Arsenic and Antimony in Drinking Water in Kohsorkh Area, Northeast Iran Possible Risks for the Public Health

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Abstract: This is the first study on antimony and arsenic contaminations of Kohsorkh area, northeast, Iran. These contaminants originate from weathering and alteration of rocks and leach into ground and surface water (geogenic exposure). Participants (200) from four villages in the study area with 3287 population were interviewed for history, diet and general health. Causes of death in the area were collected from the standard certificate that is issued by the department of health. The antimony and arsenic content in their current primary drinking water source was measured. The contamination levels for antimony and arsenic varied from 11.4 to 127.1 μg L⁻¹ and 37.4 to 376 μg L⁻¹, respectively. In highly affected area the concentration of surface water used directly as drinking water had an average concentration of 71.75 μg L⁻¹ for antimony and 191.92 μg L⁻¹ for arsenic. Antimony and arsenic analysis of tap water from houses in the study area were 35.8 to 79.3 μg L⁻¹, respectively. Antimony and arsenic concentrations are higher than the standards for drinking waters which are 18 and 30 times more than WHO recommendations, 6 and 10 μg L⁻¹ for antimony and arsenic respectively. This study indicates that the people in the villages in Kohsorkh area might be at a considerable risk of chronic arsenic and antimony poisoning. It is also add to evidence that long term ingestion of inorganic arsenic and antimony can increase the mortality due to cancer. However, there was not recorded any death due to the skin cancer in the area during the time of this study.

Key words: Arsenic, antimony, drinking water, Kohsorkh, carcinogen

INTRODUCTION

Arsenic and antimony are one of the most toxicants that are widely distributed in nature and occur in the form of inorganic and organic compounds. Exposure to inorganic compounds may occur in a variety of ways through certain industrial effluents, chemical alloys, pesticides, wood preservative agents, combustion of fossil fuels, catalysts, glass, fire retardant, occupational hazards in mining that are anthropogenic sources and natural sources. Arsenic and antimony occur as a major constituent in more than 200 minerals on the earth and are derived from ore minerals or their alteration products that naturally contaminate the environment (Smedley and Kinniburgh, 2002; Fillela et al., 2002).

The range of arsenic (As) concentrations found in natural waters is large, ranging from less than 0.5, in unpolluted area, to more than 5000 μg L⁻¹, in polluted area. Typical concentration in freshwater are less than 10 μg L⁻¹ and much higher concentrations are found in groundwater (Smedley and Kinniburgh, 2002). Worldwide, the main reason for a chronic human intoxication with arsenic is intake of contaminated drinking water. This contamination originates in As-rich ores from which inorganic As leaches into ground and surface water. Exposure to arsenic-contaminated water is associated with several diseases, especially cancer of the skin, lung, kidney and bladder. The cardiovascular phenomena such as Blackfoot disease also could be identified (Chen et al., 1985, 1986, 1988). The population cancer risk due to arsenic in water supplies may be comparable to those from environmental tobacco smoke (Smith et al., 1992).

The epidemiological studies revealed that skin, lung, liver and bladder cancers were associated with arsenic exposure via inhalation or ingestion (Bates et al., 1992, 1995; Chen et al., 1896). In addition to epidemiological studies, arsenic could act as a clastogen, thus increasing micronuclei in exfoliated bladder cell (Warner et al., 1994; Moore et al., 1997), or increasing the frequency of sister-chromatid exchanges in lymphocytes (Hansson et al., 1996; Lerdal, 1994) and it may cause increased lipid peroxidation (Lee and Ho, 1994; Ramos et al., 1995) which is related to many chronic diseases.

Studies of arsenic in humans exposed to background levels have found varying concentrations in different organs, including skin, lung, liver and kidney (Dang et al.,

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1983; Yamauchi et al., 1989). Populations in countries such as Taiwan, Mexico, India and Chile who consumed drinking water with high levels of arsenic had high rates of skin cancer (Tseng et al., 1968; Cebrian et al., 1983; Chakraborty and Sahi, 1987). In Taiwan, the prevalence of skin cancer among highly exposed males aged 60 years and older reached 25% (Tseng et al., 1968). Guo et al. (2001) also reported that, in Taiwan, the arsenic level in drinking water is associated with the incidence of squamous cell and basal cell carcinomas, but not with incidence of malignant melanoma. The evidence that arsenic in drinking water causes skin disease, including keratosis and melanosis, has been also extensively described in other populations. In Latin America, studies have been found signs of chronic arsenicism in areas of Mexico (Cebrian et al., 1983) and Chile (Borgono et al., 1977). In addition, the association between arsenic ingestion and internal cancers, including cancers of bladder, kidney, lung, liver and colon has also been documented (Chen et al., 1988; Wu et al., 1989; Chen and Wang, 1990; Guo et al., 1994). A nationwide study in Taiwan has found that associations between arsenic ingestion and urinary cancers are cell type-specific; specifically and association was observed in transitional cell cancer, but not in renal cell cancer (Gue et al., 1997). The association between transitional cell carcinoma and arsenic ingestion has also been supported by reports from other countries (Besuschio et al., 1980; Koh et al., 1989; Nomura et al., 1986; Tsuda et al., 1995). Several epidemiological studies based on data from an area of southwestern Taiwan known to have high levels of inorganic arsenic in the artesian well water supply have found elevated rates of liver cancer deaths (Chen et al., 1988; Wu et al., 1989). Respiratory effects in West Bangal were first noted in 1995 when 57% of the 156 patients who lived in arsenic-affected villages reported having cough (Guha et al., 1997). The results of epidemiological studies provide evidence that ingested inorganic arsenic increases the risk of lung cancer (Chen et al., 1986; Chen and Wang, 1990).

Antimony (Sb) is rare element and less widely distributed than arsenic in the environment (Gebel et al., 1996). Typical concentrations of total dissolved antimony are usually less than 1.0 μg L⁻¹ in unpolluted waters. However, in polluted area, concentrations can reach up to 100 times natural levels. Unfortunately, the number of cases detected exceeding the water quality has been recently increasing throughout the world (Fillela et al., 2002). Consequently, the water with high concentration of antimony could contaminate the environment and have severe effect on human as well as other aquatic biota. Arsenic and antimony can also co-exist in the environment (Gebel, 2000). Although there are many studies about exposure to arsenic, not many study address exposure to antimony or the synergistic effect of these two heavy metals.

Arsenic and antimony individually exert toxic effects. However, two in vitro studies showed that coexposure to antimony and arsenic can result in less cell damage than expected based on their individual toxicities, suggesting that coexposure to antimony and arsenic may be subadditive. In vitro study on hamster cells, Gebel et al. (1988) found that chromosome mutagenicity induced by As(III) was significantly suppressed by Sb (III) in micronuclei tests. In sister chromatid exchange tests using human lymphocytes in vitro, Gebel et al. (1997) concluded that the combined effect for As and Sb was subadditive. Gebel (2000) found that antimony and arsenic to be co-occur in the environment. Because of co-occurrence and confounding effects of arsenic and antimony, it has been suggested that antimony concentrations be measured in regions of the world where arsenic concentrations are known to be elevated and to assess the potential for antimony to act as a confounder of arsenic exposure.

This study deals with the total antimony and arsenic present in the surface water in the Kohsorkh area, northeast Iran. Arsenic and antimony in this naturally polluted area are derived from weathering and alteration of rocks and leach into ground and surface water (Mazloomi, 1992). In this study the samples have been collected from small tributaries that flow toward the major Chelipo River (40-50 L sec⁻¹), from the river itself (58°30'-58°33' E and 35°35'-35°36' N) and from tap water (surface derived). The minimum and maximum temperature for the study area, in 20 years period, is -6 to 36°C with average annual precipitation of 225 mm, from February to May. The Chelipo River is the only water source for drinking, domestic and agricultural uses in this semiarid region. The present study analyzes water sources used by people who live in the four villages in Kohsorkh area. They use the contaminated water for drinking, cooking and other domestic uses. This population is a sample from larger community in Kohsorkh region that probably using the As and Sb contaminated water. The objective of the study was to estimate the effects on health and risks associated with ingestion of antimony and arsenic-contaminated water over a long period. We analyzed the causes of death and the possible relation between these two elements and the mortality causes in the area. We also compared with a similar population unexposed to antimony and arsenic in the region.

MATERIALS AND METHODS

Water collections and analyses: A total of seventy-nine samples were seasonally collected at each of the stations
Fig.1: Location of the study area. A, Exposed area; B, unexposed area

with the exceptional circumstance of no sample from station 1 during the winter due to flooding (Fig. 1). The samples were typically collected across tributaries and Chelpo River and from surface derived tap water as drinking water samples. Tributaries and Chelpo River waters are the only sources for drinking water in the study area, however some rural people uses these waters directly for domestic and drinking and not through the water supplies system. Samples from stations 10 have been collected from groundwater from alluvial sediment at the depth of 7 m below surface. This is the only groundwater source that has been pumped and uses for domestic uses.

Water samples from tributaries and river were obtained by immersing the mouth of an acid-washed polyethylene container approximately 20 cm below the surface. Drinking water samples were collected directly from tap. The samples were kept immediately on the ice and then transported to the laboratory, Ferdowsi University for the determination of total arsenic and antimony using a Shimadzu model AA-670G with a GFA-4B graphite furnace atomizer (Apte and Howard, 1986; Chamsaz et al., 2003).

Cross sectional health evaluation: A total of about 3287 individuals have lived in the selected villages throughout their lifetime, but many of them were younger, <30 years old and unlikely to have developed any effects of the exposure. We interviewed, semi randomly, 200 adult participants from four villages about their history, height, weight, diets and general health. All of them had used the same contaminated drinking water. The age criterion was chosen because the study involved the long-term effects of the exposure (Lianfang and Jianzhong, 1994). Each subject was examined for dermatological changes in hands and feet (keratosis and melanosis) in a standard manner which is known sensitive response factors to chronic arsenic exposure.

Causes and death: We collected causes of death from available death certificates (120) from the selected villages (Bakhtiar, Chelp, Alabad and Tavala), 1995 to 2002.

Control population: Akbarabad community, which is about 10 km south of the study area, has been selected as a reference for non-exposed to the contaminants for making comparison with the exposed community. The participants from this community were 30 adult individuals with the total population of 3905 individual. From this population 204 available death certificates were analyses for causes of death.

RESULTS

Water collections and analyses: Arsenic and antimony concentrations in seasonally collected samples are
Fig. 2: Antimony and arsenic concentrations for water samples collected in spring. Each entry corresponds to a mean and standard deviation taken from three samples collected from each site.

Fig. 3: Antimony and arsenic concentrations for water samples collected in summer. Each entry corresponds to a mean and standard deviation taken from three samples collected from each site.

shown in Fig. 2. Arsenic in the samples close to naturally polluted area (sampling sites 1, 2, 3, 4 and 5) ranged from 37.4 to 376 µg L⁻¹, and for antimony was 11.4-127.1 µg L⁻¹. The range of antimony and arsenic concentrations in the samples are presented in Table 1. These concentrations of Sb and As in the tributaries and river are 11.4-127.1 and 37.4-376 µg L⁻¹, respectively and in the tap water samples are 11.4-104 µg L⁻¹ (Sb) and 25.5-104.9 µg L⁻¹ (As).

Table 2 shows the parametric results of arsenic and antimony in water samples. Arsenic concentration ranged 25.5 to 376 µg L⁻¹ and for antimony ranged 11.4 to
Fig. 4: Antimony and arsenic concentrations for water samples collected in fall. Each entry corresponds to a mean and standard deviation taken from three samples collected from each site.

Table 1: Range of antimony and arsenic in the samples from Kohsoth area

<table>
<thead>
<tr>
<th>Elements</th>
<th>Tributaries and river</th>
<th>Drinking water (tap water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony</td>
<td>11.4-127.1</td>
<td>11.4-104</td>
</tr>
<tr>
<td>Arsenic</td>
<td>37.4-376</td>
<td>25.5-104.9</td>
</tr>
</tbody>
</table>

Values are given in μg L⁻¹

Table 2: Parametric presentation of arsenic and antimony in water samples from Kohsoth area

<table>
<thead>
<tr>
<th>Parameters</th>
<th>As concentrations (μg L⁻¹)</th>
<th>Sb concentrations (μg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum</td>
<td>376.0</td>
<td>127.1</td>
</tr>
<tr>
<td>Minimum</td>
<td>25.5</td>
<td>11.4</td>
</tr>
<tr>
<td>Mean</td>
<td>97.1</td>
<td>59.9</td>
</tr>
<tr>
<td>Median</td>
<td>83.2</td>
<td>60.3</td>
</tr>
<tr>
<td>Percent of samples with As and Sb above WHO standard (%)</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

127.1 μg L⁻¹. Arsenic mean and median are 97.1 and 83.2 μg L⁻¹, and the mean and median for antimony are 59.9 and 60.3 μg L⁻¹, respectively. The drinking water standards for antimony and arsenic in Iran are 6 and 50 μg L⁻¹. All analyzed water samples contaminated with As and Sb were above WHO standards. Figure 2-5 shows the standards and the mean concentrations of arsenic and antimony. The mean antimony and arsenic concentrations were 4.2 and 7.8 μg L⁻¹ in the drinking water of the unexposed population, Akbarabad community.

Cross sectional health evaluation: General characteristics of the participants from selected villages are shown in Table 3. The table shows general characteristics of the villages and the participants. From the interview we found that most majority of the population in the study area does not consume enough meat per week and they consume more vegetables and bread. However most of them use their own grown products and they grow them with contaminated water and soil.

From dermatological attention of the participants, twenty subjects from 200 participants had dermatological problems (keratosis). Sixty-five percent of them are women with age ≥ 40 years old. They usually wash the dishes and their clothes with water showed high antimony and arsenic contaminations. No further indication of these cases was done.

Eighty percent of study participants who were all of below average height and weight appeared of malnutrition.

Causes and death: Total deaths (%) in six different causes groups, prenatal, infectious diseases, cardiovascular, cancer, accidents and others in exposed and unexposed areas are presented in Table 4. Ten percent of the total deaths in the exposed population are prenatal causes; spontaneous abortion and stillbirth. This percentage was slightly higher than the prenatal death rate in the unexposed area (5.8%). Cancer had the highest number of death between other recorded diseases in the area. This
Fig. 5: Antimony and arsenic concentrations for water samples collected in winter. Each entry corresponds to a mean and standard deviation taken from three samples collected from each site.

Table 3: General characteristics of the villages and the participants

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Faidheer</td>
<td>Chelpe</td>
</tr>
<tr>
<td>Villages Population</td>
<td>325</td>
<td>507</td>
</tr>
<tr>
<td>Male</td>
<td>161 (49.5)</td>
<td>257 (50.7)</td>
</tr>
<tr>
<td>Female</td>
<td>164 (50.5)</td>
<td>250 (49.3)</td>
</tr>
<tr>
<td>Participants (200)</td>
<td>25 (7.7)</td>
<td>35 (6.9)</td>
</tr>
<tr>
<td>Smokers</td>
<td>12 (48)</td>
<td>28 (80)</td>
</tr>
<tr>
<td>Nonsmokers</td>
<td>8 (32)</td>
<td>7 (20)</td>
</tr>
<tr>
<td>Ex-smokers</td>
<td>5 (20)</td>
<td>0 (0)</td>
</tr>
</tbody>
</table>

The values in parenthesis show percentage.

Table 4: Percentage of total deaths by cause and gender

<table>
<thead>
<tr>
<th>Gender and Causes</th>
<th>Total (%)</th>
<th>Male (%)</th>
<th>Female (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>Preterm death</td>
<td>10.0</td>
<td>3.8</td>
<td>4.2</td>
</tr>
<tr>
<td>Infections</td>
<td>2.5</td>
<td>5.8</td>
<td>1.6</td>
</tr>
<tr>
<td>Cardiovascular</td>
<td>12.5</td>
<td>19.6</td>
<td>33.8</td>
</tr>
<tr>
<td>Cancer</td>
<td>26.0</td>
<td>8.3</td>
<td>11.7</td>
</tr>
<tr>
<td>Accident</td>
<td>9.5</td>
<td>15.2</td>
<td>12.4</td>
</tr>
<tr>
<td>Others</td>
<td>39.5</td>
<td>47.0</td>
<td>35.9</td>
</tr>
</tbody>
</table>

Columns A and B are exposed and unexposed area, respectively. Column C is total death by cause in rural community, Inan (Naghavi, 2003).

record for unexposed area was about 17.7% lower than exposed area. The unexposed record is slightly lower than the nation; however the exposed record is more than the nation, almost twice (Table 4, column C).

**DISCUSSION**

Sb and As may co-occur in groundwater and surface water. However considering their average crustal abundances of 1.8 µg g⁻¹ for As and 0.2 µg g⁻¹ for Sb (Smith and Huyck, 1999), arsenic and antimony are present in environment and contaminated water, soil and air. McCarthy et al. (2004) found that mean arsenic concentration were substantially higher than antimony in water samples from wells in central Bangladesh. They reported all samples had antimony concentrations <1 µg L⁻¹ and the mean of arsenic concentrations in 25% of the samples were 299.9 µg L⁻¹. Mean Sb and As
concentrations of kohsorkh area are 59.9 and 97.1 µg L⁻¹, respectively that compare with the samples from central Bangladesh, the differences between the Sb and As means are not so high as reported in Bangladesh. Besides, high concentrations of antimony and arsenic are present in Kohsorkh area comparing to natural ranges of antimony and arsenic in freshwater, <1.0 and <10 µg L⁻¹, respectively (Filella et al., 2002; Smedley and Kinniburgh, 2002).

The results revealed that on average the sampling sites close to the visibly polluted area from natural sources (geogenic sources) had higher arsenic and antimony content than other sampling sites. Mean antimony concentrations in the samples close to naturally polluted area (sampling sites 1, 2, 3, 4 and 5) was 58.7 µg L⁻¹ and for arsenic was 127.6 µg L⁻¹. Arsenic and antimony in this naturally polluted area are derived from fault zone where the Paleogene deposits have been cut by faults and the ore deposits formed along these zones. Therefore As and Sb and other elements have formed in this area and are visible in alteration zones along the outerclips belt. The original rocks are mainly fine-grained siliciclastics that have been deposited in a relatively closed basin in central Iran within an intracontinental basin (Mazloomi, 1992). The concentration of arsenic in the contaminated soil in the study area was also high (210 to 26-10⁴ ppm) compared with non polluted soil (Ghassemzadeh et al., 2003). Thus the people in the area were not only exposed to arsenic and antimony contaminations in drinking water, they may also gain some through the vegetables and crops that they grow in the area (Filella et al., 2002; Smedley and Kinniburgh, 2002).

It is reported that malnutrition can increase the toxicity of arsenic (Smith and Hira Smith, 2004). As we interviewed the participants, they have malnutrition that probably could increase the toxicity of arsenic in the study area.

Pregnancy outcomes and arsenic in drinking water in Bangladesh was studied by Ahmad et al. (2001). They found that there is a relationship between arsenic contaminated water and spontaneous abortions and stillbirths. In Kohsorkh area, 10% of the total deaths are prenatal causes that are higher than unexposed area (3.8%). In this area, it is reported that 95% of the new born babies are under or about 2.5 kg (office from department of health, Alibad village).

The carcinogenicity of arsenic has been reported in many parts of the world (Brown et al., 1989; Chen et al., 1986; Chen and Wang, 1990; Tsuda et al., 1995). Among the population of Kohsorkh area, 26% of total death causes were by cancer. But, there is no mortality from skin lesions in the study area. However, 36.7% mortality was from digestive track cancer and 16.7% from pulmonary cancers. Digestive track which was the second highest death in the study area is also reported by Yazdanbod et al. (2005) as the most common fatal cancer in Iran. They believe this increase is due to changing in the diet and the life style in Iran. But, in Kohsorkh area it could also cause by arsenic and antimony pollution in drinking water. The coexposures of these two metals are still unknown. About 60% of people dead by cancer were farmers or sheperd that about 36.7% of them dead from digestive track, probably because they work in the field and drink more tea.

The ingestion of inorganic arsenic in drinking water results not only lung cancer also some pulmonary effects that causes cough and shortness of breath (Mazumder et al., 1998). Fifty two percents of the participants in Kohsorkh area had these two problems that most of them were men and in the age range 30-65, 35% of them are smokers. Pulmonary problems and an excess of deaths due to lung cancer has been observed among workers exposed through inhalation to inorganic in the production and use of pesticides and in gold mining (Osburn, 1969; Mabuchi et al., 1979). There was also an increased risk of lung cancer for individuals living within several kilometers of inorganic arsenic-emitting industries (Brown et al., 1984; Pershagen, 1985). They assumed a person who weighs 70 kg and inhales 20 m³ of air per day with 100% absorption, the crude lung cancer risk due to 1 µg kg⁻¹ day⁻¹ arsenic intake from air was estimated at 0.5, 1.0, 1.7 and 2.4%, respectively (Enterline and Marsh, 1982; Brown and Chu, 1983; Lee-Feldstein, 1986). Kohsorkh area is located in arid region and according to Ghassemzadeh et al. (2003), the water in the area is polluted with arsenic and arsenic particles from ores in the area. Thus, Particles contaminated with arsenic in the air can also cause health problem such as pulmonary problems and lung cancer that could happen from uptake the arsenic from the air as well as water (Roy and Saha, 2002). None of the study participants had an occupation that involved exposure to antimony and arsenic pollutants. However, they live in this area that is located in arid area with the rain fall 225 mm. Thus, particles contaminated with arsenic in the air probably important on the pulmonary problems and high risk of lung cancer (percentage of death due to pulmonary cancer was 16.7%). The main economic activity in this area is agriculture. Most men work outside the villages that exposed to arsenic and antimony pollution. Beside, some of them use water from spring or river for drinking or making tea that are highly polluted with arsenic and antimony.
The severity of chronic arsenic poisoning in the water might be magnified by exposure to Sb (Frisbie et al., 2002). Frisbie et al. (2002) found the Sb concentration ranged from 0.0015 to 1.8 μg L⁻¹ which did not exceed 6 μg L⁻¹ (WHO health-based drinking water guideline). However, this guideline is based on the toxicity of exclusively ingesting Sb, not the influence of coexposure of Sb and As. The standard was documented for decreased longevity, altered blood glucose levels and altered blood cholesterol levels in laboratory rats (WHO, 1996). It is possible that these otherwise safe levels of Sb may cause a magnification of arsenic toxicity (Engel et al., 1994; Frisbie et al., 2002). Antimony in drinking water has been also reported to modulate the toxicity of arsenic by Gebel (1999). Thus, this is an area with high arsenic and antimony contaminations that could help to scientists to investigate some unanswered questions about arsenic and antimony coexposure and the health problems. Because, this is an isolated population and rate of immigrant to other cities and villages is low, this area could be used for further study on antimony and arsenic contaminations and the health effects. Besides, most studies have been done on humid environment with lots of precipitations and the concentration of Sb is much higher than Sb. Therefore, Kohsorkh area could help the researchers to find out more about As and Sb genic coexposure.

ACKNOWLEDGMENTS

This study was supported by the Ferdowsi University of Mashhad, Iran. First author gratefully acknowledge Professor Jerry Schnoor providing the facility during visiting University of Iowa as visiting professor.

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