Arsenic concentration in water and bovine milk in Cordoba, Argentina. Preliminary results

Alejo Pérez-Carrera and Alicia Fernández-Cirelli*

Centro de Estudios Transdisciplinarios del Agua, Facultad de Ciencias Veterinarias, Universidad de Buenos Aires, Av. Chorroarín Nº 280 C1427CWO, Ciudad de Buenos Aires, Argentina

The Chaco Pampean Plain of central Argentina constitutes one of the largest regions of high arsenic (As) groundwaters known, covering around 1×10^6 km^2 (Smedley & Kinniburg, 2002; Farías et al. 2004).

The high-As groundwaters are from Quaternary deposits of loess (mainly silt) with intermixed rhyolitic or dacitic volcanic ash (Nicolli et al. 1989, Smedley et al. 1998, 2002). Early in the last century an endemic disease due to contamination of drinking water with arsenic was recognised. This disease is called HACRE (Hidroarsenicismo Crónico Regional Endémico, Chronic Endemic Regional Hydroarsenism) and is connected with a particular type of skin cancer (Astolfi et al. 1981).

One of the most affected region is the province of Cordoba, where Nicolli et al. (1989) reported As concentrations that exceed the maximun level permitted for drinking water of 50 μg/l for 82% of the groundwater samples ($n=60$) of a study area comprising approximately 10 000 km^2. The southeast of Cordoba is an important milk production zone in Argentina, where dairy product consumption is up to 192 equivalent milk l/inhabitant/year.

As a secretion of the mammary gland, milk can carry numerous xenobiotic substances, which constitute a technological risk factor for dairy products and above all for the health of the consumer (Licata et al. 2004). Nevertheless no studies on the incidence of high-As livestock drinking water in livestock health and its transfer to milk have been performed in Argentina.

The aim of the present study was the determination of arsenic content in livestock drinking water and milk from dairy farms located in an area of high-As groundwaters, to analyse the relation between As uptake through water and its transfer to milk.

Materials and Methods

The study area is located in the southeast of Cordoba province, Argentina, between 62° 33′ and 62° 57′, west longitude and 32° 12′ and 32° 50′, south latitude, in the rural area belonging to four counties: Bell Ville, Morrison, Cintra and San Antonio de Litín (Fig. 1).

Dairy farms ($n=30$) were selected according to their size: 7 small (10–20 animals); 20 medium (100–120 animals) and 3 large (>120 animals).

In all cases, groundwater samples were taken from aquifers employing existing manual drilled wells and windmill wells in August 2002 (wet season) and April 2003 (dry season). They were collected in polyethylene bottles previously rinsed with 10% nitric acid, distilled water and deionized water. Concentrated HNO$_3$ (2 ml) was added to the individual bottles. Samples were placed into an ice box (4 °C) but not frozen for transportation to the laboratory.

Cows' milk was sampled in five dairy farms selected by taking into account: (a) arsenic water concentration, (b) the farm size, and (c) the exposure period of the animal to high-As drinking water (minimum five years).

Three to five cows were chosen at random in each farm (depending on their size). Milk sampling was performed in April 2003 together with water sampling. Milk samples were taken in duplicate at separate milking times (morning – afternoon) and placed into an ice box (4 °C) but not frozen for transportation to the laboratory.

For arsenic analysis, milk samples (100 g) were weighed into a 400 ml heat resistant glass beaker and digested as previously described (Cervera et al. 1994). When white ash was obtained, it was moistened with reagent grade water, dissolved in 10 ml 6 M-HCl, filtered through Whatman No. 1 paper into a 25 ml volumetric flask, and diluted to volume with 6 M-HCl. Duplicate blanks were prepared treating the ashing solution with the same digestion procedure.

All reagents were of analytical grade. Working solutions were prepared by appropriate serial dilution of commercially available As stock standard solutions (Perkin Elmer. Atomic Spectroscopy Standard Nº 9300281).

Total As in water was determined by ICP-OES (Perkin Elmer, Optima 2000) following standardised methods (American Public Health Association, 1993).
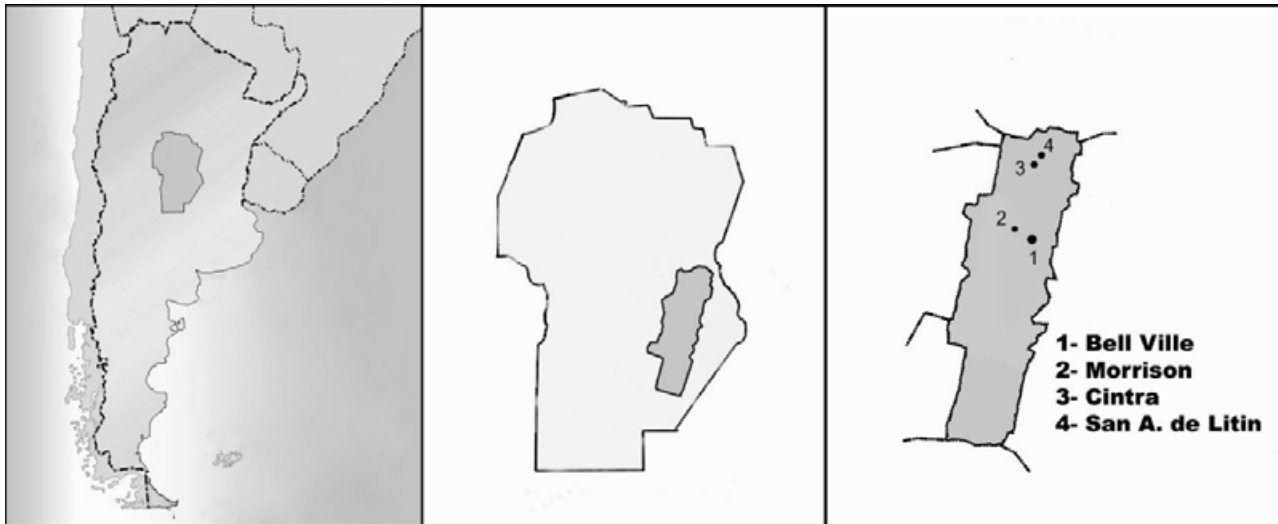
*For correspondence; e-mail: ceta@fvet.uba.ar

Fig. 1. Maps showing the location of the study area. (A) Argentina; (B) Province of Cordoba; (C) Study area.

Determinations were performed in duplicate having the relative error <1·0% for all of them.

Since As concentration in cows' milk is low, hydride generation coupled to atomic absorption spectrometry (detection limit 0·1 ng/g) was used for its determination, following the procedure previously described by Cervera et al. 1994. Determinations were performed in duplicate having the relative error <1·0% for all of them.

Results and Discussion

Groundwater is the main source of livestock drinking water. Phreatic water wells accounted for 54% of those analysed wells. The majority of phreatic water was found between 3 and 8 m, with extremes of 2 and 15 m. Arsenic concentration in all phreatic water samples was over the suggested level for occurrence of chronic intoxication in cattle (0·15 mg/l, Bavera et al. 1979) and 53% showed higher values than those recommended for livestock drinking water (0·5 mg/l; Law 24051, 1993). The remaining 46% of wells ranged in depth from around 80 to 150 m (deep wells). Arsenic concentration in deep wells was under 0·15 mg/l (Pérez-Carrera & Fernández-Cirelli, 2004). No significant differences in As groundwater content between the two sampling periods were found.

In April 2003 the As content was determined in milk from four selected farms (Holstein dairy cows), where As concentration in drinking water ranged from 0·23 to 2·54 mg/l, according to our results from the first sampling period (August 2002). Two of these establishments where medium size (100–120 dairy cows) and two were small (10–20 dairy cows). One medium size deep well establishment with As water concentration of 0·04 mg/l was also selected for comparison. In all cases, six or seven year old cows born and bred on the farm were selected to provide milk samples in order to analyse the effect of prolonged exposure to a constant As dosage.

Milk from three animals was collected at each small farm while five animals were chosen at each medium size farm. Data are summarized in Table 1. Minimum, maximum, and average values are shown. Milk As concentrations ranged from 2·8 to 10·5 ng/g for dairy farms using phreatic groundwater, while a mean value of 0·5 ng/g was obtained for the farm using deep wells. Only one sample was slightly over 10 ng/g, suggested as the permitted As level in milk (International Dairy Federation, 1986). There is little information available on the As content of cows' milk on an international level (Byrne et al. 1987: <4·85 ng/g; Cervera et al. 1994: 0·14–0·77 ng/g; Rosas et al. 1999: <0·9–27·4 ng/g; Licata et al. 2004: 37·9 ng/g). In Argentina, no information was found on the usual and abnormal contents of As in this product.

Ingestion of bovine milk has been shown to be one of the more important pathways of exposure to chemicals in the agricultural food chain model. This model requires an initial quantification of chemical levels of toxic compounds in milk. Biotransfer factors (BTF) are used to relate either estimated daily exposure dosage or feed levels of chemicals to concentrations occurring in the milk (Stevens, 1991).

$$BTF = \text{concentration As in milk (mg/l)/daily animal intake of As (mg/day)}$$

In the study area, natural forage or alfalfa without irrigation is used as the basic livestock food, with supplementation with corn silage. A soil-plant transfer of 0·02 to 0·09 has been calculated for As (Rosas et al. 1999). Since As content in soils in the study area was under the detection limit (15 ng/g, data not shown), As contribution from food might be neglected.

If As water content is considered as the only source of As available for transfer to milk, a BTF may be calculated

Table 1. Estimated bovine milk biotransfer factor

| Dairy farm | Arsenic water, µg/l | Arsenic milk, ng/g | | | Biotransfer factor |
		Cows	Range	Average	
1†	2540	3	6·2–9·3	7·8	4.4×10^{-5}
2†	1900	3	5·2–9·3	6·9	5.2×10^{-5}
3‡	829	5	2·8–10·5	5·4	9.3×10^{-5}
4‡	266	5	3·5–4·2	3·8	2.0×10^{-4}
5‡	40	5	0·3–0·7	0·5	1.8×10^{-4}

† Small size dairy farms
‡ Medium size dairy farms

according to Stevens (1991). Steady state conditions may be assumed in our outdoor experience since animals exposed to a prolonged As intake were chosen for milk sampling. BTF was estimated as above, based on an animal intake of 70 l water/day.

The values obtained (Table 1) ranged from 5.2×10^{-5} to 1.8×10^{-4} in the five farms analysed, where food is the same in all cases and one of them has very low As water content. The BTF values obtained are higher than those reported by Stevens (1991) and in accordance with those reported in Comarca Lagunera, México, by Rosas et al. (1999). It must be taken into account that in the first of these studies the value of 3.0×10^{-5} was calculated based on an indoor study where four animals (breed not specified) were dosed daily with 33 mg As_2O_3 for 15–28 months (equivalent to 1·65 ppm in feed) (Vreman et al. 1986). On the other hand, in the study performed in Mexico (BTF: 3.2×10^{-5}–6.7×10^{-4}) the daily animal intake of As was estimated through the As concentration in food and water.

Although As transfer to milk is a complex process, the fact that a BTF may be estimated through As water contribution reinforces the importance of dairy cattle drinking water quality not only from a productive point of view but also because of its incidence in the agricultural food chain. In health risk assessments, ingestion of bovine milk has been shown to be a major contributing pathway for the accumulation of persistent organic compounds in animal tissues (Stevens, 1991). The contribution of the agricultural food chain to the total human dose estimates of toxic metals has been less investigated. The fact that many of them are present in water from natural or anthropogenic sources and may be transferred to milk shows the need for further studies.

References

American Public Health Association 1993 Standard Methods for the Examination of Water and Wastes. Washington DC: American Public Health Association

Astolfi EA, Maccagno A, García Fernández JC, Vaccaro R & Stimola R 1981 Relation between arsenic in drinking water and skin cancer. *Biology Trace Element Research* **3** 133–143

Bavera G, Rodriguez E, Beguet H, Bocco O & Sanchez J 1979 Aguas y aguadas. [Water and watering places]. Ed Hemisferio Sur, Buenos Aires, Argentina

Byrne A, Camara-Rica C, Cornelis R, De Goeij J, Iyengar G, Kirkbright G, Knapp G, Parr R & Stoeppler M 1987 Results of a co-ordinated research program to improve the certification of IAEA milk powder A-11 and animal muscle H-4 for eleven difficult trace elements. *Fresenius Zeitschrift fur Analytische Chemie* **326** 723–729

Cervera ML, Lopez JC & Montoro R 1994 Arsenic content of Spanish cows' milk determined by dry ashing hydride generation atomic absorption spectrometry. *Journal of Dairy Research* **61** 83–89

Farías S, Casa V, Vázquez C, Ferpozzi L, Pucci G & Cohen I 2004 Natural contamination with arsenic and other trace elements in ground waters of Argentine Pampean Plain. *The Science of the Total Environment* **309** 187–199

International Dairy Federation 1986 Levels of trace elements in milk and milk products. Questionnaire 2386/E. Brussels: IDF

Law 24051 1993 Régimen de Desechos Peligrosos. Decreto Nacional 831/93, Reglamentación de la Ley 24051. [**Law 24051**. 1993. Regime for hazardous wastes. Argentine]

Licata P, Trombetta D, Cristiani M, Giofre F, Martino D, Calo M & Naccari F 2004 Levels of ''toxic'' and ''essential'' metals in samples of bovine milk from various dairy farms in Calabria, Italy. *Environment International* **30** 1–6

Nicolli H, Suriano J, Gomez Peral M, Ferpozzi L & Baleani O 1989 Groundwater Contamination with Arsenic and other Trace Elements in an Area of the Pampa, Province of Cordoba, Argentina. *Environmental Geology and Water Science* **14** 3–16

Pérez-Carrera A and Fernández Cirelli A 2004 Arsenic and fluoride levels in water for dairy cattle (Province of Cordoba, Argentina). *Investigación Veterinaria (INVET)* **6** 51–60

Rosas I, Belmont R, Armienta A & Baez A 1999 Arsenic concentrations in water, soil, milk and forage in Comarca Lagunera, Mexico. *Water, Air and Soil Pollutio,* **112** 133–149

Smedley PL, Nicolli HB, Barros AJ & Tullio JO 1998 Origin and mobility of arsenic in groundwater from the Pampean Plain, Argentina. In: *Water-Rock Interaction.* Proceedings 9th International Symposium, Taupo, New Zealand. pp. 275–278 (Eds GB Arehart & JR Hulston). Rotterdam: Balkema

Smedley PL, Nicolli HB, Macdonald DM, Barros AJ & Tullio JO 2002 Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina. *Applied Geochemistry* **17** 259–284

Smedley PL & Kinniburg D 2002 A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry* **17** 517–568

Stevens J 1991 Disposition of toxic metals in the agricultural food chain. 1. Steady-state bovine milk biotransfer factors. *Environmental Science and Technology* **25** 1289–1294

Vreman K, van der Veen NJ, van der Molen EJ & de Ruig WG 1986 Transfer of cadmium, lead, mercury and arsenic from feed into milk and various tissues of dairy cows: Chemical and pathological data. *Netherlands Journal of Agricultural Science* **34** 129–144