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Arsenic-Polluted Groundwater in Cambodia: Advances in Research

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Abstract

Although arsenic pollution of groundwater in Cambodia has been intensively investigated since the mid-2000s, the impacts on soil and rice as well as human health have not been sufficiently clarified. This review article showed transitions in drinking water supply, arsenic pollution of groundwater and health risks to residents, impact of arsenic on paddy soil and rice, and technologies for removal of arsenic from tube well water in Cambodia. Some rice samples from Cambodia had an arsenic content higher than 0.2 mg kg^{-1} (the maximum acceptable level of arsenic content of rice grain adopted by Codex), and some samples ranged up to 3 times above the maximum acceptable level. In such cases, arsenic exposure risk might increase if people live as self-sufficient farmers, therefore, arsenic-affected areas are deserving of more attention. It is also important that regulations insure that arsenic-contaminated rice not appear in markets. An alternative adsorbent, amorphous iron (hydr) oxide loaded activated carbon is recommended as a desirable arsenic-removal technology.

Keywords: Arsenic; Groundwater; Soil; Rice; Removal technique; Cambodia

Introduction

Arsenic (As) is a toxic metalloid element and it is well known that arsenic exposure causes lung and skin cancer, and birth defects [1]. In the case of chronic poisoning, arsenic accumulated in hair, skin and nails, resulting in strong pigmentation of hands and feet (i.e., keratosis), high blood pressure, and cardiovascular, respiratory, endocrine, neurological and metabolic dysfunctions/disorders [2]. Arsenic polluted groundwater has been identified in more than 70 countries worldwide, including Bangladesh, India, China, Vietnam, and Cambodia [3]. As many as 200 million people live in areas of high geogenic (naturally-occurring) arsenic contamination [4], and many have no other drinking or irrigation water supply [5,6], especially during the dry season. Benner and Fendorf [7] indicated that arsenic in the groundwater of South and Southeast Asia is the product of a confluence of processes initiated by the erosion of As-bearing minerals in the Himalaya. Sediments containing arsenic-bearing iron oxides are transported down the Brahmaputra-Ganges, Mekong, Irrawaddy and Red River systems, and deposited as deltaic sediments. Moreover, increasing irrigation of crop land with arsenic enriched groundwater results in elevated arsenic content of soil and rice [8], causing further exposure risk even to the people in arsenic unaffected areas.

Cambodia is one of the arsenic affected countries where the condition occurs mainly in sediments near the major rivers, Mekong, Bassac and Tonle Sap River [9]. Arsenic released from the sediments to the groundwater and pumped up by using the tube well. It is estimated that around 2.25 million people under arsenic exposure risk [9].

The country lies in continental Southeast Asia, and is bordered by Thailand and Laos to the West and North, by Vietnam on the East and South, and the Gulf of Thailand on the Southwest. It covers an area of 181,035 Km² with a total population of 13.6 million, of which 8% live in the Phnom Penh city, 10 % in other urban areas, and the remaining 82% in rural areas. There are two seasons in Cambodia. The rains come when the winds shift into the southwest monsoon from May to October, with the

most precipitation in the months of September and October. The northeast monsoon season runs from November through April, bringing sunny, dry weather, especially in January and February. The total annual average rainfall is 1000-1500 mm, with considerable yearly variation. Rainfall is heaviest in the mountains along the coast in the southwest, which receive 2,500 to more than 5,000 mm. The average annual temperature ranges 23-35°C [9,10]. The national economy depends mainly on agriculture, fisheries and forestry. Farmland covers an area of 4.34 million ha, or about 24% of the country. Cambodia has recently achieved a surplus in rice production, and is able once more to export a portion of this.

Traditionally, rainwater, surface (river and pond) water and shallow hand-dug well water have been used for daily life in Cambodia (Figure 1). However, these water sources are likely to be contaminated with microbial pathogens, which result in a high infant mortality rate [11]. Therefore, after the civil war ended in 1992, the number of tube wells has rapidly increased, along with economic development and international cooperation. The numbers of tube wells increased from 277,657 (1998) to 681,192 (2008) [12]. Currently, several kinds of wells, including hand-dug wells, hand pump tube wells and electric pump tube wells are in use (Figure 1). As Shantz [12] reported domestic water sources and usage in rural Cambodia vary according to the season. During the rainy season, most families collect and use rainwater for both drinking and non-potable uses, and during the dry season, drinking water comes both from tube wells (where available) and remaining stored rainwater or vendor-supplied water. While rainwater harvesting is commonly practiced throughout Cambodia, it is not a common primary water source but rather a secondary water source in the wet season [12].

Piped water supply coverage ratio is still very low (14% in 2011) in Cambodia, and charges for water are a considerable expense for rural people. Moreover, the piped water supply system does not supply reliable service, so most households use traditional storage jars to store piped water. A water vender system also occurs, but the water quality is poor [12].



Mekong River



Hand dug shallow well



Hand pump tube well



Electric pump tube well



Rain water harvesting tank and pipe



Figure 1: Various sources of drinking water in Cambodia

Arsenic Pollution of Groundwater and Health Risk to Residents in Cambodia

In 1993, the World Health Organization (WHO) set a standard at no more than $10 \mu\text{g L}^{-1}$ of arsenic in drinking water. However, $50 \mu\text{g L}^{-1}$ is the maximum contamination level considered acceptable in many developing countries. Figure 2 shows extent of groundwater arsenic contamination in Cambodia [12].

Arsenic in drinking water was first recognized in Cambodia during the Cambodia Drinking Water Quality Assessment between 1999 and 2000 [9]. Elevated arsenic concentrations in groundwater have been identified in at least 10 provinces, including Kratie, Kandal, and areas south and southeast of Phnom Penh [13,14]. Among these areas, Kandal Province has the highest concentration of groundwater arsenic. About 50 % of the land area of Kandal Province has groundwater exceeding $50 \mu\text{g L}^{-1}$. Arsenic concentrations exceeding typical baseline levels were detected in human nail and hair analysis, and the arsenic concentration of the groundwater used for drinking was positively correlated with both nail and hair arsenic concentration [15,16].

We conducted a survey on the quality of tube well water in Kandal, Prey Veng, and Kampong Cham Provinces in 2010 [17]. Of the 37 wells surveyed, 24 exceeded the Cambodian guideline value ($50 \mu\text{g L}^{-1}$), and 27 exceeded the WHO guideline for drinking water ($10 \mu\text{g L}^{-1}$). Levels of arsenic were extremely high in some wells ($>1,000\text{--}6,000 \mu\text{g L}^{-1}$), suggesting that arsenic pollution is a serious issue.

The symptoms of arsenicosis are generally assumed to develop after 5-20 years of consumption of water with elevated arsenic levels, depending on arsenic concentration [18]. However, new cases discovered in Cambodia have been identified with exposure times as short as 3 years [14]. Even exposure to As levels of $8.1\text{--}40.0 \mu\text{g L}^{-1}$ has been linked to skin lesions, which often develop within 5-15 years of exposure, although this risk appears to be influenced by host factors such as gender, age and body mass index [19]. Epidemiological studies on the public health effects of arsenic exposure from drinking water in Bangladesh suggested a carcinogenic effect, evidenced by an increased risk of cancers of the skin, lung, bladder, liver and kidney, and a contaminant level of $50 \mu\text{g As L}^{-1}$ could lead to cancer in 1 in 100 individuals [2]. Estimates, using groundwater quality and population data for Kandal, Cambodia, suggest that over 100,000

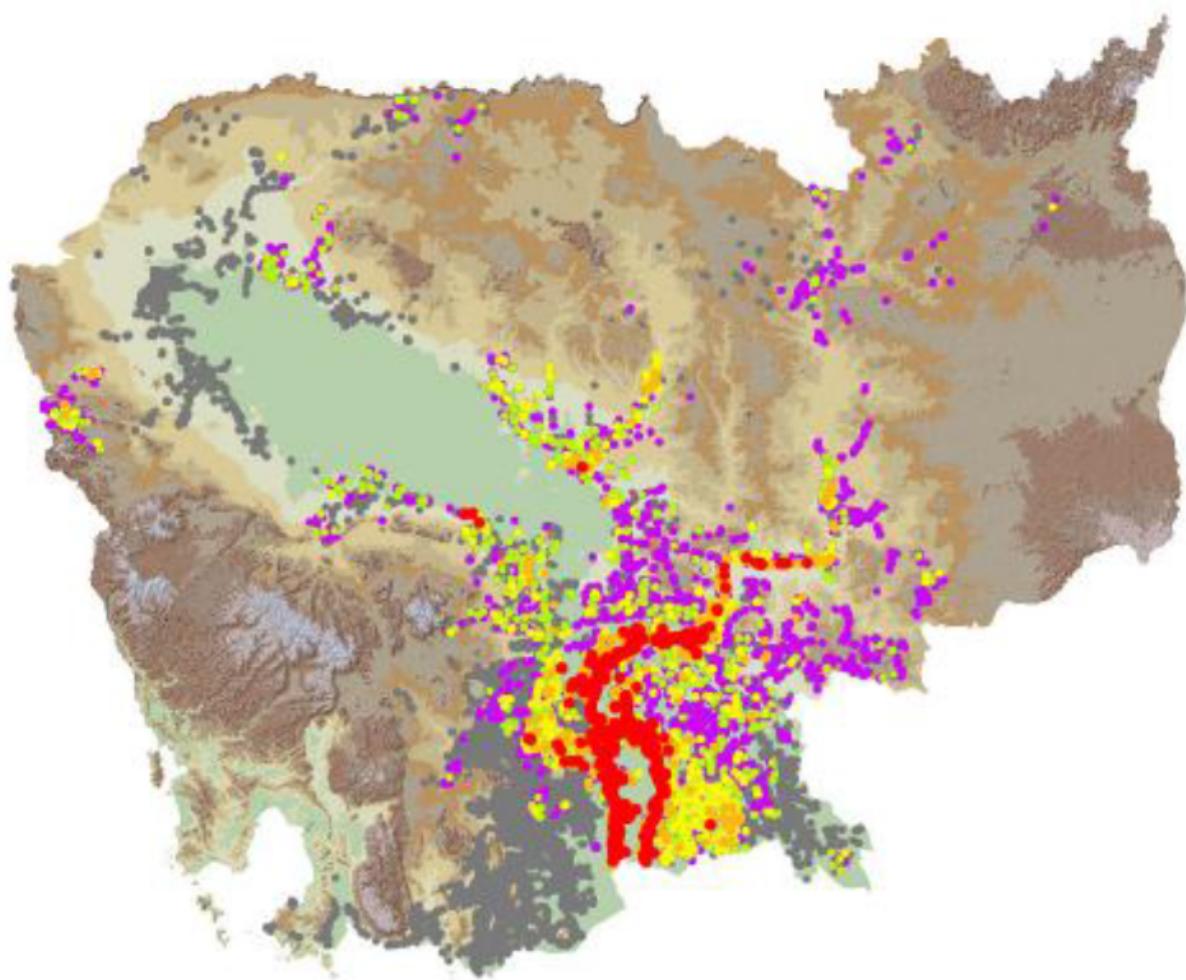


Figure 2: Extent of groundwater arsenic contamination in Cambodia
 (Purple: Non-detect; Green: $\leq 10 \mu\text{g L}^{-1}$; Yellow: $10.1\text{--}50 \mu\text{g L}^{-1}$; Orange: $0.1\text{--}300 \mu\text{g L}^{-1}$; Red: $>300 \mu\text{g L}^{-1}$)

people are at a high risk of chronic arsenic exposure in the province [14]. The first cases of arsenicosis were discovered in Cambodia in 2006 [14]. As of 2012, over 300 arsenicosis patients were identified in six different locations throughout the country [12].

Impact of Arsenic on Paddy Soil and Rice

In general, uncontaminated soils contain about 0-40 mg kg⁻¹ of arsenic with a median value of 6 mg kg⁻¹ [20]. Seyfferth et al. [21] evaluated the arsenic content of soil and rice from five provinces in Cambodia not yet impacted by irrigation with arsenic-contained groundwater. They found that total soil arsenic concentrations ranged from 0.68 to 17.8 mg kg⁻¹ and differed significantly among provinces, with Banteay Meanchey and Battambang having lower soil arsenic than Kandal and Prey Veng provinces. They pointed out that these results are consistent with lowland alluvial soils derived from Himalayan sediments. Soils within the Mekong Delta have a higher total arsenic concentration than lowlands of upland soils far from the Mekong. Total arsenic content in rice averaged 0.2 mg kg⁻¹, and ranged from 0.1 to 0.371 mg kg⁻¹. There was no difference in average rice arsenic content between Kandal and Battambang provinces [21]. Phan et al. [22] collected paddy soil and rice from Kandal and Kampong Cham provinces in households where groundwater was used to irrigate paddy fields. They found that the total arsenic content of soils ranged from 3.07-26.3 mg kg⁻¹ in Kandal and 0.68-0.93 mg kg⁻¹ in Kampong Cham. Arsenic content of rice grain were 0.014-0.649 mg kg⁻¹ and 0.008-0.085 mg kg⁻¹ in the two provinces, respectively. There was no significant difference in total arsenic content of soil and rice grain between the two studies. The main reason for the relatively low contents of arsenic in the irrigated soil and rice are attributed to limited irrigated groundwater usage.

However, as the authors indicated, arsenic content of rice grain is not significantly correlated with the total soil arsenic content. Rice grain with the highest arsenic (0.371 mg kg⁻¹) was in a sample from Kampong Thom province, where the total soil arsenic content was only 1.1 mg kg⁻¹. This suggests that arsenic uptake by rice is not only dependent on the total soil arsenic content, but also greatly affected by other soil properties, such as pH, redox potential, silicon and phosphorous content, etc. Seyfferth et al. [21] indicated that even irrigation with uncontaminated groundwater will result in arsenic uptake by rice, especially under flooded conditions. Under flooding, reductive dissolution of arsenic (V) bearing iron (III) oxides results in the release of adsorbed arsenic in soil solution, which is subject to plant uptake [22] (Table 1).

Panaullah et al. [23] investigated the impact of long-term irrigation with As-contaminated groundwater on soil arsenic levels, rice yield and rice arsenic content in Bangladesh. They found that after 16-17 years of tube well use, a spatially variable buildup of arsenic was observed in the paddy field, namely a gradient in soil As content from up to 70 mg kg⁻¹ near the well to around 10 mg kg⁻¹ distant from the well. They also indicated that 96% of the added arsenic from tube well water was retained in the soil. Moreover, rice yield declined progressively from 7-9 t ha⁻¹ to 2-3 t ha⁻¹ with increasing soil arsenic concentration, and arsenic contents of rice ranged from 0.3-0.6 mg kg⁻¹.

Arsenic contents of rice grain vary widely depending on rice species and soil conditions. All the values of Cambodian rice described above were within the range reported worldwide (0.02-0.9 mg kg⁻¹) [24]. However, Banerjee et al. [25] found that urinary arsenic strongly correlated with cooked rice arsenic, indicating that rice could be one of the major dietary exposure routes. They also found that groups consuming rice with mean cooked rice arsenic content >0.2 mg kg⁻¹ had significantly higher induction of genetic damage compared to groups with mean cooked rice arsenic ≤ 0.2 mg kg⁻¹. In July 2014, the Codex Alimentarius Commission of FAO (Food and Agriculture Organization of the United Nations) and WHO (World Health Organization of the United Nations) [26] adopted

a maximum acceptable level for arsenic in rice of 0.2 mg kg⁻¹. This is the upper limit of the normal range without additional arsenic burden from drinking water. Therefore, areas where people are using arsenic polluted tube well water for daily life should receive critical attention. As revealed above, some rice samples from Cambodia had arsenic content higher than 0.2 mg kg⁻¹, with some up to 3 times the limit value. In these cases, arsenic exposure risk may be enhanced, especially in self-sufficient farmers. Regulations preventing rice contaminated with high levels of arsenic from reaching the market are needed.

In Cambodia, 85% of agricultural land is planted to rice in the rainy season with only 13% used during the dry season [27]. The main reasons for the relatively low rice planting intensity, compared to other countries such as Bangladesh, Thailand and Vietnam, are the long dry season, irregular rainfall during the wet season, and an insufficient irrigation system [28]. The government of Cambodia, as a major component of its economic development plans, is now promoting agricultural water management, particularly irrigation [29]. Priority should be given to establishing arsenic removal technologies and systems before increasing groundwater irrigation in arsenic-affected areas.

Arsenic Removal Technologies for Groundwater

Presently, most of the arsenic removal techniques are still at a laboratory testing stage, although there are some hopeful prospects. Arsenic removal methods have been intensively investigated since the 1990s. Although precipitation, ion exchange, zero-valent iron, membrane separation and filter [30], electrochemical methods [31] have been used for arsenic removal, the adsorption of As from aqueous arsenic systems has received more attention due to its high removal efficiency, low cost, and easy-to-recycle property. It is well known that there exists a high affinity between inorganic arsenic species and iron. This behavior was utilized to develop Fe (III)-bearing materials like goethite and hematite, ferrihydrite, and Fe (III)-loaded resins, iron oxide-coated sand, and iron-doped activated carbon [17]. Chen et al. [32] pointed out that the combination of activated carbon and iron loading would take advantage of the strength of these two materials. They indicated that activated carbon serves as an ideal support media for iron preloading, and iron offers high affinity for arsenate and arsenite.

Aluminum-based adsorbents include activated alumina, gibbsite (mineral Al(OH)₃), aluminum hydroxide and layered double hydroxides [33]. Arsenic (V) has long been known to be strongly adsorbed by aluminum hydroxides, whereas arsenic (III) is considerably less readily adsorbed. The arsenic (V) adsorption maximum on amorphous aluminum hydroxide occurs at approximately pH 4 - 4.5. Ranjan et al. [34] reported that arsenic (V) adsorption on hydrous iron (III) oxide strongly depended on the system's concentration and pH, while arsenic (III) adsorption was pH insensitive. Iron hydroxide is usually considered to be a superior arsenic adsorbent when compared to aluminum hydroxide, but iron (III) hydroxide can release arsenic if its environment causes it to be reduced to soluble iron (II) hydroxide [35].

Sarkar et al. [36] developed an arsenic removal unit which consists of a stainless steel column filled with about 100 L of activated alumina or hybrid anion exchanger, and found that As concentration in treated water remains under 50 µg L⁻¹ over 5 years with adequate operation and management of the units. In Cambodia, a modified BioSand filter containing rusting nails was investigated by Chiew et al. [37]. They indicated that the overall arsenic removal was low and suggested that such amended filters should not be widely deployed until improvements are made to address the consistency and efficacy of treatment.

An arsenic removal equipment using amorphous iron (hydr)oxide adsorbent has been developed and a monitoring trial in Cambodia

Table 1: Arsenic contents of soil and rice grain in Cambodia

	As in soil (mg kg ⁻¹)	As in rice grain (mg kg ⁻¹)	Reference
Banteay Meanchey	1.4 - 9	0.153 - 0.28	Serfferth et al. [22]
Battambang	2.8 - 8.2	0.146 - 0.239	
Prey Veng	8.3 -15.6	0.1 - 0.245	
Kandal	12.4 - 17.8	0.13- 0.298	
Kampong Thom	1.1	0.371	
Kandal	3.07 - 26.3	0.014 - 0.649	Phan et al. [23]
Kampong Cham	0.68 - 0.93	0.008 - 0.085	
Worldwide	unpolluted soils 0 - 40 (Median 6.82)	0.02 - 0.9	Bowen [21]
Maximum acceptable level	-	0.2	Codex [28]

Table 2: Arsenic adsorption amount of iron loaded activated carbon compared with amorphous iron (hydr)oxide

Adsorbent (reference)	Particle size of AC* (mm)	Fe loaded	Fe content (%)	Form of Fe	As(V) adsorbed (mg g ⁻¹)
Am-Fe** Kang et al. [17]	-	-	58.1	Ferrihydrite	42.4
Fe-AC1*** (Kang, unpublished data)	1.4-2.8	Fe(NO ₃) ₃ · 9H ₂ O	7.5	Ferrihydrite	8.7
Fe-AC2*** Jang et al. [39]	0.126	Fe(NO ₃) ₃ · 9H ₂ O	7.5-13.2	Ferrihydrite	18-20

*Activated carbon; **Amorphous iron (hydr)oxide; ***Iron loaded activated carbon

was conducted from April 2011 to February 2012 by Kang et al. [17]. The adsorbent cartridge is packed in layers consisting of the adsorbent, palm husk-activated charcoal, coarse sand, and fine sand. Monitoring results showed that arsenic concentration of the treated water could be reduced to <10 µg L⁻¹ by managing the arsenic removal equipment properly, suggesting that the amorphous iron (hydr)oxide adsorbent has a high arsenic adsorbing capacity not only in the laboratory but also under field conditions for daily use. This latter study demonstrates one of the successful arsenic removal techniques that could reduce arsenic concentration of water below the WHO guideline in situ.

Lata and Samadder [38] reviewed the past and current available information on potential of nano adsorbents for arsenic removal from water which include nano-particles of metals such as titanium, cerium and zirconium etc. They found that more studies are required on suitable holding materials for the nano adsorbents to improve the permeability and to make the technologies applicable at the field condition.

Choices in Arsenic Removal Systems and Future Perspectives to Solve Arsenic Water Problem

In spite of the severity of the groundwater arsenic pollution problem, unfortunately there is presently no perfect solution in the affected areas. Among the countermeasures recommended are in the following order: (1) piped surface water, (2) rainwater harvesting, (3) deep tube well water, (4) dug well water, (5) shallow tube well water purified by a reliable and sustainable arsenic removal technology [12]. However, as described in section 1, residents in the areas have no choice but to use, or partially use, tube well water for their daily life and/or irrigation of crop land. Therefore, the establishment of arsenic removal systems in these areas must have the highest priority. Arsenic removal systems for daily use water and irrigation water can be considered separately. The water quality for daily use must consistently meet WHO drinking water standards, and the desired removal style is set up for larger communities so that maintenance and reliability issues can be addressed. On the other hand, arsenic removal systems for irrigation water can be individual or group maintained, depending on the area of crop land and distance to the tube well. This water quality must meet the standards for irrigation water of the specific country.

In general, more than 1 mm diameter of adsorbent is recommended for water treatment. The amorphous iron (hydr)oxide with a diameter of 3mm we used in Cambodia collapsed in some equipment [17]. One alternative way to apply the iron (hydr) oxide is loading it on activated carbon. Table 2 shows As adsorption of two kinds of iron-loaded activated carbon (Fe-AC) compared with amorphous iron (hydr)oxide (Am-Fe). Arsenic adsorption amount of iron-loaded activated carbon Fe-AC1 and Fe-AC2 were 8.7 and 18-20 mg g⁻¹ [39], respectively, while that of amorphous iron (hydr) oxide was 42.4 mg g⁻¹ [17]. Moreover, arsenic adsorption was higher in Fe-AC2, which has a smaller particle size than Fe-AC1. We can get same arsenic removal efficiency by increasing Fe-AC amount and/or lessening the particle size of Fe-AC.

The advantages of Fe-AC for arsenic polluted groundwater can be summarized as follows.

(1) Fe-AC can be prepared in arsenic affected countries at low cost, since it can be synthesized by iron salt and activated carbon, both available in most countries.

(2) Because Fe-AC only instead of activated carbon currently using in the general water treatment system, therefore the techniques and knowledge for present water treatment system can be directly apply for arsenic removal system.

(3) Managers and technicians currently operating the general water treatment systems can be advisor and technical director training new managers and technicians for arsenic removal systems.

Arsenic recovery and disposal of activated carbon from arsenic removal systems with Fe-AC is one remaining issue. Laboratory studies revealed that addition of phosphorous resulted in an increase in arsenic desorption from allophonic soil [40]; however, this result needs to be verified in groundwater.

Efficient remediation of arsenic polluted groundwater requires the cooperation of researchers, technicians, and managers both working with general water treatment and arsenic contamination. Furthermore, establishment of arsenic removal systems should be under strong leadership of the national and local government. Financial support from government and international agencies is also indispensable.

Conflicts of Interest

The authors declare no conflict of interest.

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