential carcinogenic risk at that concentration.

According to the analysis results shown in Section 3.1, the concentration of arsenic in 56% of 725 centralized drinking water sources exceeded 0.002 mg/L, which means that the residents served by almost half of the investigated centralized drinking water sources have a significant potential health risk by consumption. For lacking of complete statistics, we do not really know what is the percentage of distributed drinking water sources with high risk when the concentration of arsenic exceeded 0.002 mg/L, and more than 20% distributed drinking water sources with high risk can be estimated through the analysis mentioned in Section 3.2.

6. Risk management of arsenic in China

6.1. Methods available to lower potential health risk

In order to reduce the cancer risk and hazard index of arsenic by consumption, some methods such as control of contamination sources and end treatment can be used to reduce the concentration of arsenic in source water and drinking water.

6.1.1. Supervision to be reinforced for contamination sources

There are two arsenic sources in the natural environment, one is the mobilization of arsenic under natural conditions, such as natural weathering reactions, biological activity, geochemical reactions, volcanic emissions and so on, and the other is anthropogenic activities, including mining activities, combustion of fossil fuels, use of arsenic pesticides, herbicides, crop desiccants and the use of arsenic additives in livestock feed [13]. Therefore, the first thing to do is to identify the sources of arsenic in source waters before measures are taken. If high-arsenic concentration is caused by anthropogenic activities, it is necessary to take actions to reinforce the supervision of contamination sources, otherwise, the use of alternative drinking water sources should be considered.

6.1.2. Investment to be increased for application of advanced purification technologies

It is known through risk analysis that the adverse effect of arsenic to people is acceptable when the concentration of arsenic in drinking water was less than or near to 0.002 mg/L. Unfortunately, it is difficult to use traditional purification processes to produce cleaned water with a low arsenic concentration, say 0.01 mg/L. The investment should be increased accordingly for the application of advanced purification technologies including membrane filtration and ion exchange for centralized drinking water sources and the purchase of small purification equipment for distributed and decentralized drinking water sources.

6.2. Cost-effectiveness analysis

Cost-effectiveness analysis is essential for the development of effective measures for risk management. Cancer risk and risk management measures are listed in Table 4 for permissible content of arsenic in source waters. The current economic status of China says the investment will not be affordable if the permissible content of arsenic in source water was set at 0.002 mg/L. Additionally, the lifetime carcinogenic risk by consumption will not be acceptable if the permissible content of arsenic in source water was set at 0.05 mg/L. Therefore, it is prudent to set the permissible content of arsenic at 0.01 mg/L while necessary risk management measures are taken.

6.3. Current risk management measures for arsenic in China

When the permissible content of arsenic is set at 0.01 mg/L, there is still 2.9% of centralized drinking water sources and 12.9% of distributed drinking water sources which cannot meet the requirement, so effective measures should be developed and used to reduce the hazard risk as much as possible. On the one hand, it is necessary to identify the contaminated sources to prevent the discharge of arsenic containing wastewater without treatment. On the other hand, purification efficiency should be improved by optimizing the operational parameters in a more rational way. While 0.002 mg/L is set as the long term goal for control of arsenic in

source water, advanced purification processes should be applied in some well-developed economic regions to reduce the risk of adverse health effects.

7. Conclusions

Protection of source water aims at maintaining high quality of drinking water by simple purification of the source water. As part of our efforts to find effective methods to control the deterioration of water sources, the concept of risk assessment and management is introduced in this paper for risk management of arsenic in source water based on the health risk assessment by analyzing the arsenic removal efficiency of traditional purification process. It is justified through analyses that risk assessment and management is suitable for China to control pollution of drinking water sources. The permissible content of arsenic in source water should be 0.01 mg/L at present in China, and risk management measures include necessary control of contamination sources and improvement of purification efficiency.

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References

 E.E. Chang, P.C. Chiang, S.H. Chao, C.L. Chuang, Development and implementation of source water quality standards in Taiwan, Chemosphere 39 (1999) 1317–1332.

- [2] P. Roccaro, G. Manicni, F.G.A. Vagliasindi, Water intended for human consumption. Part I. Compliance with European water quality standards, Desalination 176 (2005) 1–11.
- [3] M.J. Focazio, D.W. Kolpin, K.K. Barnes, E.T. Furlong, M.T. Meyer, S.D. Zaugg, L.B. Barber, M.E. Thurman, A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States-II untreated drinking water sources, Sci. Total Environ. 402 (2008) 201–216.
- [4] F.X.R. Van Leeuwen, Safe drinking water: the Toxicologist's approach, Food Chem. Toxicol. 38 (2000) S51–S58.
- [5] USEPA, States must prioritize drinking water protection efforts—EPA issuing source assessment guidance, Water Qual. Prof. 1 (1997), 1, 4.
- [6] J.M. Davies, A. Mazumder, Health and environmental policy issues in Canada: the role of watershed management in sustaining clean drinking water quality at surface sources, J. Environ. Manage. 68 (2003) 273–286.
- [7] R. Sams, D.C. Wolf, S. Ramasamy, E. Ohanian, J. Chen, A. Lowit, Workshop overview: arsenic research and risk assessment, Toxicol. Appl. Pharm. 222 (2007) 245–251.
- [8] USEPA, Risk Assessment Guidance for Superfund. Human Health Evaluation Manual Part A, Interim Final, vol. 1, EPA/540/1-89/002, 1989.
- [9] USEPA, Water Quality Standards—Establishment of Numeric Criteria For Priority Toxic Pollutants; States' Compliance; Final Rule: Washington, DC, Federal Register vol. 57, no. 246, 1992, pp. 60848–60923.
- [10] USEPA, Final Water Quality Guidance for the Great Lakes System; Final Rule: Washington, DC, Federal Register vol. 60, no. 56, 1995, pp. 15365–15425.
- [11] S.R. Wickramasinghe, B. Han, J. Zimbron, Z. Shen, M.N. Karim, Arsenic removal by coagulation and filtration: comparison of groundwaters from the United States and Bangladesh, Desalination 169 (2004) 231–244.
- [12] S. Song, A. Lopez-Valdivieso, D.J. Hernandez-Campos, C. Peng, M.G. Monroy-Fernandez, I. Razo-Soto, Arsenic removal from high-arsenic water by enhanced coagulation with ferric ions and coarse calcite, Water Res. 40 (2006) 364–372.
- [13] D. Mohan, C.U. Pittman Jr., Arsenic removal from water/wastewater using adsorbents—a critical review, J. Hazard. Mater. 142 (2007) 1–53.
- [14] M. Bissen, F.H. Frimmel, Arsenic-a review. Part II. Oxidation of arsenic and its removal in water treatment, Acta Hydroch. Hydrob. 31 (2003) 97–107.
- [15] L. Wang, A.S.C. Chen, T.J. Sorg, K. Fields, Field evaluation of as removal by IX and AA, J. Am. Water Works Ass. 94 (2002) 161–174.
- [16] USEPA, Technologies and Costs for Removal of Arsenic from Drinking Water, EPA/815/R-00/028, 2000.
- [17] USEPA, Integrated Risk Information System (IRIS), 2006.