Risk Analysis of Acute and Chronic Exposure to Arsenic of the Inhabitants in a District of Buenos Aires, Argentina

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ABSTRACT

The arsenic occurrence in the water constitutes a serious world health concern due to its toxicity. Depending on the intensity and duration of exposure, this element can be acutely lethal or may have a wide range of health effects in humans and animals. In Argentina, the origin of arsenic is mainly natural, and related to different geological processes. The Argentinean concern about arsenic and its influence on human health dates back to the previous century. The disease ascribed to arsenic contamination was called 'chronic regional endemic hydroarsenism'. It is produced by the consumption of water with high levels of this element. In our study, we focused in La Matanza district, a very populated site in the Buenos Aires Province. An increasing concern of the inhabitants of the area regarding health problems was detected. In order to establish a full view of arsenic exposure in the area, several matrices and targets were analyzed. As matrices, water and soil samples were analyzed. As targets, canine and human hair was studied. The aim of this study was to investigate acute and chronic exposure to arsenic of La Matanza inhabitants.

KEYWORDS

Arsenic, Water contamination, Human hair, Canine hair, Chronic regional endemic hydroarsenism.

INTRODUCTION

The environmental situation in the Buenos Aires Metropolitan Area is characterized by a marked deterioration of urban ecosystems. This deterioration in life quality is caused by non-controlled anthropogenic pollutant discharges. Surface water, groundwater as well as soils and sediments have been widely polluted by industrial and municipal wastewaters, household wastes, and agricultural activities over the past several decades. At the same time, due to population growth in urbanized areas, the risk of exposition to polluted waters through drinking water has grown [1].

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La Matanza district, located in the Buenos Aires Province, with an area of 325.71 km^2 and a population of 1,249,958 inhabitants is divided into 15 villages. Among them, Virrey del Pino, with an area of 116,520 km^2 and a population of 90,382 inhabitants is located near the 3rd National Road. In our study, we focused the investigation in Los Alamos neighborhood which is affected by industrial activity in the area and a lack of monitoring. This vicinity is classified as residential, but lacks the most essential public services such as tap drinking water, natural gas and sewers. Population has to get water by particular pumping wells drilling from 14 to 40 m depth to reach the aquifer. There are no paved roads, complicating the access to the vicinity particularly in rainy days and aggravating the situation of urban hygiene [2].

A large area of Argentina is affected by chronic endemic regional hydroarsenism (HACRE, hidroarsenicismo crónico regional endémico, in Spanish). Symptoms and health problems for humans were densely studied by physicians and toxicologists. Cancer [3, 4], dermatitis [5] and Bowen disease [6] was associated to the presence of As in drinking water. La Matanza lies within this area. In this region, volcanic material is the principal component of loessic and eolic deposits causing a natural presence of arsenic in water as a product of different geological processes, what was studied in different regions of Argentina, like Córdoba [7, 8], La Pampa [9] and Santiago del Estero provinces [10]. Matanza population drink water exceeding the recommended 10 $\mu gAsL^{-1}$ (WHO drinking water standard) [11].

Consuming such water for long periods of time can cause chronic contamination in people, implying a higher risk of skin [12], bladder [13], lung and kidney [14] cancers as was suggested by several authors.

For that reason it is important to bring new forms of monitoring of this element in the environment, being the biomonitoring an evaluation methodology which includes all absorption pathways and all sources of pollution.

Dog (*Canis lupus familiaris*) has long been an important research model and a promising tool as a target and bioindicator for metal contamination [15-17]. This is due to the fact that dogs share the same environment as humans [18] and, as mammals, have similar responses to pollutants [19].

Blood and hair particularly appear as interesting monitoring tools for arsenic exposure risk assessment [20, 21]. Horse [22], reindeer [23], cat and dog [24] hair has been studied by several authors as targets to assess the potential exposure of these animals to arsenic.

In order to establish a full view of arsenic exposure in the area, during this study several matrices and targets were analyzed. As matrices, water and soil samples were analyzed; as targets, canine and human hair samples were selected.

The aim of this study was to investigate acute and chronic exposure to arsenic among the Virrey del Pino inhabitants. The analytical techniques used in this study were selected by considering the available amount of sample, sensitivity, accuracy, reproducibility and detection limits of the method.

X-ray fluorescence spectrometry was used for the direct analysis of water samples and, after an in situ microwave digestion for dog hair and soil samples [25]. Hydride generation atomic absorption spectrometry was used for the analysis of human hair samples.

EXPERIMENTAL

Environmental issues were assessed after the first visit to the district on the 20th February 2012. This inspection defined a preliminary sampling plan based on the observation at a glance of pollution sources and informal interviews with neighbors concerning its health status. With this information, a sampling plan which included sampling of drinking water and soil as well as human and dog hair was developed.

The criterion for the final sampling was determined by designing a grid about 10 by 10 blocks on either side of Route 3, 44.5 km. The sampling was random class, defining 24 houses along the Chacon stream, tributary of the La Matanza river. All points were recorded using a Geographic Positioning System (GPS). Water samples were collected in each of the 24 houses. A volume of 1,000 mL, previously filtered through a 0.45 Millipore, were placed in Nalgene bottles, previously treated with 10% nitric acid for 48 h, washed with distilled water and then with deionized water, two or three times. The samples were acidified with concentrated HNO_3 (1 mL per bottle) and transported and stored under refrigeration (4 °C) until analysis.

Soil and sedimented dust nearby Los Alamos samples were obtained with plastic shovels. Each portion of 500 g was taken and ground again using tungsten carbide mortars in a Shatter box mill. This sub-sample was sieved through a nylon sieve of 60 μm were left. A portion of 10 g was weighted and pressed in a hydraulic (press 17 tons cm^{-2}) without any binder obtaining pellets (30 mm diameter) for EDXRF measurement. The standard reference materials SRM 270 San Joaquin Soil and SRM 2710 Montana Soil Highly Elevated Traces were used for calibration curve. The IAEA Soil 7 and GBW07405 (China National Publishing Trading Corporation) were employed for validation.

Canine hair samples were obtained from dogs located within 100 meters around a metal factory located in the neighborhood of Los Alamos. All of the sampled dogs were clinically healthy and under normal food regime as reported by the owners. A survey was completed by the owners for each dog in their household during the sample collection procedure. The survey provided information on breed, age, gender, time of residence in the house, type of surface in the home yard (e.g. grass, cement), hours spent outdoors, and use of pesticides, medications or oral supplements that might affect hair arsenic levels. Inhabitants of the houses provided human hair. Freshly cut human scalp hair samples were collected from 18 individuals, male and female, aged between 7 to 35 years. The samples were quickly put in a pre-code polyethylene bag and sealed. 0.1 g of hair was weighted and put into a beaker with 5 mL of concentrated HNO_3. The beaker was placed on a hot plate, adjusting heating to a gentle boil record. Then 0.5 mL of 30% H_2O_2 was added. Finally the digested sample was transferred to an aphorized 1.00 mL Eppendorf tube. Total arsenic concentration was measured by TXRF previous adding Co internal standard.

RESULTS AND DISCUSSION

Water samples were analyzed by TXRF. In addition to As, the analysis also allowed the determination of other elements such as P, K, Ca, Ti, V, Cr, Mn, Fe, Cu, Zn, Br, Sr and Pb, as presented in Table 1.

Copper, strontium, iron and zinc distributions show higher concentration values than the average of their limits of quantification. Chromium, manganese and vanadium show a greater accumulation of class frequencies near their limits of quantification. It should be noted that the use of TXRF allows detection level concentrations in the order of μgL^{-1}. This condition is mandatory to assess the contamination of natural groundwater and the effectiveness of applied treatment strategies. The level of arsenic in all water samples is higher than permitted by Argentine Food Code values (10 μgL^{-1} by Argentinean National Law N°18284) (Table 2). This is a factual data that the study area is within the affected chronic regional endemic hydroarsenism zone. This pathology, typical of regions with high concentrations of As in the water, affecting large areas of the provinces of

Argentina: Buenos Aires, Chaco, Salta, Santiago del Estero, Santa Fe, La Pampa, further comprising the entire province of Cordoba. However, in the soil samples studied (Table 3), no large quantities of As were found (compared with those found in contaminated soils [7]), which indicates that this element is present in the rocks that water must cross to reach the aquifer but not in the land of the surface soils.

The average concentrations found in the hair of the studied dogs was 24 ± 2 mg gDW^{-1}, that is significantly higher than the concentration measured in controls (1.0 ± 0.4 mg gDW^{-1}; $p<0.001$). According to the US Department of Health and Human Services, arsenic levels above 1.00 mg gDW^{-1} represent excessive exposure, so the dogs sampled appear to be contaminated by chronic exposure.

In human hair samples, normal level of arsenic was detected evidencing non chronical contamination.

Pb and Cr were found in sedimented dust from the smelter nearby Los Alamos (Table 4). Dust pollution can be exposed and being in contact with human's body in various ways besides through inhalation. Therefore, continuous accumulation of pollutants in the neighborhood streets can lead to chronic contamination of the inhabitants with other metals.

Table 1. TXRF results of drinking water samples

Sample	Ca	K	V	Cr	Mn	Fe	Cu	Zn	As	Sr
	[mgL^{-1}]		[μgL^{-1}]							
1	33	9.8	<5.0	<5.0	125	41	85	18	37	690
2	10	23.0	15	10	55	100	55	50	64	890
3	21	7.3	25	9	45	85	65	64	49	450
4	32	7.8	10	8	44	45	45	45	55	680
5	13	7.9	25	8	40	66	55	60	48	770
6	34	12.0	23	10	25	45	85	85	59	660
7	55	13.0	15	<5.0	23	98	74	75	59	1,000
8	26	8.0	12	<5.0	10	88	63	85	58	890
9	59	8.2	20	<5.0	15	45	46	45	49	560
10	29	7.4	<5	<5.0	12	99	40	56	67	780
11	31	8.2	20	<5.0	30	120	32	55	70	690
12	19	11.2	10	8	20	110	54	110	63	890
13	33	12.1	25	<5.0	21	80	45	80	59	450
14	16	10.0	23	<5.0	15	90	55	70	59	680
15	21	9.8	15	<5.0	11	100	40	60	58	700
16	32	7.6	25	<5.0	15	80	33	65	49	450
17	13	7.8	30	8	16	70	50	78	67	660
18	30	8.9	20	<5.0	20	80	45	80	76	890
19	55	7.2	20	<5.0	32	90	40	60	63	780
20	26	15.0	16	10	41	110	33	85	59	560
21	60	24.0	20	<5.0	40	120	45	74	58	800
22	29	14.0	<5	<5.0	30	110	33	56	49	700
23	32	13.6	<5	10	20	105	52	85	67	650
24	40	11.8	10	<5.0	33	100	40	60	70	850

Table 2. Detection Limits (DL), Maximum Measured Value (MMV), minimum Measured Value (mMV) and Maximum Guidelines Value (MGV) for the studied analytes (μgL^{-1}) in water samples

Element	DL	MMV	mMV	MGV
			[μgL^{-1}]	
K	7	60	26	−
Ca	10	24	11	400[a] (as $CaCO_3$)
V	5	30	<5	100[b]
Cr	5	10	8	50[a]
Mn	5	125	11	100[a]
Fe	5	120	45	300[a]
Cu	6	85	32	1,000[a]
Zn	2	110	18	5,000[a]
As	5	76	37	10[a]
Sr	30	1,000	450	4,000[b]

[a] Argentinean National Law 18284 − Argentinean Food Code
[b] US Environmental Protection Agency

Table 3. EDXRF results from soil samples

Sample	Ca	Fe	Ti	Cr	Mn	Ni	Cu	Zn	Sr	Zr	Pb	As
		[%]						[mgL^{-1}]				
1	0.55	3	0.47	20	1,036	34	10	136	210	690	30	>5
2	1.30	3	0.45	20	898	32	10	180	200	590	40	10
3	0.94	3	0.44	20	742	28	10	207	190	540	50	>5
4	0.93	3	0.41	20	638	28	10	167	180	590	35	14
5	1.60	3	0.42	31	1,118	25	28	122	190	540	35	>5
6	1.40	4	0.41	21	756	29	10	221	200	500	38	>5
7	1.40	4	0.40	40	857	31	301	564	190	470	40	>5
8	1.20	4	0.43	37	875	25	11	112	180	520	45	9
9	0.93	4	0.43	29	826	31	16	237	170	540	48	>5
10	0.70	3	0.47	23	970	35	10	147	200	700	49	>5
11	0.53	4	0.47	37	1,075	27	10	137	210	380	55	25
12	1.20	3	0.39	132	925	26	10	266	220	410	58	>5
13	1.80	3	0.36	104	672	25	19	286	190	350	59	>5
14	0.98	3	0.45	23	789	35	15	284	200	480	56	18
15	1.40	3	0.42	150	725	32	11	189	210	490	56	>5
16	0.79	3	0.46	20	710	29	10	121	200	580	58	>5
17	1.40	3	0.46	27	666	28	10	118	210	530	57	>5
18	1.27	4.60	0.47	20	888	27	10	92	220	420	20	17
19	0.34	4.30	0.55	132	932	41	15	156	230	330	50	25
20	1.20	4.50	1.10	140	500	50	30	100	200	350	70	14
21	1.00	5.60	0.80	90	1,200	80	30	200	300	600	20	>5
22	1.00	6.00	0.90	80	1,300	60	20	230	320	860	50	8
23	1.00	6.10	0.70	60	150	80	25	150	230	960	60	>5
24	1.50	5.00	0.60	60	600	90	30	120	260	860	30	7

Table 4. Metal concentrations found in sedimented dust from smelter in Los Alamos and in Buenos Aires

	Los Alamos	Buenos Aires (control)
Pb in sedimented dust from smelter [mgkg^{-1}]	356	soil mean: 10
Cr in sedimented dust from smelter [mgkg^{-1}]	136	soil mean: 48

CONCLUSIONS

During this study, water and soil samples were analyzed as matrices and canine and human hair samples were selected as targets to investigate acute and chronic exposure to arsenic at the Los Alamos neighborhood in Virrey del Pino, La Matanza, Buenos Aires, Argentina.

The results of the present study provide evidence of arsenic contamination at Los Álamos neighborhood; probably it is due to the use of groundwater for drinking and cooking. Chronic accumulation of arsenic in dogs was found. These results serve as an alert for local population concerning arsenic exposure risks. This work is a preliminary test about the use of canine hair as sentinel of arsenic exposure. The goal of this research was to demonstrate that monitoring other matrices and targets can be achieved in a simple and economically way using TXRF technique. Such a monitoring is needed either to check this analyte in soils and water as well as in hair and dust bringing a complete panorama of the risk of this element for leaving organism.

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