



Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Review

One century of arsenic exposure in Latin America: A review of history and occurrence from 14 countries

Jochen Bundschuh^{a,b,c,*}, Marta I. Litter^{d,e,f}, Faruque Parvez^g, Gabriela Román-Ross^h, Hugo B. Nicolliⁱ, Jiin-Shuh Jean^c, Chen-Wuing Liu^j, Dina López^k, María A. Armienta^l, Luiz R.G. Guilherme^m, Alina Gomez Cuevasⁿ, Lorena Cornejo^{o,p}, Luis Cumbal^q, Regla Toujaguez^m

^a Faculty of Engineering and Surveying, University of Southern Queensland, Toowoomba, Queensland 4350, Australia

^b KTH-International Groundwater Arsenic Research Group, Department of Land and Water Resources Engineering, Royal Institute of Technology (KTH), Teknikringen 76, SE-10044 Stockholm, Sweden

^c Department of Earth Sciences, National Cheng Kung University, University Road, Tainan City 701, Taiwan

^d Gerencia Química, Comisión Nacional de Energía Atómica, Av. Gral. Paz 1499, San Martín, 1650, Prov. de Buenos Aires, Argentina

^e Instituto de Investigación e Ingeniería Ambiental, Universidad Nacional de General San Martín, Peatonal Belgrano 3563, 1° piso, 1650 San Martín, Prov. de Buenos Aires, Argentina

^f Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Av. Rivadavia 1917, 1033 Ciudad Autónoma de Buenos Aires, Argentina

^g Department of Environmental Health Sciences, Mailman School of Public Health, Columbia University, 60 Haven B-1, New York, NY 10032 USA

^h Department of Chemistry, Faculty of Sciences, University of Girona, Campus Montilivi s/n, 17071 Girona, Spain

ⁱ Instituto de Geoquímica (INGEOQUI), Centro de Investigación San Miguel, Av. Mitre 3100, 1663 San Miguel, Provincia de Buenos Aires, Argentina

^j Department of Bioenvironmental Systems Engineering, National Taiwan University, No. 1, Sec. 4, Roosevelt Road, Taipei, 106-17, Taiwan

^k Department of Geological Sciences, 316 Clippinger Laboratories, Ohio University, Athens, OH, USA

^l Universidad Nacional Autónoma de México, Instituto de Geofísica, Ciudad Universitaria Del. Coyoacán México D.F. C.P. 04510, Mexico City, Mexico

^m Departamento de Ciência do Solo, Universidade Federal de Lavras, Campus Universitário, Caixa Postal 3037, CEP: 37200-000, Lavras, Minas Gerais, Brazil

ⁿ Hospital Metropolitano Vivian Pellas, Managua, Km. 9 3/4 Carretera a Masaya, Nicaragua

^o Centro de Recursos Naturales y Medioambiente, CERENAYMA, Facultad de Ciencias, Universidad de Tarapacá, Casilla 7-D, Arica, Chile

^p Laboratorio de Investigaciones Medioambientales de Zonas Áridas, LIMZA, Centro de Investigaciones del Hombre en el Desierto, CIHDE/CODECITE, Universidad de Tarapacá, Casilla 7-D, Arica, Chile

^q Laboratorio de Remediación Ambiental, Centro de Investigaciones Científicas, CEINCI, Escuela Politécnica del Ejército, Casilla 1715-231B, Quito, Ecuador

ARTICLE INFO

Article history:

Received 14 October 2010

Received in revised form 5 June 2011

Accepted 7 June 2011

Available online 29 September 2011

Keywords:

Latin America

Geogenic arsenic

Arsenic occurrence and mobilization

Groundwater

Surface water

Mining

ABSTRACT

The global impact on public health of elevated arsenic (As) in water supplies is highlighted by an increasing number of countries worldwide reporting high As concentrations in drinking water. In Latin America, the problem of As contamination in water is known in 14 out of 20 countries: Argentina, Bolivia, Brazil, Chile, Colombia, Cuba, Ecuador, El Salvador, Guatemala, Honduras, Mexico, Nicaragua, Peru and Uruguay. Considering the 10 µg/L limit for As in drinking water established by international and several national agencies, the number of exposed people is estimated to be about 14 million. Health effects of As exposure were identified for the first time already in the 1910s in Bellville (Córdoba province, Argentina). Nevertheless, contamination of As in waters has been detected in 10 Latin American countries only within the last 10 to 15 years. Arsenic is mobilized predominantly from young volcanic rocks and their weathering products. In alluvial aquifers, which are water sources frequently used for water supply, desorption of As from metal oxyhydroxides at high pH (>8) is the predominant mobility control; redox conditions are moderate reducing to oxidizing and As(V) is the predominant species. In the Andes, the Middle American cordillera and the Transmexican Volcanic Belt, oxidation of sulfide minerals is the primary As mobilization process. Rivers that originate in the Andean mountains, transport As to more densely populated areas in the lowlands (e.g. Rímac river in Peru, Pilcomayo river in Bolivia/Argentina/Paraguay). In many parts of Latin America, As often occurs together with F and B; in the Chaco–Pampean plain As is found additionally with V, Mo and U whereas in areas with sulfide ore deposits As often occurs together with heavy metals. These co-occurrences and the anthropogenic activities in mining areas that enhance the mobilization of As and other pollutants make more dramatic the environmental problem.

© 2011 Elsevier B.V. All rights reserved.

* Corresponding author at: Faculty of Engineering and Surveying, University of Southern Queensland, Toowoomba, Queensland 4350, Australia.

E-mail addresses: jochenbundschuh@yahoo.com (J. Bundschuh), litter@ceia.gov.ar (M.I. Litter), mp844@columbia.edu (F. Parvez), gabriela.roman@udg.edu (G. Román-Ross), hbnicolli@arnet.com.ar (H.B. Nicolli), lcw901015@gmail.com (C.-W. Liu), lopezd@ohio.edu (D. López), victoria@geofisica.unam.mx (M.A. Armienta), guilherm@dcs.ufpa.br (L.R.G. Guilherme), alinagomezcuevas@hotmail.com (A.G. Cuevas), lorenacp@uta.cl (L. Cornejo), luis.cumbal@espe.edu.ec (L. Cumbal), toujague@yahoo.com (R. Toujaguez).

Contents

1. Introduction	3
2. Arsenic species and mobilization in groundwater of Latin America	7
2.1. Arsenic species	7
2.2. Mechanisms of arsenic mobilization	8
3. Arsenic in the Precolumbian Era	8
4. Few findings until the 1960s	8
4.1. Arsenic detection in groundwater of Argentina	10
4.2. Arsenic discoveries in groundwater of Mexico.	14
4.3. Arsenic detections in surface water and groundwater of Chile	15
5. Arsenic: from the 1970s to the 20th century.	16
5.1. Arsenic detection in groundwater and surface water resources of Peru	16
6. Arsenic in the 21st century	18
6.1. Central America	18
6.1.1. Guatemala	18
6.1.2. Honduras	19
6.1.3. El Salvador	20
6.1.4. Nicaragua	21
6.1.5. Costa Rica	22
6.2. Caribbean.	22
6.2.1. Cuba	22
6.3. South America	23
6.3.1. Colombia	23
6.3.2. Ecuador	24
6.3.3. Bolivia	24
6.3.4. Brazil	28
6.3.5. Uruguay	28
7. Conclusions	29
Acknowledgments.	29
References	29

1. Introduction

Recent studies from northern Chile have showed that the indigenous population of Latin America¹ may have suffered arsenicism 7000 years ago caused by high arsenic (As) exposure of geogenic origin in drinking water and in food (Arriaza et al., 2010; Byrne et al., 2010; Rivadeneira et al., 2010, see Section 3). However, it was not until 1913 when the first cases of human As poisoning were described from the locality of Bell Ville in the Chaco–Pampean plain in Argentina and related to As in drinking water from groundwater (Goyenechea, 1917). There were few studies in the Chaco–Pampean plain in the following decades. However, it took until the end of the 1950s and the beginnings of the 1960s that the problem of ground- and surface water contaminated predominantly by geogenic As was detected in other Latin American countries, i.e. in Mexico and Chile. However, at the beginning of the 21st century, the findings of high As concentrations in water resources in Latin American countries increased sharply. Contamination has been detected for the first time in 10 Latin American countries only within the last 10 to 15 years. As by today, high As levels have been detected in ground- and surface water in 15 of the 20 Latin American countries (2011) (Fig. 1). Much of the As contamination was detected and/or described within the last 10 to 15 years, but in many cases, these data were published much later or never in the international literature. Examples of countries where As was detected in waters (not including the geothermal ones) detected or reported since the end of the 1990s are El Salvador (1998), Nicaragua (1996/2000), Brazil (1998/2000), Bolivia (2001), Cuba ((1985) 2002), Ecuador (2005), Honduras

(2006), Uruguay (2005/06), Colombia (2007), and Guatemala (2007) (Bundschuh et al., 2009).

In most mid-sized and large urban areas with centralized water supply, the problem of As-contaminated drinking water resources has been mitigated by the installation of water treatment plants or tapping alternative water resources. In Latin America, accommodation to the allowable limit of As in drinking water has been a step-by-step approach where limits were set-up according to the affordable technology in each country at that moment. Nowadays, the tested methods are able to reach the 10 µg/L limit recommended by the WHO. The technologies used are based mainly on coagulation–flocculation–filtration and reverse osmosis (RO) (Bundschuh et al., 2010; Litter et al., 2010a,b, 2012). Conventional large-scale As removal plants using coagulation methods and reverse osmosis were installed in some places. In northern Chile, plants were installed in Antofagasta (since 1970), Calama (since 1978), San Pedro and other cities (Fig. 2). Currently, four plants working with a coagulation-based technology using ferric chloride for low to medium production capacity (30 to 520 L/s) are operative and achieve As removals complying the Chilean regulation (Sancha, 2003). As described, in Chile the problem has been partially solved by installation of plants in some large and medium cities; however, the problem persists at the north of the country, typically associated to small rural communities. Solutions for these areas are proposed in the paper of Litter et al. (2012).

In Argentina, plants using a coagulation–adsorption–filtration process with polyaluminum chloride (PAC) or ferric chloride, followed by a double filtration, allowed the simultaneous removal of As and F⁻, achieving also concentrations in accordance with national and international regulations (Fernández et al., 2009). Although several RO plants have been installed in Argentina to remove As and salinity in the last decades, the high levels of solids and the high silica content cause severe fouling and scaling problems (Fernández and

¹ In this paper, Latin America will be referred to as the region comprising those countries in the Americas where the Spanish or Portuguese languages prevail: Mexico, all countries of Central America with the exception of Belize, all South American countries (with the exception of Guyana, Suriname and Trinidad and Tobago) and, in the Caribbean, Cuba, Dominican Republic and Puerto Rico.

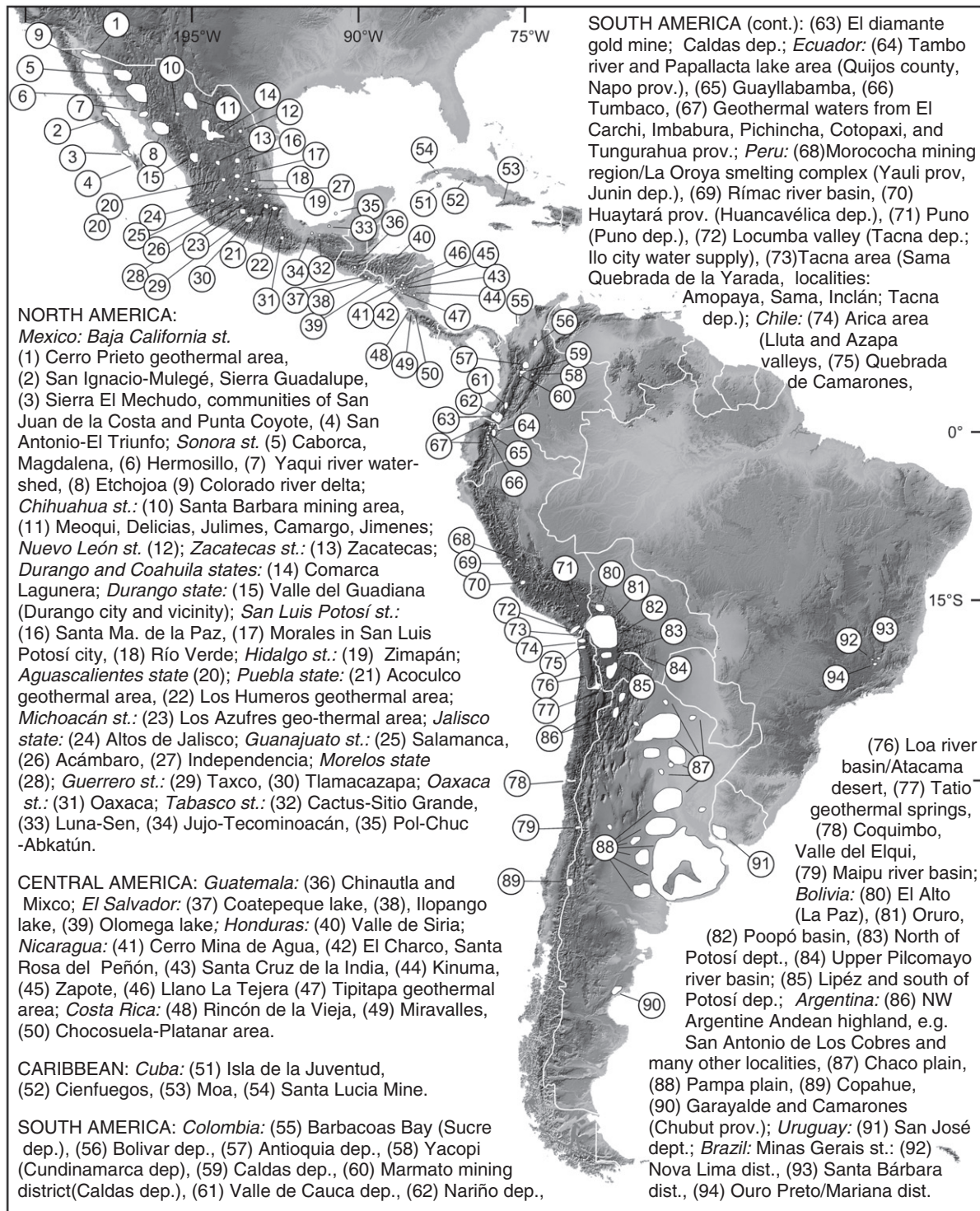


Fig. 1. Latin America: distribution of aquifers and surface water bodies with high concentrations of dissolved As as known today. Compiled from Armienta et al. (2008), Bundschuh et al. (2008, 2009 a,b, 2010) and from unpublished information available to the authors. Abbreviations: st: state, prov.: province, dep.: department, dist.: district. The digital elevation model digital model of the world PIA3388 (<http://photojournal.jpl.nasa.gov>) is courtesy of NASA/JPL-Caltech.

Ingallinella, 2010). Examples of As removal plants have been reported in Guatemala (Bundschuh et al., 2010) and in Peru (Castro de Esparza, 2006). The Latin American experience provides valuable information that could be used to solve these problems in other regions of the world, especially in countries of Asia where the first option is to find other water sources not contaminated with As. Finally, treatment plants for As immobilization and stabilization in industrial effluents, as the case

of copper and gold mining and metallurgical operations in Chile and Brazil (Pantuzzo and Ciminelli, 2010), respectively, are also described. Coprecipitation technologies with iron salts have demonstrated to provide mineral forms with a high geochemical stability on the environment as landfills (Pantuzzo and Ciminelli, 2010). In Argentina, similar action was taken in some cities and big towns of the provinces of La Pampa, Santa Fe and Santiago del Estero (all in the Chaco-

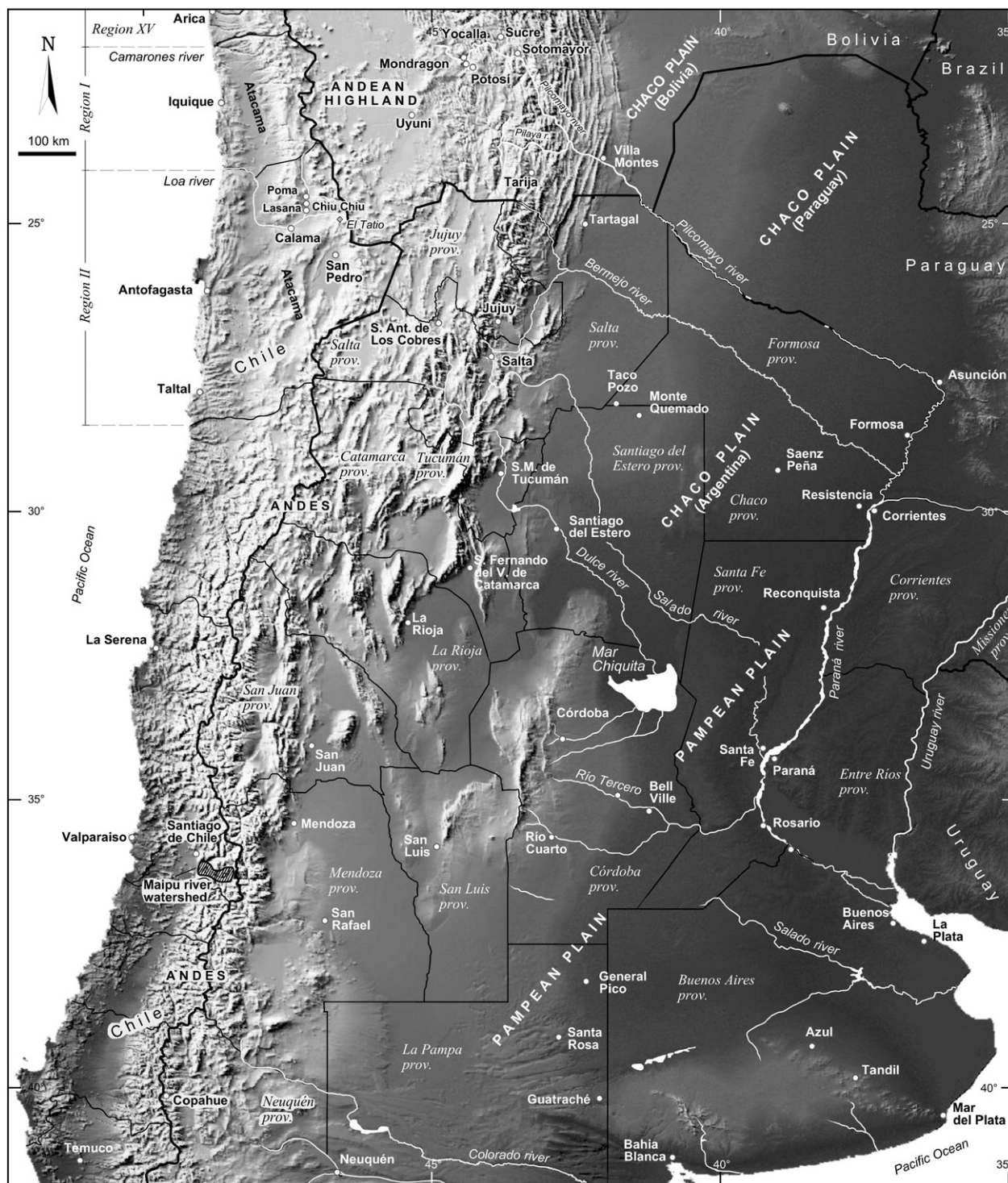


Fig. 2. Geomorphological setting of Argentine, Paraguay Chile and southern Bolivia. The digital elevation model digital model of the world PIA3388 (<http://photojournal.jpl.nasa.gov>) is courtesy of NASA/JPL-Caltech.

Pampean plain, Fig. 2) and fortunately many plants are presently operating since the 1990s in Santa Fe, Salta, San Juan and Buenos Aires provinces. In Guatemala, a first conventional As treatment plant was installed in 2008 in Mixco, close to Guatemala City (Fig. 1), and gave excellent results: an effluent with As concentration below $10 \mu\text{g L}^{-1}$ was obtained, in accordance with the water quality standard of Guatemala (Bundschuh et al., 2010; Litter et al., 2010a,b). In Peru, a treatment plant in the city of Ilo, built in 1982, used initially massive doses of 90% lime (CaO), but many difficulties were encountered and

it was necessary to use new methods in order to reduce costs, increase efficiency and improve the quality of the treated water. After laboratory and pilot trials, the solution taken was based on the use of ferric chloride or ferric hydroxide and sulfuric acid, removing As at high pH through coagulation and flocculation with natural $\text{Mg}(\text{OH})_2$ (Castro de Esparza, 2006).

In contrast to these urban areas, practically no solutions were provided for As mitigation in isolated Latin American rural and periurban populations (not connected to a centralized water supply

system). In another article of this issue and in other publications, some small-scale and household methods to remove arsenic from water for drinking purposes in Latin America have been reviewed (Litter et al., 2012; Bundschuh et al., 2010; Litter et al., 2010b).

Most of the inhabitants of rural and urban poor communities affected by As problems in Latin America are typically not aware of the toxicity of As. In this paper, we will not address remediation actions taken to reduce As in drinking water. These have been discussed in different recent review papers (Bundschuh et al., 2010; Litter et al., 2010a,b) and in a paper of this special issue (Litter et al., 2012).

In 1993, the World Health Organization (WHO) provisionally lowered the As guideline value for drinking water from 50 to 10 µg/L (WHO, 2003). This reduction resulted in a several fold increase of the number of population exposed to As. In Latin America, this new As provisional guideline value became law (in chronological order) in Honduras (1995), Costa Rica (1997), El Salvador (1997), Colombia (1998), Guatemala (1998), Nicaragua (1999), Panama (1999), Bolivia (2004), Brazil (2005), Argentina (2007), and Chile (2008). Other Latin American countries such as Uruguay, Peru, and Venezuela still maintain the 50 µg/L limit; Mexico has a regulatory limit of 25 µg/L (2005). It must be stated that in Argentina the national limit is not applied to all provinces but they regulate the permissible As concentration by their own norms. However, the national limits for

other uses of water are often much higher in the different Latin American countries. National limits in irrigation water vary significantly from 10 µg/L in Chile to 200 µg/L in Peru; in some countries, they further depend on the type of plant, e.g. whether it is applied for irrigation of vegetables, fruits, forage, etc. and whether the plants are consumed raw or cooked. In addition, the limit of As in water for animal husbandry is regulated individually in some Latin American countries; the national limits vary between 10 µg/L (Chile) and 500 µg/L (Argentina). Table 1 gives an overview of respective regulations of some of the Latin American countries. To our knowledge, no national regulations for irrigation water and water for animal husbandry exist in Nicaragua, El Salvador and Guatemala.

Toxic manifestations and health impacts due to human As exposure have been reported from many areas in Latin America. However, at present it is not possible to precisely assess the number of persons potentially exposed to As. Castro de Esparza (2009) estimates that in Latin America at least 4.5 million people are exposed to drinking water with more than 50 µg/L of As. However, if we consider the 10 µg/L limit, adopted by most of the Latin American countries, then the number of exposed people estimated by the authors would increase by a factor 3–4 to around 14 million.

Numerous studies from Latin America have reported an array of adverse health effects including cancer, reproductive outcomes,

Table 1
National regulations for permitted arsenic concentrations in irrigation water and water for livestock of selected countries of Latin America.

Use of water	Limit (µg/L)	Regulation ^a
<i>Mexico</i>		
Agricultural irrigation	100	Criterios Ecológicos de Calidad del Agua. CE-CCA-001/89.
Animal husbandry	200	12-13-89. Secretaría de Desarrollo Urbano y Ecología.
Wastewater discharged into rivers used for irrigation		NOM 001-ECOL-1996 NOM 001-ECOL-1996. SEMARNAT. Límites máximos permisibles de contaminantes en las descargas de aguas residuales en aguas y bienes nacionales
Monthly average	200	
Daily average	400	
<i>Venezuela</i>		
Water used for agriculture	50	DECRETO No. 883, FECHA: 11 de Octubre de 1995
<i>Ecuador</i>		
Agricultural water	100	Texto Unificado de Legislación Ambiental Secundaria (TULAS, 2003), Ecuador
Water for animal husbandry or cattle	200	
<i>Peru</i>		
Irrigation of vegetables of crude consumption	200	Ley General de Aguas, Decreto Legislativo No.17,752 y modificatorias a los Artículos 81 y 82 de los Reglamentos de los Títulos I, II y III introducidos por el DS No. 007-83-S.A.
Animal husbandry	200	
<i>Bolivia</i>		
Water for irrigation	50	Ley 1333 (Ley de Medio Ambiente de 27 de abril de 1992)
<i>Chile</i>		
Water for irrigation	100	NCh1333. of 1978 MOD.1987. Requisitos de calidad del agua para diferentes usos
Animal husbandry	10	Norma chilena oficial NCh1333.Of1978 MOD.1987 (referenciado a la NCh409/1.Of2005). Requisitos de calidad del agua para diferentes usos
<i>Brazil</i>		
Irrigation of vegetables that are consumed raw and fruits grown in soils and consumed raw without skin	10	Resolução CONAMA no. 357, de 17 de março de 2005: Dispõe sobre a classificação dos corpos de água e diretrizes ambientais para o seu enquadramento, bem como estabelece as condições e padrões de lançamento de efluentes, e dá outras providências.
Irrigation of vegetables, fruit plants and parks, gardens, sport and leisure fields with what people can have direct contact	10	and Deliberação Normativa Conjunta COPAM/CERH-MG n° 01, de 05 de maio de 2008: Dispõe sobre a classificação dos corpos de água e diretrizes ambientais para o seu enquadramento, bem como estabelece as condições e padrões de lançamento de efluentes, e dá outras providências.
Aquiculture	10	
Irrigation of trees, cereals and forages	33	
Watering of animals	33	
<i>Argentina</i>		
Agricultural irrigation water	100	Decreto Nacional 831/93, Reglamentario de la Ley 24.051
Animal husbandry	500	

NCh = Norma chilena oficial = Official Chilean norm.

^a NOM = Norma Oficial Mexicana = Official Mexican Norm.

cardiovascular, lung diseases, and cognitive impairment in children from high As exposure. Epidemiological investigations from As-endemic areas of Antofagasta in Chile and Córdoba province of Argentina have consistently linked high levels of As exposure with elevated risk of bladder and lung cancer mortality (Hopenhayn-Rich et al., 1996; Smith et al., 2006; Marshall et al., 2007; Bates et al., 2004a). A few studies from the same region have also documented As-induced kidney, liver and skin cancer (Hopenhayn-Rich et al., 1998; Yuan et al., 2010). Studies from Latin American countries revealed that smoking, male gender, long latency period, exposure at early life and incomplete metabolism of As, considerably increase cancer risk (Ferrecio et al., 2000; Marshall et al., 2007; Smith et al., 2006; Steinmaus et al., 2010). Higher mortality and inductance from pulmonary and cardiovascular diseases have also been observed within relatively shorter period of peak exposure (Smith et al., 2006; Yuan et al., 2007). A few years ago, a study among Andean women showed that arsenic crosses into placenta (Concha et al., 1998a,b). Subsequently low birth weight, and neonatal mortality from As exposure was observed (Hopenhayn-Rich et al., 2000). Studies from Mexico reported that in children cognitive development is impacted by As exposure (Rocha-Amador et al., 2007; Calderon et al., 2001). An in-depth review of the health effects, biomarkers, genetic susceptibility, and mechanistic studies from Latin American countries is included in this issue of the journal (McClintock et al., 2012).

In this paper we will give a short overview on As mobilization and As species in groundwater followed by an overview on the discoveries of As in Latin America made during the last 100 years related to geogenic As contamination of water resources. Thereby, more focus would be paid to those countries where the As problem is internationally less known compared to the countries where the problem has been already described in the international literature for several decades. We discuss the countries in chronological order when the occurrence of As in water resources and related health effects have been made. After a short description of the relevance of As already in the Pre-Columbian Era, we address the findings in Argentina at the beginning of the 20th century, followed by the discoveries in Mexico and Chile at the end of the 1950s and beginning of the 1960s, respectively. In the next section we address the countries where the problem of As in water resources has been made from the 1970s to the end of the 20th century comprising only the country Peru. The last section describes the explosive findings of areas with As in water resources made in the 20th century comprising 10 countries (Guatemala, Honduras, El Salvador, Nicaragua, Cuba, Colombia, Ecuador, Bolivia, Brazil and Uruguay).

Concerning As-rich geothermal waters, which mix with aquifers used for water supply or which flow into surface water bodies, constitute an important additional source of geogenic As at several sites in Latin America, especially in Mexico, Central America, Ecuador, Chile and Argentina. This topic will be not discussed in this article because it is described in detail in the paper of López et al. (2012). Although in the present paper the most relevant human health related studies will be mentioned, the topic will be presented in detail by McClintock et al. (2012). Regarding the release of As from geogenic sources through As-contaminated water and soil into plants and animals and into the human food chain, we refer to the paper of Bundschuh et al. (2012).

2. Arsenic species and mobilization in groundwater of Latin America

2.1. Arsenic species

In natural waters (not considering geothermal waters), dissolved As is generally present in inorganic forms either as oxyanions or as neutral species. Depending on Eh and pH of the water, inorganic As is found in different species of As(V) and As(III). Arsenate is present as H_3AsO_4 ; its corresponding anions are H_2AsO_4^- , HAsO_4^{2-} and AsO_4^{3-}

with dissociation constants of $\text{pK}_{a1}=2.3$, $\text{pK}_{a2}=6.8$ and $\text{pK}_{a3}=11.6$, respectively, whereas arsenite occurs as H_3AsO_3 and its hydrolysis products are H_4AsO_3^+ , H_2AsO_3^- , HASO_3^{2-} and AsO_3^{3-} with dissociation constants $\text{pK}_{a1}=9.2$ and $\text{pK}_{a2}=12.7$, respectively (Smedley and Kinniburgh, 2002; Adriano, 2001; Lillo, 2003). Under oxidizing conditions, As(V) predominates and is found in the common pH range of most natural ground- and surface waters as the oxyanions H_2AsO_4^- ($\text{pH}<6.8$) and HAsO_4^{2-} ($\text{pH}>6.8$). In water with reducing conditions, As(III) is the predominant oxidation state and, in most reduced natural waters, the neutral species H_3AsO_3 predominates ($\text{pH}<9.2$) (Yan et al., 2000).

In Latin America there are only very few data about As speciation in groundwater (not considering geothermal waters). Smedley et al. (2002) studied the As speciation in the northern part of La Pampa province (Chaco-Pampean plain, Argentina). These authors found total As concentrations of 7–5280 $\mu\text{g/L}$ (mean \pm SD: $429 \pm 925 \mu\text{g/L}$, median: 171 $\mu\text{g/L}$, $n=108$). The As(III) concentrations were <4.4–136 $\mu\text{g/L}$ (mean \pm SD: $20.4 \pm 26.8 \mu\text{g/L}$, median: 11.1 $\mu\text{g/L}$, $n=108$); in the water samples with As(III)>4.5 $\mu\text{g/L}$ (detection limit), the percentage of As(III) referred to total As was 1.5–42.2% (mean \pm SD: $4.0 \pm 5.4\%$, median: 2.8%, $n=60$). Another study from the Chaco-Pampean plain is those of Claesson and Fagerberg (2003) and Bejarano Sifuentes and Nordberg (2003), who studied the As speciation in groundwater of the Río Dulce cone (Santiago del Estero Province, NW Argentina). They analyzed $n=74$ samples and reported total As concentrations of 7.0–14,969 $\mu\text{g/L}$ (mean \pm SD: $800 \pm 2596 \mu\text{g/L}$, median: 108 $\mu\text{g/L}$). The As(III) concentrations were 1.2–8991.2 $\mu\text{g/L}$ (mean \pm SD: $296 \pm 1216 \mu\text{g/L}$, median: 17.4 $\mu\text{g/L}$); the percentage of As(III) referred to total As was 1.9–73.6% (mean \pm SD: $26.1 \pm 17.6\%$, median: 19.2%), which is significantly higher than that found by Smedley et al. (2002). In the western part of Nicaragua, As speciation was studied in 7 areas in alluvial sedimentary aquifers composed by weathering products of volcanic rocks and hydrothermal alterations (Barragne-Bigot, 2004). Total As concentrations of $n=76$ samples were 0.40–106 $\mu\text{g/L}$ (mean \pm SD: $11.4 \pm 20.8 \mu\text{g/L}$, median: 3.65 $\mu\text{g/L}$). The As(III) concentrations were 0.1–56.4 $\mu\text{g/L}$ (mean \pm SD: $3.9 \pm 10.9 \mu\text{g/L}$, median: 1.1 $\mu\text{g/L}$); the percentage of As(III) referred to total As was 4.8–100% (mean \pm SD: $27.8 \pm 23.9\%$, median: 18.7); these values are similar to those of the Río Dulce aquifer groundwater. The Eh values in the 3 regions were 131–492 $\mu\text{g/L}$ (mean \pm SD: $330 \pm 374 \mu\text{g/L}$, median: 325 $\mu\text{g/L}$), 177–362 $\mu\text{g/L}$ (mean \pm SD: $274 \pm 42 \mu\text{g/L}$, median: 289 $\mu\text{g/L}$) and 40–331 $\mu\text{g/L}$ (mean \pm SD: $182 \pm 72 \mu\text{g/L}$, median: 184 $\mu\text{g/L}$), respectively. In all the studied areas from Argentina and Nicaragua, there was no correlation between the percentage of As(III) and the Eh value; the respective correlation coefficients (r) were 0.08, 0.03, –0.07 for La Pampa, Río Dulce cone and Nicaragua, respectively. It can be recognized that the percentage of As(III) species is quite different in the La Pampa and the Río Dulce aquifers despite that the redox conditions are similar. On the other hand, it can be seen that the percentage of As(III) in the Río Dulce and Nicaraguan aquifers is similar, although the redox potential in the Nicaraguan case is significantly lower compared to that of the Río Dulce aquifer. This indicates that no redox equilibria exist between the different As species.

Although total As concentrations have been measured in various parts of Mexico, few studies report the redox states of As in water. At Comarca Lagunera, about 90% of As in groundwater correspond to As(V) (Del Razo et al., 1990; Rosas et al., 1999); however, no redox potentials were given in these studies. A similar predominance of As(V) (more than 95%) was measured in the most As-polluted samples from an alluvial and a fractured limestone aquifer in Zimapán Valley (Armienta et al., 2001). Differences in oxidation state predominance were measured in the Rio Verde basin; a higher proportion of As(III) was measured in the aquifer within lacustrine deposits compared to fluvial sediments where most of the As occurs as As(V) (Planer-Friedrich et al., 2001).

2.2. Mechanisms of arsenic mobilization

The concentration of As dissolved in ground- and surface-water bodies is a function of space and time and depends on the available primary and secondary As sources, the fluid properties (pH, redox potential, ions present, ionic strength, contents of organic matter, etc.) and interfacial processes between solid and fluid which comprise: (i) chemical processes such as dissolution/precipitation, (ii) microbiological transformations and (iii) physicochemical processes such as adsorption/desorption and ion exchange. The As mobilization is governed by (i) the As source and (ii) site- or zone-specific hydrogeochemical conditions that may result in extremely heterogeneous lateral and vertical distributions of As in groundwater, as typical for different parts of Latin America such as the Chaco-Pampean plain, Argentina (Smedley et al., 2005; Bundschuh et al., 2004; Bhattacharya et al., 2006), and Sébaco Valley, Nicaragua (Altamirano Espinoza and Bundschuh, 2009).

In Latin America, the processes relevant for As mobilization and remobilization are:

- Sulfide oxidation in mineralized areas: (hydrothermal deposits, sulfide ore deposits).
- Formation of secondary As minerals: metal oxyhydroxides (as principal As source in many sedimentary aquifers) are formed by different geogenic processes such as sulfide oxidation, and generally dissolution/leaching of rocks and minerals followed by precipitation of these secondary minerals as a function of local hydrochemical conditions (especially redox and pH) on sediment particles of sedimentary aquifers.
- As remobilization from metal oxides and oxyhydroxides, by (i) dissolution of metal oxyhydroxides under very acid conditions and (ii) by desorption of As from metal oxyhydroxides at high pH (>8) and oxidizing conditions.

Sulfide oxidation, especially those of pyrite and arsenopyrite, forms an important mechanism for As mobilization in all areas with sulfide mineralization (non-authigenic As source). Hence, this is a very common process found in the Andes, the Middle American cordillera and the Transmexican Volcanic Belt with volcanism or plutonism-related mineralization, which can release substantial amounts of As into the groundwater. These oxidation processes are often catalyzed by abiotic microbe activity, which increases the reaction rate (Nordstrom and Southam, 1997; Nordstrom and Alpers, 1999). The Fe released by the oxidation reaction tends to precipitate as sulfate, oxide or oxyhydroxide with re-adsorption and co-precipitation of As and forms an important reduction of As mobility. However, under very acidic conditions, the Fe oxyhydroxides are unstable.

Oxides and oxyhydroxides of Fe, Mn and Al form the principal secondary As minerals, which can act – depending on the present geochemical conditions – as sources and sinks for dissolved As. The retention/release of As by oxides and oxyhydroxides is predominantly controlled by sorption and precipitation/dissolution. These processes can explain the concentrations of many arseniferous aquifers, especially those formed by unconsolidated and consolidated sediments. Desorption is the principal control of dissolved As concentrations in many aquifers composed of consolidated and unconsolidated sediments.

Adsorption of ions on the solid phase surface depends on the surface charge of the solid. Generally, the metal oxides and oxyhydroxides have a variable surface charge, which is function of its mineral-specific pH point of zero charge (pH_{pzc}) where the mineral surface has no net charge on its surface, and the pH of the water (pH_w). If $pH_w < pH_{pzc}$, the mineral surface is positively charged and can adsorb As if present as oxyanions (adsorption capacity increases with decreasing pH_w). Highest adsorption affinity of As(V) on metal oxides and oxyhydroxides ranges

according to their pH_{pzc} between 7 and 9 (Dzombak and Morel, 1990; Sigg and Stumm, 1981; Davies and Kent, 1990; Fuller et al., 1993). Iron oxides and oxyhydroxides are considered as principal adsorbents of As(V) in many sand and silt aquifers (Smedley and Kinniburgh, 2002). The kinetics of these adsorption processes is fast (range of minutes), which allows a fast adaptation, e.g. if water flows within an aquifers with variable geochemical conditions (Fuller et al., 1993).

3. Arsenic in the Precolumbian Era

In northern Chile, there are evidences that chronic arsenicosis has affected human populations for more than 7000 years; mummies of the *Chinchorro culture*, whose individuals lived between about BC 7000 and BC 2000 in the coastal zone of northern Chile and southern Peru (between Ilo and Antofagasta, about 17–22° S; Fig. 3) presented typical manifestations due to As ingestion. Most of the mummies were found in zones rich in minerals containing As and most of the water resources in the region contained high As concentrations (200–5000 µg/L). This culture developed a complex funeral by including an intricate process of mummification of its defuncts (Arriaza et al., 2010; Rivadeneira et al., 2010), which permitted its conservation and provides material for analyses on bones, skin and hair of the mummies (Table 2) (Byrne et al., 2010). Arsenic concentrations in hair are very variable from one site to the other. High As mean values are reported from Morro, Iquique and Camarones, whereas the mean contents from the other sampling sites are much lower. The highest average As contents in hair were found at Morro Sanitary Station, close to Arica (696 mg/kg).

Throughout time, the funeral preparations of the *Chinchorro culture* have undergone various variations which have led behind different types of mummies: the black, the red, the bandaged, and the mud-coated mummies (Uhle, 1917, 1919; Arriaza, 1995a,b; Arriaza and Standen, 2008; Bittmann, 1982; Guillén, 1992; Schiappacasse and Niemeyer, 1984; Standen, 1991, 1997). The study of the external paints of 6 black mummies (Table 3) from the city of Arica (Fig. 3) resulted in an ample range of As contents of 31–6891 mg/kg whereas 6 red mummies, also from Arica, indicated a smaller range (1172–5392 mg/kg) but higher average values (Table 3). The only black mummy from Playa La Lisera (~2.5 km S of Arica) presented high As concentration (1771 mg/kg) within As concentrations range of paint from the black mummies of Arica. The As concentrations in external paints of mummies from the Camarones valley (250 km southeast of Arica) is very different for black and red mummies (black: 116 mg/kg; red: 7299 mg/kg); reasons may be the changes of the construction of the mummies or the different geological sources of the primary materials used for paints (Table 3). The clayey materials with which the 5 black mummies were filled have very variable As contents in the different sectors from where the mummies are coming (Table 3); this is probably due to different As contents in the clays of the different sites. In the area of Arica city, As contents are low (6.0–51.6 mg/kg) compared to those from Playa La Lisera (66.8 mg/kg) and Caleta Camarones (Camarones cave) (73.0 mg/kg); however, the limited number of studied mummies does not allow to establish tendencies for the individual areas (Parra, 2007; Mella, 2007; Gutierrez, 2007).

4. Few findings until the 1960s

From the beginning of the 19th century to the 1960s, only few discoveries of natural As contaminations of water resources were reported from Argentina, Chile and Mexico. In this section, these findings will be described and the updated knowledge of levels of As in water resources in these countries will be presented.

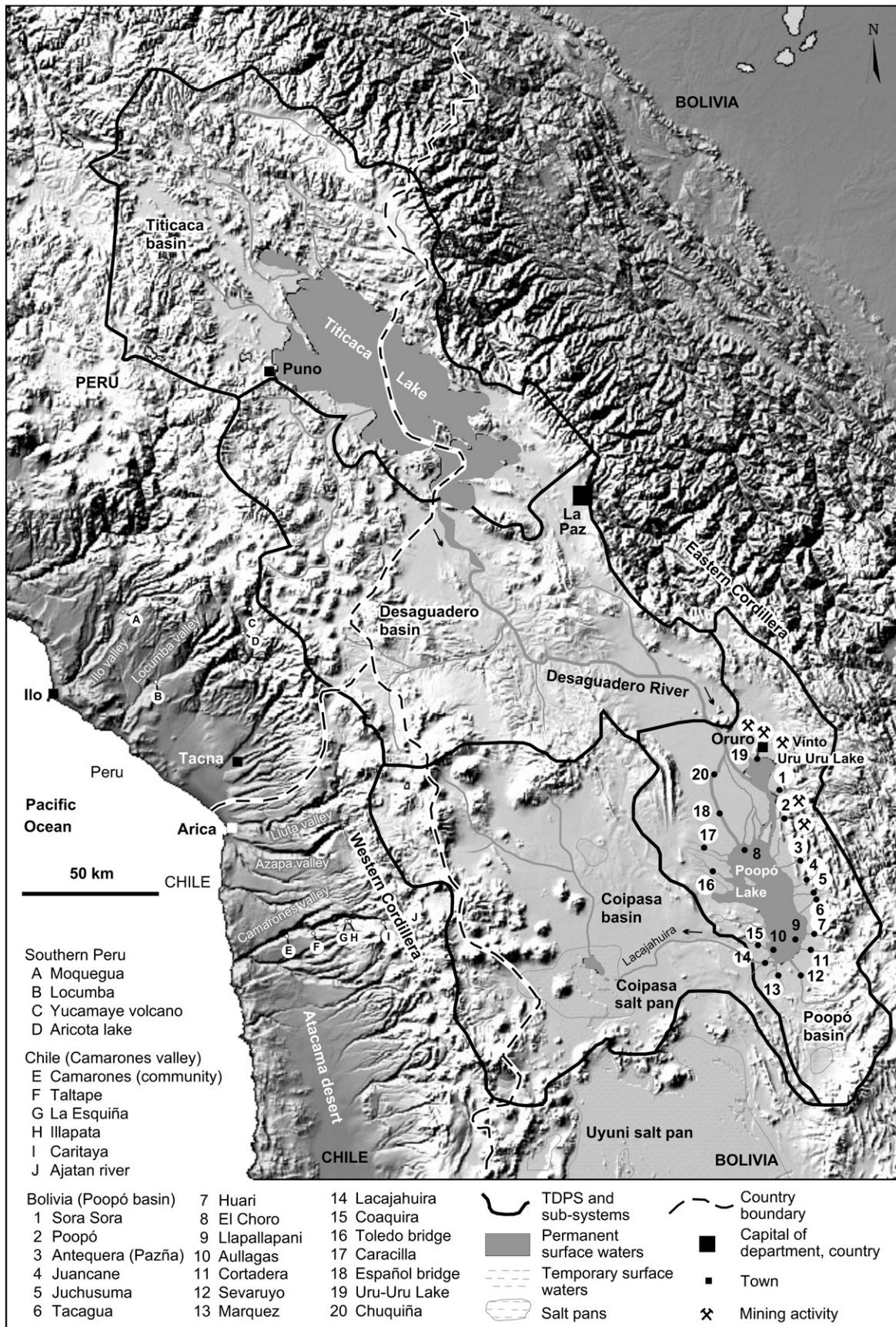


Fig. 3. Geomorphological setting of northern Chile, southern Peru and the Andean part of Bolivia. The digital elevation model digital model of the world PIA3388 (<http://photojournal.jpl.nasa.gov>) is courtesy of NASA/JPL-Caltech. Modified from Bundschuh et al. (2008).

Table 2

Arsenic contents (AsH) of mummy hair from different burial sites in Atacama desert area (northern Chile) and arsenic concentrations in water resources. Modified from Byrne et al., 2010.

Burial site (total n = 46)	AsH ^a (mg/kg)	Total As in water ^b (mg/L)
Camarones (n = 10)	Average 37.8 ± 48.0 Range 147.5 – 1.9	1.00 (Camarones River)
Morro (n = 9)	Average 58.8 ± 103.8 Range 262.2 – 0.8 ^c	<0.01 (Azapa river)
Iquique (n = 6)	Average 45.7 ± 92.5 Range 234.3 – 2.6	–
Yungay (n = 8)	Average 2.8 ± 3.6 Range 11.4 – 0.8 ^c	<0.01 (Azapa river)
Azapa (n = 12) ^d	Average 6.9 ± 9.9 Range 37.7 – 0.8 ^c	<0.01 (Azapa river)
Morro Sanitary Station ^e	Average ≈ 696 ± 151	<0.01 (Azapa river)

^a AsH average for each burial site ± standard deviation; AsH concentrations >20.5 mg/kg were estimated.

^b Current nearest water course.

^c Below the detection limit <0.8 mg/kg.

^d Post-Chinchorro agriculture community.

^e This mummy was first reported by Max Uhle in 1922.

4.1. Arsenic detection in groundwater of Argentina

Argentina was the first country in Latin America from where As occurrence in groundwater has been reported. In the beginning of the 20th century, in the locality of Bell Ville (Córdoba province, central Chaco–Pampean plain, Fig. 2), the toxic effects of As on the public health were mentioned in several publications during the years 1913–1917. The Argentine physician Dr. Mario Goyenechea described in 1913 for the first time skin lesions in his work “About a new disease detected in Bell Ville” (published in Spanish as “*Sobre una nueva enfermedad descubierta en Bell Ville*”) (Goyenechea, 1917) and related it to As in drinking water and for food preparation. From here, the new illness was termed as “Bell Ville disease”. In 1917/18, Dr. Abel Ayerza described exhaustively the cardiovascular and cutaneous manifestations of this disease and named it “Chronic Endemic Regional Arsenicism” (in Spanish: “*Arsenicismo Regional Endémico*”) (Ayerza, 1917a,b, 1918). Ayerza (1917a,b) found that 1300 (15%) of the 8534 inhabitants in the rural area of Bell Ville town suffered from the homonymous disease. Trelles et al. (1970) transcribed the data statistics of patients registered by the regional hospital of Bell Ville in

Table 3

Content of total arsenic (mg/kg) in exterior paint and internal clay fillings of Chinchorro mummies from northern Chile.

Material type	Arica city	Playa La Lisera (sector south of Arica city)	Caleta (cave) Camarones
<i>Black mummies</i>			
Clayey material (internal filling)	6.0 ± 0.5 (n = 1)	66.8 ± 6.8 (n = 1)	73.0 ± 0.9 (n = 1)
	20.0 ± 0.6 (n = 1)		
	51.6 ± 1.9 (n = 1)		
Black paint (exterior)	31 ± 1.31 (n = 1)	1771 ± 2.45 (n = 1)	116 ± 5.5 (n = 1)
	4585 ± 163 (n = 1)		
	6891 ± 164 (n = 1)		
	3328 ± 68 (n = 1)		
	410 ± 9.52 (n = 1)		
<i>Red mummies</i>			
Black paint (exterior)	1172 ± 101 (n = 1)	–	7299 ± 306 (n = 1)
	3647 ± 151 (n = 1)		
	2116 ± 84 (n = 1)		
	364 ± 35 (n = 1)		
	5392 ± 239 (n = 1)		
	2887 ± 225 (n = 1)		

Each sample was analyzed in triplicate, given are the respective means and standard deviation.

the years 1934–1944 and found 511 patients affected by arsenicism. Later, in 1921, Reichert and Trelles discovered As in groundwater in many agricultural areas of the Chaco–Pampean plain (Reichert and Trelles, 1921), and found the highest concentration in the groundwater of the Río Tercero river basin (Córdoba province, Fig. 2), and in the north of the Santa Fe province (Fig. 2). In the early 1950s, the physician Prof. Dr. Enrique E. Tello introduced in his work “Chronic Endemic Regional Hydroarsenicism (CERHA), its Clinical Manifestations” (published in Spanish as “*Hidroarsenicismo Crónico Regional Endémico (HACRE), Sus Manifestaciones Clínicas*”) a new name for the disease that relates it to its source water (Tello, 1951). Three decades later, Tello described the health effects of 339 registered patients originating from the provinces of Buenos Aires, Córdoba, Chaco, Santa Fe and Salta (Tello, 1986, 1988). In the 1990s, Biagini et al. (1995) reported that between 1972 and 1993, 87 persons affected by As-related health effects were predominantly from the northern part of the Chaco–Pampean plain (provinces Santiago del Estero, Chaco and Salta, Fig. 2). The Chaco–Pampean plain comprises the principal cattle-raising areas of Argentina, which is the largest milk producer in the world; the evaluation of As content in bovine milk and the biotransference from As-contaminated water intake carried out by Pérez Carrera and Fernández Cirelli (2007) in the Córdoba province and by Sigríst et al. (2010) in the Santa Fe province, acquire thus special significance (see Bundschuh et al., 2012). The Chaco–Pampean plain is the largest one in Latin America and one the largest geographic units in the world affected by As-contaminated groundwater, as will be discussed in detail in a paper of this special issue (Nicolli et al., 2012).

In the next few decades, new regions with high concentrations of As in groundwater were identified, mostly in the Chaco–Pampean plain, and some in the Andean highlands (e.g. Astolfi et al., 1981, 1982; Nicolli et al., 1985; Smedley et al., 2005; Bundschuh et al., 2004, 2008, 2009). In Argentina, until the end of the 20th century, As-rich groundwater and, to some extent, surface water from the provinces of Córdoba, Tucumán, Santa Fe, La Pampa, Santiago del Estero, Salta, Chaco and Formosa in the Chaco–Pampean Plain, and from the provinces of Jujuy and Salta in the Andean highlands were found to have high levels of As (Table 4, Fig. 2). Furthermore, the problem of As in groundwater was detected in several other provinces, mostly in smaller alluvial basins at the Andean foothills in the provinces of Mendoza, San Luis, San Juan, La Rioja, Catamarca, and in Patagonia (Chubut province, Fig. 1) from where only few data have been reported (Table 4, Fig. 2) (Ministerio de Salud, 2005). In Copahue area (Neuquen province), As is released from the crater lake of the Copahue volcano into a river, but no report on the adjacent groundwater has been published (Fig. 2).

The about 1 million km² covering Chaco–Pampean plain of Argentina is the largest identified area in the world with high As concentrations in groundwater (e.g., Nicolli et al., 1989, 2001a,b, 2004, 2009a,b; Smedley et al., 2002, 2005; Bhattacharya et al., 2006; Farías et al., 2003; Bundschuh et al., 2004, 2008, 2009). The plain is very uniform regarding morphology, sedimentological composition and regional groundwater recharge in the Andean regions and their foothills to the west. The redox conditions of the aquifers are moderately reducing to oxidizing, and As(V) is the predominant As species (for discussion of As species see Section 2.1). Arsenic and other trace elements such as V, Mo, U, and minor elements such as B and F are assumed to have their original source in volcanic ash (originating from the volcanism in the Andes), which is contained to 5–25% in the loess-type sediments of the Chaco–Pampean plain. The volcanic ash, contains over 90% glass of rhyolitic composition, which has generally As concentrations of 5–8 mg/kg; due to its amorphous structure it is highly soluble in water (Nicolli et al., 1989; Smedley et al., 2002, 2005; Bundschuh et al., 2004). In geological time spans, this As was dissolved under favorable conditions and precipitated or adsorbed on Fe, Al, Mn oxyhydroxides from where desorption can occur as a fast process, according to changing

Table 4

Overview of arsenic concentrations in groundwater of different areas of Argentina obtained in the principal studies performed. n>L gives number of samples exceeding 10 µg/L and percentage of n. Studies with only punctual arsenic data are not included. In many cases the original data of the mentioned studies were used rather than the data presented in the references.dat.

Location ^a	Area (km ²)	Depth (m b.s.)	Spec.	As range (µg/L)	As mean (µg/L)	SD	median (µg/L)	n	n>L	References of study
<i>Chaco-Pampean Plain</i>										
SE Salta prov. (Chaco–Salteña plain)	10,000	na	t-As	50–3200	na	na	na	na	na	Farfán Torres et al. (2006)
Flooded lowlands (limit between Salta and Chaco provinces)										
shallow-medium levels	na	12–90	t-As	200–1500	na	na	na	na	na	Rodríguez de Sastre et al. (1993)
deep	na	190–220	t-As	130–270	na	na	na	24	24(100%)	Farfán Torres et al. (2006)
Chaco prov. (11 departments of central Chaco region: Comdte. Fernández, Independencia, Quitilipi, Maipú, Almirante Brown, Gral. Belgrano, 9 de Julio, 25 de Mayo, 12 de Octubre, Mayor Jorge Fontana and San Lorenzo)	33,200	Shallow	t-As	10–5000	na	na	na	79	56	Osicka et al. (2002)
W Chaco prov. shallow	na	4–20						28		
deep		20–100	tAs	6–250	61.5	na	na	13	38(93%)	Blanes et al.(2006)
Centre-W Chaco province Shallow	na	4–20	tAs	3–180	48	na	33	na	37 (86%)	Blanes and Giménez (2004)
Deep		20–100	tAs	11–246	68	na	23	na	19 (95%)	Blanes and Giménez (2004)
W Santiago del Estero prov. (1) Copo dep. (disperse rural communities)	3000									Ministerio de Salud (2005)
Lujan		na ^b	t-As	515–697	618	94	643	3	3	
La Firmeza		na ^b	t-As	<10–651	173	237	40	14	10	
Monte Quemado		na ^b	t-As	<10–710	112	264	10	7	2	
Santos Lugares		na ^b	t-As	133–519	376	146	401	5	5	
Urutaú		na ^b	t-As	<10–84	13	15	10	24	5	
Las Termas		na ^b	t-As	<10–278	57	100	10	7	2	
San Bernardo		na ^b	t-As	450	–	–	–	1	1	
Venado Solo		na ^b	t-As	926	–	–	–	1	1	
Malvinas		na ^b	t-As	37	–	–	–	1	1	
(2) Río Dulce alluvial cone	1500									
Robles dep.		6–13	t-As	2–2400	172	391	45	65	47 (72%)	Bundschuh et al. (2004)
La Banda and Robles dep.		3–10	t-As	7–14,969	732	2640	54	40	39 (98%)	Claesson and Fagerberg (2003)
			As-III	1.2–1813	125	371	9.9	40	–	
La Banda and Robles dep.		1.9–10	t-As	11.5–13,494	520	2008	81	58	58 (100%)	Bejarano Sifuentes and Nordberg (2003)
			As-III	6.8–8991	498	1740	41	34	–	
Banda dep.		62–70	t-As	9.0–10.0	9.5	29	9.5	2	0 (0%)	
		4–10	t-As	10–1900	432	153	30	19	18 (63%)	Mellano and Ramirez (2004)
Capital, Robles, and Silipica dep.		6–17	t-As	6.6–3278	289	707	56	26	25 (96%)	Lindbäck and Sjölin (2006)
S Santa Fe prov.	40,000	na		100–700	na	na	na	na	na	Madiec et al. (2000)
Center-north Santa Fe prov.	12,000	0.60–110	t-As	0.015–780	97.8	94	70.6	141	139 (99%)	Nicolli et al. (2008a,b, 2009b)
Central Santa Fe Prov., Las Colonias dep.	224	8–12	t-As	6–201	58	40	46	82	2	Ministerio de Salud (2005)
SE Córdoba prov.	10,000	2–22	t-As	103–3810	390	712	150	54	54 (100%)	Nicolli et al. (1985, 1989)
SE Córdoba prov. Shallow	10,000	3–15	t-As	80–4500	1100	1.4	na	19	19 (100%)	Pérez Carrera and Fernández Cirelli (2004)
Deep		80–150	t-As	<20–200	40	0.04	na	18	na	Pérez Carrera and Fernández Cirelli (2004)
S Córdoba prov.		Phreatic								
Los Jagüeles basin	na	2–10	t-As	<20–500	173	137	100	na	na	Cabrera et al. (2005)
Vicuña Mackena	na	2–10	t-As	<20–300	80.9	96.6	50.0	na	na	Cabrera et al. (2005)
Alejo Ledesma rural zone	na	2–10	t-As	5–1700	412	417	300	na	na	Cabrera et al. (2005)
San Basilio-Monte de los Gauchos	na	2–10	t-As	50–400	150	110	100	na	na	Cabrera et al. (2005)
Río Cuarto rural zone	na	2–10	t-As	<20–750	84	162	na	na	na	Cabrera et al. (2005)
Moldes rural zone	na na	2–10	t-As	<20–250	63	57	50	na	na	Cabrera et al. (2005)
El Barreal Stream basin	na	2–10	t-As	<20–900	108	176	45.0	na	na	Cabrera et al. (2005)
La Colacha basin	na	2–10	t-As	27–239	93.5	57.7	77.6	na	na	Cabrera et al. (2005)
Chaján Stream basin	na	2–10	t-As	<20–400	136	116	70.0	na	na	Cabrera et al. (2005)
S Córdoba prov.										
El Barreal Stream basin		10–15	t-As	0.5–900	89.7	146	35.0	49	na	Matteoda et al. (2007)
Córdoba, B. Aires, Santa Fe, San Luis prov.	150,000	Phreatic	t-As	10–593	108	127	67	66	66	Farías et al. (2003)
SE Buenos Aires prov.	6000	na	t-As	100–2000	na	na	na	na	na	La Dymas (1975)

(continued on next page)

Table 4 (continued)

Location ^a	Area (km ²)	Depth (m b.s.)	Spec.	As range (µg/L)	As mean (µg/L)	SD	median (µg/L)	n	n>L	References of study
S Buenos Aires prov, Bahía Blanca area	31,400	2–40	t-As	<10–4000	na	na	na	79	56 (71%)	Blanco et al. (2003)
	46,000	3–35	t-As	0–4000	na	na	na	93	48 (52%)	Fiorentino et al. (1998)
N La Pampa prov.	8000	2–130	t-As	<4–5280	372	847	137	111	102 (92%)	Smedley et al. (2002, 2009)
General Pico-Dorila	2930	0.60–4	t-As	<100–400	100	na	na	1370	(>90%)	Medus et al. (2005)
<i>Andean Highlands</i>										
W Jujuy (Tumbaya, Susques in Cochinoa dep.)	5000	Phreatic	t-As	6–9770	625	2181	30	36	32 (89%)	Fariás et al. (2009)
NW Salta prov. (San Antonio de Los Cobres in Los Andes dep.)	-	na	t-As	179–248	209	35	200	3	3 (100%)	Fariás et al. (2009)
<i>Subandean Valleys/Andean Foothills (alluvial fills)</i>										
S Jujuy prov. (Manuel Belgrano, Palpalá in San Antonio dep.)	3200	na	t-As	5–10	6.8	1.8	6.0	6	0 (0%)	Fariás et al. (2009)
Tucumán prov.										
Salí River basin	7300									
Shallow		3–15	t-As	12.2–1660	159	349	45.8	42	42 (100%)	Nicolli et al. (2001a, 2004)
Deep		30–150	t-As	11.4–107	37.9	20.2	33.7	26	26 (100%)	Nicolli et al. (2001a, 2004)
Artesian		200–>400	t-As	16.2–76.9	36.4	18.2	26.5	17	17 (100%)	Nicolli et al. (2001a, 2004)
Burrucacú basin	2700									
Shallow		3–15	t-As	15.8–1610	160	363	43.2	20	20 (100%)	Nicolli et al. (2001b, 2009a)
Deep		30–150	t-As	13.8–36.6	25.0	8.3	22.3	21	21 (100%)	Nicolli et al. (2001b, 2009a)
Artesian		200–>400	t-As	15.7–144	41.1	35.1	28.4	28	28 (100%)	Nicolli et al. (2001b, 2009a)
Burrucacú basin, Los Pereyra (shallow)			t-As	19.7–758	418	na	185	31	na	Warren (2001)
Burrucacú basin, Los Pereyra (deep)		208–477	t-As	0.25–70	12	na	8.9	25	na	Warren (2001)
S part of Salí River basin (NW of Guasayán ranges)			t-As	27–76	52.0	na	na	9		García et al. (2009)
N Mendoza prov. (departament of Lavalle)	10,212	2–5	t-As	<12–584	102	125	290	25	23 (92%)	Pérez Carrera et al. (2008)
N Mendoza prov. (department of Lavalle)	na	na	t-As	<10–822	125	190	48.0	37	34 (92%)	Cáceres et al. (2005)
S and E San Luis prov. (dep. Coronel Pringles, Gen. Pedernera, Gob. Dupuy)	na	na	t-As	>50	na	na	na	na	na	González et al. (2003, 2004)
	na	na	t-As	43–170	na	na	na	na	na	González et al. (2003, 2004)
Buena Esperanza: (13 wells)										
S San Luis prov. Quinto River basin shallow	na	10–12	t-As	11.1–103	34.5	na	na	11	11(100%)	Galindo et al. (2007)
La Rioja prov. (alluvial fan of La Rioja city)	1000									Martinez and Carrillo-Rivera (2006)
Group I: N and NE of La Rioja city		na	t-As	≤38	na	na	na	na	na	
Group II: S of La Rioja city		na	t-As	≤380	na	na	na	na	na	
Group III: W of La Rioja city; groundwater with origin at Sierra de Velasco		na	t-As	7–12	na	na	na	na	na	
Group IV: SE of La Rioja city corresponding to regional groundwater flow		na	t-As	127	na	na	na	na	na	
San Juan prov. (12 departments: Jáchal, Iglesia, Rawson, Pocitos, Zonda, Rivadavia, Caucete, Ullum, Valle Fétil, Calingasta, 25 de Mayo, Sarmiento).	na	na	t-As	<10–280	29.7	40.0	18.5	60	44 (73%)	Cáceres et al. (2005)
San Juan prov. (25 de Mayo dep.)	na	na	t-As	10–280	80.8	94.2	39.5	6	5 (83%)	Cáceres et al. (2005)
<i>Patagonia</i>										
Chubut prov. (public system of water supply of 27 localities)	18,088									
Garayalde (Florentino Ameghino dep.)		na	t-As	30–100	na	na	na	na	na	Sandali and Diez (2004)
Camarones (Florentino Ameghino dep.)		na	t-As	50–100	na	na	na	na	na	Sandali and Diez (2004)
Other 25 localities (Florentino Ameghino dep.)		na	t-As	<20	na	na	na	na	na	Sandali and Diez (2004)

na: not available.

^a G: geothermal; M: mining; dep. Department; prov. province; Gen: General.; Gob: Gobernador; n: number of samples. t-As: Total arsenic.^b Water source not stated for the individual water samples, but in most cases well water from the phreatic aquifer (30–40 m depth) with few deeper perforations and few rainwater harvesters.

geochemical conditions in time and space. Such changing conditions result in a very patchy distribution of concentrations of dissolved As on short distance with so-called “hotspots” (Bundschuh et al., 2004; Bhattacharya et al., 2006), as we can also find in other areas of Latin America, e.g. in Sébacco valley (Nicaragua; Altamirano Espinoza and Bundschuh, 2009).

The hot spots are characterized by presence of Na–HCO₃ type groundwater and high pH (>8), whereas low concentrations of dissolved As are found in zones with Ca–HCO₃ type of groundwater with about neutral pH. Ion exchange (due to longer residence time in these sections of the aquifer) where Na from the solid phase is exchanged by Ca²⁺ and Mg²⁺ from the groundwater, and further by

dissolution of carbonates, can explain the genesis of these NaHCO_3 type groundwater and the pH increase, which favors As desorption from oxyhydroxides of Fe, Al, and Mn (pH of water becomes more positively depleted versus pH_{pzc} of the adsorbent). However, other processes must be considered as co-acting As mobility controls such as the presence of ions competing for the As adsorption sites: anions and oxyanions of V, Mo, PO_4^{3-} and HCO_3^- . This process is favored within As hot spots due to the often highly mineralized groundwater and high concentrations of V and Mo. Additionally, evaporative As concentration increase is locally of importance, especially in small internal drainage systems, leading to an increasing concentration of dissolved As toward depressions without flushing, which are very common all over the Chaco–Pampean region (Nicolli et al., 1989; Nicolli et al., 2010; Smedley et al., 2002, 2005; Bundschuh et al., 2004; Bhattacharya et al., 2006).

In the following, we compile the concentrations of As, V, Mo, U, B and F for five study areas A_1 to A_5 of Chaco–Pampean plain, which are described in detail by Nicolli et al. (2012): (i) northwestern Chaco–Pampean plain (Salí and Burrucacú basins: A_1); (ii) Central areas of the Chaco–Pampean plain comprising Río Dulce cone (A_2); (iii) the area in the east of the Córdoba province (A_3); (iv) eastern areas of the Chaco–Pampean plain comprising the northern part of the Santa Fe province (A_4); and (v) southern areas of Chaco–Pampean plain comprising the northern part of the La Pampa province (A_5). More details about the individual areas and the aquifers can be found in Table 4. In total 633 data sets were compiled from different resources (A_1 : Nicolli et al. (2004, 2009a); A_2 : Claesson and Fagerberg (2003), Bejarano Sifuentes and Nordberg (2003), Mellano and Ramirez (2004), Bundschuh et al. (2004), Lindbäck and Sjölin (2006); A_3 : Nicolli et al. (1985); A_4 : Nicolli et al. (2009b); A_5 : Smedley et al. (2002)). The compilation shows the following concentrations: As: $<1\text{--}14,969 \mu\text{g/L}$ (mean \pm SD: $294 \pm 1067 \mu\text{g/L}$, median: $65.6 \mu\text{g/L}$, $n = 633$), V: $0.1\text{--}3550.0 \mu\text{g/L}$ (mean \pm SD: $177 \pm 316 \mu\text{g/L}$, median: $90 \mu\text{g/L}$, $n = 497$), Mo: $<1\text{--}6280 \mu\text{g/L}$ (mean \pm SD: $88.2 \pm 341 \mu\text{g/L}$, median: $21.1 \mu\text{g/L}$, $n = 488$), U: $<1\text{--}515 \mu\text{g/L}$ (mean \pm SD: $25.6 \pm 37.0 \mu\text{g/L}$, median: $15.8 \mu\text{g/L}$, $n = 413$), B: $34.0\text{--}18,865 \mu\text{g/L}$ (mean \pm SD: $1702 \pm 1777 \mu\text{g/L}$, median: $1230 \mu\text{g/L}$, $n = 362$) and F: $<1\text{--}24,382 \mu\text{g/L}$ (mean \pm SD: $1308 \pm 2122 \mu\text{g/L}$, median: $758 \mu\text{g/L}$, $n = 477$), aquifers indicate moderate reducing to oxidizing conditions; respective Eh data are: $90\text{--}570 \text{ mV}$ (mean \pm SD: $325 \pm 70 \text{ mV}$, median:

328 mV , $n = 483$). The mobilization and re-precipitation of these elements have led to secondary minerals; for example, the Fe, Al, and Mn oxyhydroxides, which coprecipitated and/or adsorbed As, constitute important secondary As minerals, which – under alkaline conditions ($\text{pH} > 8$) – release As into the water due to desorption. In the Chaco–Pampean plain, high pH waters generally correspond to Na-HCO_3 waters whose genesis can be explained by high residence time in the aquifer, which favored ion exchange where Na from the solid phase is exchanged for Ca^{2+} and Mg^{2+} from the liquid phase. This explains the positive correlations between As and pH and between As and Na as well as the negative correlations between As and As and Mg concentrations in the water. However, since many processes interact to very different extent in the different studied areas, the correlation is very variable in the different areas as well as within the individual areas themselves (e.g. related to different geochemical conditions and occurring processes within different vertical and horizontal zones); the correlation (as r) is therefore moderate but clearly existing: As with pH: 0.18, 0.12, 0.33, 0.51 and 0.47; As with Na: 0.55, 0.16, -0.01 , -0.12 and 0.01; As with Ca: 0.16, -0.15 , -0.25 , -0.29 and -0.21 and As with Mg: 0.10, -0.15 , -0.23 , -0.25 and -0.19 for the areas A_1 to A_5 , respectively.

This also explains the correlation of As with the previously mentioned elements, which can be observed in many regions of the Chaco–Pampean plain (Nicolli et al., 1989; Nicolli et al., 2010; Smedley et al., 2002, 2005; Bundschuh et al., 2004; Bhattacharya et al., 2006). Despite of the described uniform regional pattern (sediments, regional groundwater flow, regional recharge, etc.), local processes, especially local groundwater recharge may result in local deviations and can explain why the previous correlations are not observed in all areas of the plain. Since mobilities of the elements V, Mo, U, B, and F are different, the process of aquifer flushing and related changes of the geochemical conditions (especially of pH and Eh) can lead to mobilization or sequestration of the mentioned elements; the mode and grade depends thereby on the individual element. This can explain why the correlation between As and the other specific elements is dissimilar in the different regions of the Chaco–Pampean plain. In the following, we compare relations of concentrations of As and other elements for the previously mentioned areas A_1 to A_5 . Correlation coefficients (r) for the correlation of As with V, Mo, U, B and F are as follows: As with V: 0.66, 0.58, 0.57, 0.86, 0.85; As with Mo: 0.64, 0.62, -0.02 , 0.76, 0.26; As with U: 0.60, 0.22, 0.42, 0.30, 0.32; As

Table 5

Reported arsenic concentrations in groundwaters (except otherwise stated) of Mexico and possible sources (for locations see Fig. 1).

Location	Maximum As concentration ($\mu\text{g/L}$)	Origin	References
Comarca Lagunera	800	Geogenic; Alluvial aquifer	Del Razo et al., 1990; Cebrián et al., 1994; Rosas et al., 1999; Ortega-Guerrero, 2003; Molina, 2004; Gutierrez-Ojeda, 2009
(Durango, Coahuila, Chihuahua)			
Hermosillo, Sonora	305	Geogenic	Wyatt et al., 1998
Zimapán, Hidalgo	1100	Geogenic and anthropogenic; Mining zone	Armienta et al., 1997, 2001; Sracek et al., 2010
Baja California Sur	410	Mining residues	Carrillo-Chávez et al., 2000
Río Verde, San Luis Potosí	50	Geogenic	Planer-Friedrich et al., 2001
Villa De la Paz, San Luis Potosí	265 (reservoir) 5900 (channels)	Anthropogenic and geogenic; Mining zone	Castro-Larragoitia et al., 1997; Yáñez et al., 2003; Razo et al., 2004a,b
Acapulco, Puebla	206	Geogenic (geothermic)	Quinto et al., 1995
Valle de Guadiana, Durango	167	Geogenic (volcanic rocks?)	Alarcón-Herrera et al., 2001
Guanajuato	80 (Acámbaro)	Anthropogenic and geogenic	http://proteccioncivil.guanajuato.gob.mx/atlas/sanitario/acambaro.php
	300 (El Copal)		Rodríguez et al., 2006
	180 (Salamanca)	Anthropogenic	Mejía et al., 2007
	220 (Cuerámaro)	Geogenic (geothermal)	Martínez and García, 2007
	120 (Independencia aquifer)	Geogenic, possible mineralization	Mahlknecht et al., 2004
Los Azufres, Michoacán	24,000	Geogenic (geothermal)	Birkle, 1998, Birkle et al. 2010
Aguascalientes	14.5	Geogenic	Trejo-Vázquez and Bonilla-Petriciolet, 2002
Zacatecas	500	Unknown?	Leal-Ascencio and Gelover-Santiago, 2006
Jalisco	263	Geogenic (geothermal)	Hurtado-Jiménez and Gardea-Torresdey, 2009
Oaxaca	178	Geogenic?	Caballero-Gutiérrez et al., 2010
Chihuahua	170 (Las Vírgenes reservoir)	Anthropogenic and geogenic	Hernández-García, 2007
	474	Geogenic, mineralization	Reyes-Cortés et al., 2006; Mahlkecht et al., 2008

with B: 0.54, 0.75, 0.78, 0.28, 0.27; As with F: 0.38, 0.87, na, 0.83, 0.70, for the areas A₁ to A₅, respectively (na: not available).

Though there are many sites with As contamination of groundwater resources in Argentina, there are relative fewer epidemiological and risk assessment studies, which described the health effects of As exposure from the provinces of Córdoba (e.g., Hopenhayn-Rich et al., 1996, 1998), Chaco (e.g., Concha et al., 1998a,b; Medina et al., 2004) and Santa Fe (e.g., Corey et al., 2005) in the Chaco–Pampean plain, but also in the Andean Highlands in the areas of San Antonio de Los Cobres (Salta province; e.g., Concha et al., 1998a,b) and in the province of Jujuy (Fig. 2) (e.g., Fariás et al., 2003, 2009). A nationwide assessment was performed by the Argentine Ministry of Health (Ministerio de Salud, 2005). These studies will be discussed in detail together with others in this volume (McClintock et al., 2012).

It has been estimated that between 1.2 and 2 million people are exposed to As considering the safe limit of 50 µg/L in drinking water. However, the number of people chronically exposed would increase somewhat between 3 and 8 million if the safety limit is considered to be the 10 µg/L introduced in 2007 in Argentina.

4.2. Arsenic discoveries in groundwater of Mexico

In Mexico, the chronic exposure to As from groundwater originating from sedimentary aquifers was identified in 1958 from the Lagunera region, in the northern part of the country (Durango and Coahuila states, Fig. 1; Cebrián et al., 1994; Armienta and Segovia, 2008). In 1962, 40 cases and one fatality were reported from the urban area of Torreón (Comarca Lagunera, Coahuila state, Fig. 1) (Castro de Esparza, 2009). Since then, an increasing number of studies related to As in the environmental, health and geochemical sciences were undertaken in Mexico. Today, As in supplied water have been found in 13 out of the 31 Mexican states including Durango, Coahuila, Zacatecas, Morelos, Aguascalientes, Chihuahua, Sonora, Puebla, Nuevo León, Jalisco, Oaxaca, Guanajuato and San Luis Potosí (Fig. 1, Table 5). From these locations, an estimated 450,000 people are found to be exposed to >50 µg/L of As (Castro de Esparza, 2009; Armienta et al., 2008). However, if the current national regulatory limit (25 µg/L) is used, the number of exposed people would increase by several folds.

Most of the research on As in Mexico was focused on the identification of signs and symptoms of chronic As poisoning. Studies dealing with the environmental assessment of As contamination in specific areas, although less abundant, is growing. However, research focused on the recognition of specific processes releasing As to groundwater was only performed in certain zones. Development of treatment alternatives to remove As from water had started since the last decade. An overview of toxicological studies, treatment options, co-occurrence of As and F in groundwater, and As in geothermal areas of Mexico is presented in other articles of this special volume (Armienta and Segovia, 2008; Litter et al., 2012 and López et al., 2012). Arsenic on fluids of high-enthalpy volcanic and low-enthalpy geothermal systems of petroleum reservoirs are discussed in a review paper by Birkle et al. (2010). This paper will focus on the information not included in other papers, mainly on research dealing with the environmental fate and identification of As sources in contaminated zones.

Studies on the behavior of As in the environment started with the determination of total As concentrations in drinking water of zones where As health effects were observed in the population (Chávez et al., 1964; Cebrián et al., 1994). Later on, speciation determinations and research to determine specific As sources in polluted areas were also included (Del Razo et al., 1990). At Comarca Lagunera (Fig. 1), the first publications reported pesticides used in cotton fields, extensively raised since 1930, as one of the causes of groundwater As pollution. A natural source related with an extinct hydrothermal system was also proposed, based on the co-occurrence of boron, fluoride and lithium

in As-polluted water (González-Hita et al., 1991). Subsequent hydrogeological, geological and hydrogeochemical studies led to the recognition of other natural processes like evaporation, dissolution of Fe and Mn oxides and sulfides oxidation, as causes for groundwater As enrichment (Ortega-Guerrero, 2003; Molina, 2004; Gutierrez-Ojeda, 2009). About 400,000 people were considered to be exposed to As concentrations >50 µg/L in that zone (Cebrián et al., 1994). Comarca Lagunera is one of the most important cattle-raising areas of Mexico. The evaluation of As content in cow-milk and the translocation factors from polluted water intake carried out by Rosas et al. (1999) has thus special significance (see Bundschuh et al., 2012).

The As concentration in groundwater was also determined at other zones in northern Mexico, such as Sonora and Chihuahua states (Wyatt et al., 1998; Alarcón-Herrera et al., 2001) (Fig. 1). A geogenic origin of As was assumed based on the correlation between As and fluoride concentrations in Chihuahua water samples, and also on the geology and hydrogeology of the Guadiana valley in Durango state (Fig. 1) (Alarcón-Herrera et al., 2001).

Detailed hydrogeological and hydrogeochemical studies were also performed at other zones like the Independencia aquifer, the Río Verde, and the Zimapán valleys in Central Mexico (Fig. 1), which recognized natural As water sources (Armienta et al., 1997, 2001; Planer-Friedrich et al., 2001; Mahlknecht et al., 2004; Ortega-Guerrero, 2009).

Arsenic pollution in aquifers, superficial water bodies, soils and wastes were studied in several mining zones of the country. Natural and anthropogenic origin of As in groundwater was identified at certain locations (Castro-Larragoitia et al., 1997; Armienta et al., 1997, 2001; Carrillo-Chávez et al., 2000; Razo et al., 2004a; Rodríguez et al., 2005). At Zimapán, central Mexico, hydrogeochemical modeling jointly with mineralogical and chemical analyses of rock formations showed arsenopyrite oxidation and scorodite dissolution as plausible processes releasing As to the fractured deep limestone aquifer (Armienta et al., 1997, 2001). Isotopic and chemometric studies revealed a distinction between the characteristics of deep wells contaminated by natural sources, and those of shallow wells polluted by tailings (Sracek et al., 2010). In Santa María de la Paz, San Luis Potosí state (Fig. 1), Castro-Larragoitia et al. (1997) determined As contents in soils, water and tailings. Further studies by Razo et al. (2004a) proposed arsenopyrite oxidation and natural dissolution of sulfides under high alkalinity and anaerobic conditions to cause the presence of As in groundwater. Carrillo-Chávez et al. (2000) measured high As contents in groundwater near mine waste piles in San Antonio-El Triunfo Area Baja California Sur (Fig. 1), and identified main geochemical processes of As along the flow-path. An overview of the information on groundwater As presence in Mexico may be found in Armienta et al. (2008) and Armienta and Segovia (2008).

Environmental impact of mine wastes and smelter dust and fumes including As dispersion was also addressed in various zones of San Luis Potosí, Hidalgo, Chihuahua, Guerrero, Sonora, Guanajuato and Baja California states (Fig. 1). These studies included the determination of heavy metals and As mobilization processes in tailings, based mainly on chemical and mineralogical characteristics (Talavera et al., 2005; Gutiérrez-Ruiz et al., 2007; Romero et al., 2006, 2008). Geochemical mobility of As was assessed by means of physico-chemical and mineralogical and sequential fractionation determinations of diverse tailing waste piles at Hidalgo and Guanajuato states (Méndez and Armienta, 2003; García-Meza et al., 2004, 2006; Ramos-Arroyo and Siebe, 2007). Leachate analyses, leaching experiments and geochemical modeling were carried out to determine As and heavy metals mobility from tailing piles and smelter slags at Guanajuato, Taxco and Santa María de la Paz mining districts (Fig. 1) (Manz and Castro, 1997; Carrillo-Chávez et al., 2003; Talavera et al., 2006; Mendoza Amézquita et al., 2006).

Arsenic contents in soils contaminated by tailings and smelting operations were also assessed at several sites. Ongley et al. (2007) determined the influence of old smelters and tailings on As

concentration and distribution in soils at Zimapán mining district (Fig. 1), and studied its liability and concentration variations with depth. Gutierrez, 2007) measured total and soluble contents of As and heavy metals in soils to assess the influence of inactive tailings in the mining district of Santa Barbara in Chihuahua state (Fig. 1). Naranjo-Pulido et al. (2002) determined As contents in an abandoned mining zone of Baja California Sur. Bioaccessibility experiments in soils of the mining district of Santa Maria de la Paz in San Luis Potosí state, developed by Razo et al. (2004b), showed more than 4 times As bioaccessibility determined by the PBET method (simulation of the human digestion process) in soils impacted by a smelter with respect to those impacted by mine wastes.

Arsenic concentration, sources and mobility were studied also in some rivers and coastal sediments including Sonora, Hidalgo, Guerrero, Chihuahua and Baja California states. Coastal sediments of the La Paz lagoon and the Sonora state did not show As contamination (Shumilin et al., 2001; Jara-Marini and García-Rico, 2006). However, sediment cores from the Colorado river remnant delta (Fig. 1) showed a probable contamination of As from pesticides used in the first half of the past century (Daesslé et al., 2009). River sediments at mining zones reflected the influence of mines and tailings settled on their shores (García et al., 2001; Gutiérrez-Ruiz et al., 2007; Gutiérrez and Carreón, 2008). Studies on As fractionation evidenced a predominance of As in the fractions with the lowest environmental mobility (residual, and oxides and hydroxides of iron) (García et al., 2001; Gutiérrez-Ruiz et al., 2007). Concentration of As in sediments and water of three storage lakes of Chihuahua state (La Boquilla, El Granero, Las Vírgenes) was measured in 2005 and 2006. Average As contents in sediments ranged from 9.11 to 16.62 mg/kg without significant differences among the lakes or the seasons (Hernández-García et al., 2008). Average As concentrations in water ranged from 6 to 21 µg/L except for the sample taken from Las Vírgenes in spring that had 170 µg/L (Hernández-García, 2007). Arsenic concentrations in other water reservoirs in Chihuahua have also been determined: Chuiscar, El Rejón, San Marcos and Chihuahua. Sediments collected in spring, summer and autumn of 2008 contained from 3.147 to 7.307 mg/kg As on average; the highest water As concentration in water (10 µg/L) was measured in Chuiscar storage lake in winter (Cano de los Ríos, 2010; Pérez-Vargas, 2010). While the input of residual waters has been suggested as the origin of As in the storage lakes (Hernández-García, 2007), agrochemicals may also be important source. Further As mobilization of acid igneous rocks and sulfide mineralization may be a further source.

4.3. Arsenic detections in surface water and groundwater of Chile

As already reported in Section 2, in northern Chile, in the wider area of Atacama Desert (Figs. 2 and 3), the inhabitants have been exposed to As from drinking water and food for a long time as found in mummies of the Chinchorro culture (Arriaza et al., 2010; Byrne et al.,

2010; Rivadeneira et al., 2010). However, it was not until 1962 that first cases of As-related health effects were reported from the city of Antofagasta (Fig. 2). In Antofagasta, As exposure was a consequence of the new drinking water supply introduced in 1958 that pumped water from the Loa river and its tributaries containing high As (average 800 µg/L; Bundschuh et al., 2008, 2009). Arsenic in river water is predominantly released from volcanic rocks and sulfide ore deposits and their weathering products at the Andean volcanic chain. Here, it is mobilized by snow melt and rain and transported into the rivers and springs. These rivers were the only freshwater resource in northern Chile at that time (Romero et al., 2003; Bundschuh et al., 2008, 2009). Additionally, geothermal manifestations are locally important sources of As, as the geothermal springs from El Tatio (Fig. 2) (Landrum et al., 2009), which will be discussed in another paper of this special issue (López et al., 2012).

In northern Chile, the first skin lesion cases were detected in the beginning of the 1960s, especially in children and, later on, other As-related health effects were described. At that time, a total of 500,000 people were exposed in northern Chile to As by drinking water (Castro de Esparza, 2009). In the city of Antofagasta, 130,000 inhabitants were exposed from 1958 to 1970 (12 years) to high As levels in drinking water. In Calama (Fig. 2), the second largest city of the affected area, a removal plant was installed in 1978. These As removal plants solved the problem in Antofagasta, Calama and in some other larger urban areas (Rivara et al., 1997; Cortina et al., 2012). At present, additional several seawater desalination plants are operating in northern Chile to provide drinking water (Bundschuh et al., 2010; Cortina et al., 2012). The well-defined exposure time to As allowed to study extensively the epidemiological aspects of the Chilean As case through the following decades (e.g., Borgoño and Greiber, 1972; Pizarro and Balabanoff, 1973; Puga et al., 1973; Klohn, 1974; Borgoño et al., 1977; Smith et al., 1998; Karcher et al., 1999; Ferreccio et al., 2000; Sancha and Frenz, 2000; Sancha et al., 2000; Hopenhayn-Rich et al., 2000; Bates et al., 2004b; Christian and Hopenhayn, 2004; Cáceres et al., 2005).

However, in many smaller towns, villages and isolated houses in northern Chile, water with As is still used for drinking and irrigation purposes. For example, the Chiu Chiu area (Fig. 2) (Smith et al., 2000) and some rural settlements in the region of Arica and Parinacota (XV Region) (Fig. 3), where the population still suffers from chronic arsenicism as a consequence of As exposure through water and soil (Table 6), and transference to animal fodder and human food (Lara et al., 2006; Cornejo et al., 2006a,b, 2008; Bundschuh et al., 2008). This was shown by high As accumulation in human hair, nails and urine. Yáñez et al. (2005) took samples from two communities, Esquiña and Illapata, located in the Camarones valley (Fig. 3). The population of Esquiña consumes drinking water coming from small waterfalls (As: 12.2–74.0 µg/L), whereas the population of Illapata consumes drinking water from the Camarones river and waterfalls (As: 48.7 and 1252 µg/L, respectively: 92.0–99.5% as As(V)), though river water is

Table 6

Contents of total arsenic in water and soil of the valleys of the region Arica and Parinacota (northern Chile); for locations see Fig. 3. Modified from Bundschuh et al., 2008.

Site	Location (Latitude, Longitude)	As in water ^a (mg/L)	As in soil ^a (mg/kg)
Río Lluta	18.39400° S, 70.29047° W	0.20 ± 0.010	40 ± 2
Río Azapa	18.51317° S, 70.21317° W	0.02 ± 0.001	8 ± 1
Río Lluta (Puente Chacabuco)	18.40883° S, 70.10742° W	0.28 ± 0.002	38 ± 2
Río Lluta (Humedal)	18.40319° S, 70.32303° W	0.03 ± 0.001	32 ± 2
Río Caritaya	18.94197° S, 69.41497° W	5.10 ± 0.030	489 ± 15
Río Camarones (Illapata)	18.94144° S, 69.50856° W	1.24 ± 0.090	300 ± 7
Río Camarones (Taltape)	19.00211° S, 69.81958° W	1.10 ± 0.020	105 ± 6
Río Camarones (Camarones town)	19.00356° S, 69.85656° W	1.04 ± 0.010	100 ± 8
Río Camarones (embouchure into Pacific)	19.18197° S, 70.27047° W	0.92 ± 0.020	120 ± 6

^a Each value corresponds to the mean value and the standard deviation from three determinations.

Table 7
Arsenic species in hair of the Esquiña and Illapata populations; for locations see Fig. 3.
Modified from Yáñez et al., 2005.

Village	Population	As in hair (mg/kg) average (min–max.)			
		As (III)	DMA	MMA	As(V)
Esquiña (n = 22)	Children (n = 11)	0.40 (nd–1.53)	nd	0.01 (nd–0.02)	0.15 (nd–0.37)
	Adults (n = 11)	0.13 (0.02–0.71)	nd	0.02 (nd–0.03)	0.17 (nd–0.41)
	SD	0.37		0.01	0.11
	Average Esquiña	0.26	nd	0.02	0.15
Illapata (n = 21)	Children (n = 8)	2.15 (0.56–3.24)	0.18 (nd–0.35)	0.02 (nd–0.03)	0.18 (0.1–0.47)
	Adults (n = 13)	4.74 (0.23–13.72)	0.07 (nd–0.07)	0.05 (nd–0.15)	0.614 (0.21–1.52)
	SD	3.87	0.11	0.04	0.38
	Average Illapata	3.75	0.16	0.04	0.45

nd: not detected. For calculation of averages, only values over the detection limits were considered.

preferred by the population (Yáñez et al., 2005). The authors found that the average total As (AsT) contents in hair from 21 individuals of Esquiña and 22 individuals from Illapata were 0.7 and 6.1 mg/kg, respectively (Table 7). Most of the As (98%) corresponds to inorganic As (AsI); respective mean As(III) contents were 0.25 and 3.75 mg/kg in Esquiña and Illapata, and the respective mean As(V) contents were 0.15 and 0.45 mg/kg. The analyzed organic species, DMA(V) and MMA(V) amount to less than 2% of the extracted AsT. The study found that the contents of AsT, As(III) and As(V) in hair depend on the age of the exposed individuals from Illapata ($r=0.65$, 0.69 , 0.57 , respectively) and on the exposure time, which corresponds to the residence time in Illapata ($r=0.54$, 0.71 and 0.58 , respectively). In another study, As contents in water, urine, hair, and nails (Fig. 4) were studied in people from the same localities (Cornejo et al., 2008). In this study, the As concentration of drinking water from Esquiña and Illapata were found to be 50 and 1090 $\mu\text{g/L}$, respectively. Total As concentrations in the two villages were 0.20 and 1.10 $\mu\text{g/L}$ in urine, 0.30 and 3.8 mg/kg in hair, and 3.2 and 11.2 mg/kg in nails, respectively (Fig. 4), confirming the influence of the As levels in both geogenic sources.

Another study in northern Chile is from the region of Coquimbo, in Elqui valley (9800 km^2) (Fig. 1). Elqui river and its tributaries, which rise in the Andes at 3500–4000 m above mean sea level (a.s.l.), drain areas with important hydrothermal alterations and epithermal ore deposits; these include As-rich copper dikes at the well-known locality of El Indio (gold mining at El Indio–Tambo district; 29.32028°S 70.02778°W). Recent studies found that As in the sediments of the valley amounts to 55–485 mg/kg (202 ± 45 mg/kg, $n = 14$) in river

sediments and 119–2.344 mg/kg (747 ± 544 mg/kg, $n = 14$) in Holocene lake sediments, mostly associated to iron oxides and iron oxyhydroxides (Oyarzun et al., 2004). Since the enrichment of As is found not only in the river sediments, which are influenced by mining activities, but also in the Holocene lacustrine sediments ($BP 9640 \pm 40$, Oyarzun et al., 2004), the authors conclude that the As contamination of Elqui valley arises not only from mining activities but also from erosion and natural leaching. A high erosion is caused by heavy rainfalls related to the El Niño (Oyarzun et al., 2004).

Due to the same geological setting (volcanic mountain chain of the Andes, geothermal activities, mining operations), it is expected that As concentrations can be at elevated levels in other areas of Chile. Thus, the Maipo river basin (SE of Santiago de Chile (Fig. 2), which drains the area of San José and Tupungatito volcanoes, contains geothermal springs with predominantly NaCl-type water and As concentrations between 300 and 1300 $\mu\text{g/L}$, which affect the river water quality (Mohammad Ayaz Alam, personal communication).

5. Arsenic: from the 1970s to the 20th century

After the description of the first identification of As in water resources in Argentina, Mexico, and Chile, As problem was detected from 1970s to 1990s in an increasing number of regions in these and in new countries. For example, the problem was described in Peru in the 1970s from Ilo valley (Kirchmer and Castro, 1979; Castro de Esparza, 2009; Bundschuh et al., 2008, 2009) and later from Rímac river basin in the east of Lima, capital of Peru (Castro, 1993; Infante Fernández and Sosa Palomino, 1994; MEM-DGAA, 1997; Bedregal et al., 2001; Juárez Soto, 2006; Bundschuh et al., 2008). In Mexico, Argentina, and Chile, new regions were found (Sections 4.1, 4.2 and 4.3). In the following, the detections in Peru, where the As problem has been reported in the period from the 1970s on and followed by the studies performed until today will be described.

5.1. Arsenic detection in groundwater and surface water resources of Peru

In Peru, there are several sites where water resources are affected by high As concentrations (Figs. 1 and 3). In most cases, As is of geogenic origin and released predominantly in the Andean region by natural weathering and by mining activities. From Andean region, As is transported predominantly by water and river sediments to the low lying semi-desertic, more densely habited areas. These waters are used there for irrigation before being discharged into the Pacific Ocean. In 2000, it was estimated that in Peru at least 250,000 people drink water with As concentrations exceeding 50 $\mu\text{g/L}$, the current national regulatory limit (2011) (Sancha and Castro de Esparza, 2000; Castro de Esparza, 2002, 2010). The rural population that relies on untreated water is the most exposed to high As in Peru.

In 2002, elevated concentrations of As were reported in the Locumba river basin (200–400 $\mu\text{g As/L}$, Castro de Esparza, 2002)

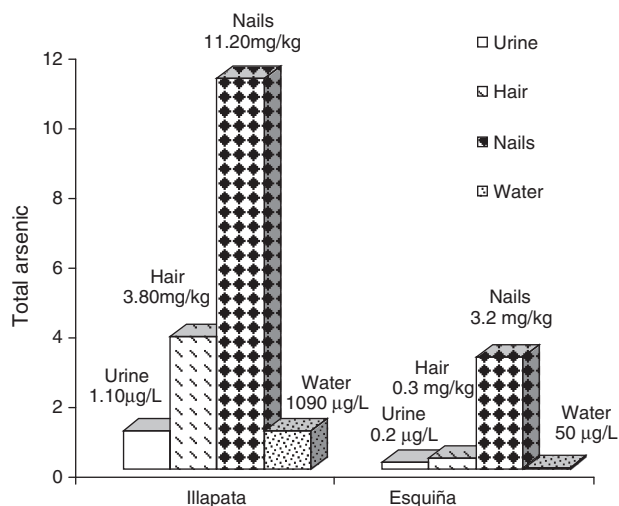


Fig. 4. Total arsenic content in urine, hair and nails of residents from Illapata and Esquiña (Camarones valley, northern Chile).
Modified from Cornejo et al., 2006b.

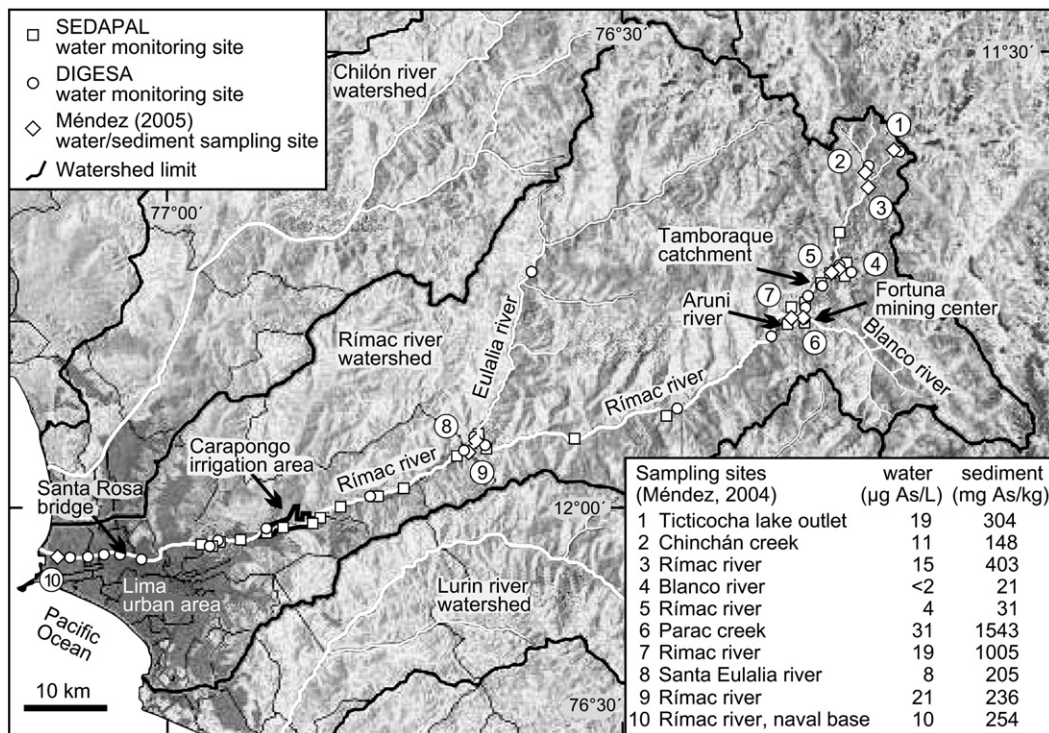


Fig. 5. The Rímac watershed (central Peru) with surface water monitoring station of the Water and Sewage Service of Lima (*Servicio de Agua Potable y Alcantarillado de Lima*, SEDAPAL) and the General Division of Environmental Health (*Dirección General de Salud Ambiental*, DIGESA) (compiled from Juárez Soto (2006)). Additional plotted are the surface and riverbed sediment sampling sites and respective arsenic concentrations of Méndez (2005).

(Fig. 3). In the homonymous valley, the population living along the river is exposed to As from drinking water exceeding the national regulations (50 µg/L). At present, the population is supplied by drinking water from a cistern; however, the As-contaminated water is still used for other purposes including irrigation and animal husbandry. Though the population in the Locumba valley consumed drinking water with toxic As concentrations for a long period, no visual evidence of health effects can be found (Castro de Esparza, 2002, 2003).

Ilo city uses water from the Locumba river basin (Fig. 3), which is conducted by a channel to Ilo. The water from the Locumba river and its tributaries contains 400–1500 µg As/L (CEPIS, 1975). Kirchmer and Castro (1979) investigated different technologies for As removal and, in 1982, a treatment plant for As removal was installed in Ilo (Siveroni, 1989; Castro de Esparza, 2009; see also Cortina et al., 2012). The tributaries of the Locumba river, the Collazas and Salado rivers, having As concentrations of 640 and 1680 µg/L, respectively, pass through the area of the Yucamane volcano (Fig. 3), where As mobilization from volcanic rocks and pyroclastic materials occurs. These rivers discharge As-contaminated water into the Aricota lake (Siveroni, 1989).

From December 2004 to September 2006, As contents were studied in samples of the basins of Sama and Quebrada de la Yarada rivers (a wider area of Tacna city, Fig. 3) (Jorge et al., 2006). Here, in the localities of Amopaya, Sama and Inclán, As concentrations in the range of 140–230 µg/L were found in river water with an As(III)/As(V) ratio of 0.1.

In the area of Puno (Andean highland, Fig. 3), 44% of the groundwater wells installed to provide the population microbiologically safe drinking water, As concentrations exceeded the provisional WHO guideline value and 10% exceed the Peruvian regulatory limit (Castro de Esparza et al., 2005; Castro de Esparza, 2010). The highest observed As concentration was 180 µg/L.

In 1999, a study of As in drinking water was performed in Huaytará (the largest province of the Huancavélica department) (Fig. 1). The

average As concentration of the 31 analyzed samples was 246 µg/L; the highest values were from Pachac, probably due to anthropogenic contamination by As-based fertilizers and pesticides (Flores, 1999).

Other As sources exist in the Morococha mining region and in the La Oroya smelting complex (Yauli Prov, Junin Department; Fig. 1), which influence the water of the Yauli river, where As concentrations of up to 460 µg/L have been found (Zenitagoya et al., 2004).

The Rímac river basin (Figs. 1 and 5), situated east of Lima, at the occidental flank of the Andes, is also contaminated by As. The contamination originates predominantly from mining activities in the middle and upper part of the basin and from natural leaching of Andean volcanic rocks and sulfidic ore deposits (Infante Fernández and Sosa Palomino, 1994; MEM-DGAA, 1997). Arsenic is mined as arsenopyrite and orpiment (Méndez, 2005). The Rímac river basin

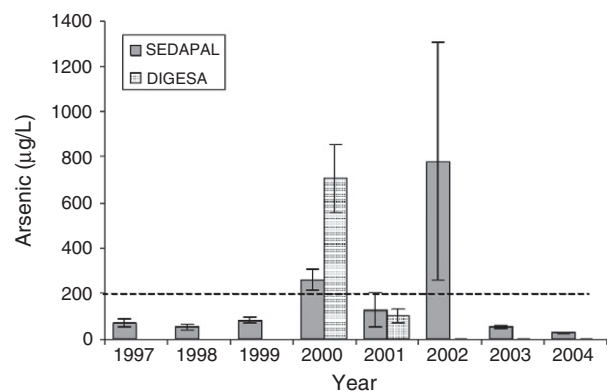


Fig. 6. Mean arsenic concentrations by year in surface water of Rímac river basin performed by SEDAPAL (1997–2004) and DIGESA (2000–2001). The vertical bars represent the standard deviation. The 200 µg/L concentration line corresponds to the regulatory limit established in Peru for As in irrigation water. Modified from Juárez Soto, 2006.

Table 8

Mean arsenic concentrations in river water by year and part of the Rimac watershed basin in the years 1997–2004 (in $\mu\text{g/L}$); for location see Figs. 1 and 5. Modified from Juárez Soto (2006).

Year	As ($\mu\text{g/L}$)		
	Upper basin	Middle basin	Lower basin
1997	100 \pm 40	50 \pm 10	60 \pm 10
1998	80 \pm 20	30 \pm <10	40 \pm 10
1999	50 \pm 10	130 \pm 10	100 \pm 10
2000	220 \pm 80	360 \pm 60	240 \pm 30
2001	190 \pm 140	50 \pm <10	40 \pm 10
2002	1160 \pm 1000	410 \pm 30	290 \pm 40
2003	40 \pm 10	50 \pm <10	60 \pm 20
2004	20 \pm <10	30 \pm <10	30 \pm <10

Each value corresponds to the mean value and the standard deviation from three determinations.

(3300 km^2) is one of the most important Peruvian hydrographic basins, with an average width of 16 km and extending over 200 km from the Andes to the area of Lima. This river provides 71.8% of the drinking water to Lima through the La Atarjea Drinking Water Treatment Plant (SEDAPAL, 2004). The Rimac river basin includes the Santa Eulalia (1098 km^2) and Río Blanco (194 km^2) sub-basins (Fig. 5). The geological units that crop out in the basin are sedimentary, metamorphic, volcanic and intrusive rocks; a large number of mines that exploit polymetallic deposits containing zinc, copper, silver and lead, are located in the upper part of the Rimac river watershed (Méndez, 2005). The presence of As adversely influences the quality of water and the soils and vegetables in the lower part of the basin, and constitutes a severe human health risk (Castro, 1993; Infante Fernández and Sosa Palomino, 1994; MEM-DGAA, 1997; Bedregal et al., 2001; Juárez Soto, 2006). The first investigations were performed in 1994, where As concentrations were determined in 53 samples of drinking water, river, well and spring water. It was found that 84.9% (Infante Fernández and Sosa Palomino, 1994) of the samples exceeded the limit recommended by the WHO. Nevertheless, no cases of As poisoning have been recorded.

The water quality of the Rimac basin is periodically monitored by the Water and Sewage Service of Lima (*Servicio de Agua Potable y Alcantarillado de Lima*, SEDAPAL), and by the General Division of Environmental Health (*Dirección General de Salud Ambiental*, DIGESA). Using data from both institutions, Juárez Soto (2006) studied the spatial and temporal historical data on the water quality of the Rimac river basin.

The annual average As concentrations in 1997, 1998, 1999, 2001, 2003 and 2004 were <200 $\mu\text{g/L}$ (acceptable for irrigation according to national regulations) (Fig. 6). However, in 2000 (260 $\mu\text{g/L}$; SEDAPAL and 710 $\mu\text{g/L}$, DIGESA), 2001 and 2002, the 200 $\mu\text{g/L}$ limit was exceeded. There are large spatial variations. This can be seen considering the year 2000 (average 260 $\mu\text{g/L}$ SEDAPAL, 710 $\mu\text{g/L}$ DIGESA), when the highest concentrations (1630 $\mu\text{g/L}$ As) were detected in Puente Santa Rosa, and for 2001 (average 130 $\mu\text{g/L}$ SEDAPAL, 100 $\mu\text{g/L}$ DIGESA), when the highest As concentrations (1330 $\mu\text{g/L}$) were reported from Aruri river, area of Toma Tamboraque (650 $\mu\text{g/L}$) and Santa Rosa bridge (380 $\mu\text{g/L}$) (Fig. 5). The highest As concentrations of 9160 $\mu\text{g/L}$ were measured in the river water in the area close to the mining center Fortuna (Centro Minero Fortuna; sulfide ore deposits; Fig. 5). High As concentrations are generally found in river waters of the upstream area of Rimac river basin (Table 8); however, temporal variations of As concentrations are high in the entire area. All the annual average As concentrations from the upper, middle and lower part of Rimac watershed exceed the provisional WHO guideline value of 10 $\mu\text{g/L}$ (Table 8). Within the observation 1997–2004 period, the years with the highest concentrations were 2000–2002. This indicates that the enforced environmental regulations of Peru resulted in a significant reduction of As released by mining activities into the Rimac river basin. However, the large amounts of As, uptaken especially

in the years 2000–2002 by the soils in the lowest part of the basin, extensively used for agriculture, constitute a severe problem and require periodical future monitoring by the respective authorities. The As contamination of vegetables in the Carapongo irrigation area (lower Rimac basin, Lurigancho–Chosica district; Fig. 5) was investigated by Juárez Soto (2006) and is discussed in this special issue (Bundschuh et al., 2012).

Méndez (2005) investigated the influence of mining activities on water and riverbed sediments in Rimac river watershed. River water and sediment samples were taken in October 2004 from 10 sites. At most (60%) sampled locations in Rimac watershed, As exceeds the WHO provisional guideline value of 10 $\mu\text{g/L}$ but not the Peruvian regulatory limit of 50 $\mu\text{g/L}$ (Fig. 5). Arsenic concentrations are the lowest at Blanco river (≤ 2 $\mu\text{g/L}$, detection limit) and the highest at Parac creek (31 $\mu\text{g/L}$) (Fig. 5); the median was 13 $\mu\text{g/L}$. In riverbed sediment, As contents ranged from 21 to 1543 mg/kg (median: 245 mg/kg). Eight sediment samples had high As contents (148–1543 mg/kg); the highest value was found at Parac creek (1543 mg/kg), the lowest at Blanco river (21 mg/kg) (Fig. 5).

6. Arsenic in the 21st century

In 10 of the 14 Latin American countries where high As concentrations in groundwater and surface waters (not including geothermal aquifers) are known today (Fig. 1), this problem was detected/described since the turn of the 20th century in Nicaragua (1996/2000), El Salvador (1998), Brazil (1998/2000), Bolivia (2001), Venezuela (2005), Ecuador (2005), Honduras (2006), Uruguay (2005/06), Colombia (2007), Guatemala (2007), and Costa Rica (2005/2009) (Bundschuh et al., 2009). These new findings show that at least 94 localities in Latin America (Fig. 1) are affected by high As levels in a significant manner. The increased number of sites with As also suggests that many other sites of similar geological settings may have high As in ground- and surface water.

6.1. Central America

High levels of As were detected in surface water and groundwater used for drinking and irrigation purposes in several places in Central America. In most cases, the origin of As is natural due to the tectonic setting of the Pacific coast at a subduction zone with numerous volcanoes. Leaching predominantly from volcanic rocks and hydrothermal vents and their weathering products are common sources for As in freshwater resources. Geothermal fluids, often rich in As, are another important As source. The presence of faults and contacts between different rock types channelize the circulation of hydrothermal fluids surrounding the magmatic chambers of active and dormant volcanoes (e.g. López et al., 2004; Pérez et al., 2004; Birkle and Bundschuh, 2007a,b); this allows geothermal fluids emerge toward the earth's surface (fumaroles, hot springs). Geothermal fluids may contaminate groundwater and surface water resources that are used for water supply. Arsenic of geothermal origin will be discussed in this issue in detail in the paper by López et al. (2012). Furthermore, there are several sites where As is released into the environment from mining activities and related metallurgical processing. With exception of Nicaragua, no epidemiological studies have been performed yet in Central America. To our knowledge, As in the food chain was only studied rudimentarily in Nicaragua and El Salvador, where As contents in fishes were investigated (see Bundschuh et al., 2012).

6.1.1. Guatemala

In June 2007, there were several announcements in the mass media about the presence of As in the public water supply system (groundwater) in different areas of the municipality of Mixco (Fig. 1) in the department of Guatemala whose origin is natural due to leaching from volcanic rocks (Cardoso et al., 2010). The average As

concentration in the well was 15 µg/L (Garrido Hoyos et al., 2007; Garrido Hoyos and Avilés Flores, 2008; Bundschuh et al., 2010; Cardoso et al., 2010).

In a recent study, Archer and Elmore (2010) investigated the release of As from ceramic pot filters in the region of Antigua and, they found that the source of As contamination was the clay itself. They stated that some clay sources in Guatemala have been excluded from use because they could release more than WHO standard for As exposure of 10 µg/L.

Other water quality studies by Elmore et al. (2005) at the village of San Sebastian de Lemoa, located at the Guatemala Highlands, did not show As concentrations above the detection limit. The test kit used here was “ArsenicCheck for Water” manufactured by Hybrivet Systems, Inc. This procedure has a detection limit of 10 µg/L (Elmore et al., 2005). However, the geology of Guatemala with a chain of active volcanoes and geothermal systems (see López et al., 2012) and the presence of ore deposits containing arsenopyrite (e.g. the Sb–W–Au deposits at Ixtahuacan, Guillimette and Williams-Jones, 1993) suggest that As could be a water quality problem in Guatemala that has not been fully assessed.

The health and environmental impacts produced by the Marlin Mine have been studied recently by researchers from the Physicians for Human Rights at the University of Michigan (Basu and Hu, 2010). The study includes analysis of water samples from Tzala and Cuilco rivers above the mine, Tailings creek (a discharge from the tailings) that discharges into Quivichil Creek, and at Quivichil Creek. Inhabitants from five communities around the mine were also investigated. The results of this research show that individuals residing closer to the mine had higher levels of urinary mercury, copper, arsenic, zinc when compared to those living in villages away from the mine. For the 23 individuals that participated in the study, the range of As concentration in blood samples was 3.20–8.50 µg/L (mean ± SD: 4.18 ± 1.14 µg/L). The range of As concentration in urine samples was from 0.04 to 16.71 µg/L (mean ± SD: 3.22 ± 4.81 µg/L). Arsenic levels in the river waters were 0.160, 0.060, 0.400, and 0.050 µg/L for samples from the Tzala river, the Tailings creek, the Quivichil Creek, and the Cuilco river, respectively. For the sediment in the same order, the concentrations were 830, 520, 310, and 880 µg/kg. In addition, levels of blood aluminum, manganese, and cobalt were elevated with values ranging from 16.5 to 107.1, 7.3 to 24.3, and 0.2 to 1.5 µg/L, and median values of 52, 13.2, and 0.4 µg/L, respectively. These values are high in comparison to established reference ranges or thresholds of 16, <1, and <2 µg/L, respectively (Basu and Hu, 2010). Besides, for the river water and sediments, several metals such as

aluminum, manganese and cobalt were found at elevated levels in the river water and sediment sites adjacent to the mine when compared to the farther sites. This suggests that human exposures to certain metals may be elevated near the mine but it is not clear if these elevations pose a significant threat to health yet because the concentrations are still relatively low. The recommendation is to conduct more investigation and to communicate between the different water governing bodies actively involved in remediation this problem.

In another more comprehensive study (E-Tech International, 2010) of the Marlin Mine site, the quality of the water studied included long term monitoring and several databases (e.g. Ministry of Environment and Natural Resources in Guatemala (MARN), the mining company (Goldcorp)). Problems with the initial environmental impact assessment of the mine prior to exploitation are reported, as well as failures to comply with regulations during the 5 years of exploitation of the mine. The concentration of As in Quebrada Seca (they give this name to Tailing Creek in Elmore et al. study) was 120 µg/L at the end of April or early May, 2009. The large difference between the values encountered by Basu and Hu (2010) and the E-Tech International report can be explained by the seasonal variations in rainfall in Guatemala. With 2 seasons (rainy from May to October, and dry from November to April) and often the first heavy rains early at the end of the dry season. Data from two recently installed wells to monitor the groundwater downgradient from the tailing impoundment showed As concentrations of 261 and 46 µg/L, respectively. The authors report that the concentration of the supernatant in the tailing impoundment was only 38 µg/L in 2006 making the interpretation of the data not clear. However, seasonal effects could also explain this inconsistency because large seasonal variations in concentrations are observed in the data reported for other ions, suggesting that the tailings could be a variable source of contaminant input to the groundwater.

6.1.2. Honduras

Arsenic in Honduras has not been fully studied to understand the magnitude of the problem. Bibliographic references, if they exist, are not accessible. However, two types of industries have been identified that have the potential to contaminate the environment with As: geothermal energy exploitation and gold mining. Goff et al. (1986b) studied the geochemistry of springs in seven geothermal sites in Honduras and detected As in four of them: Azacualpa, Pavana, Platanares, and Vanes Caldera, presenting concentrations of As of 70, 110, 1260, and 1160 µg/L, respectively. However, only one sample is

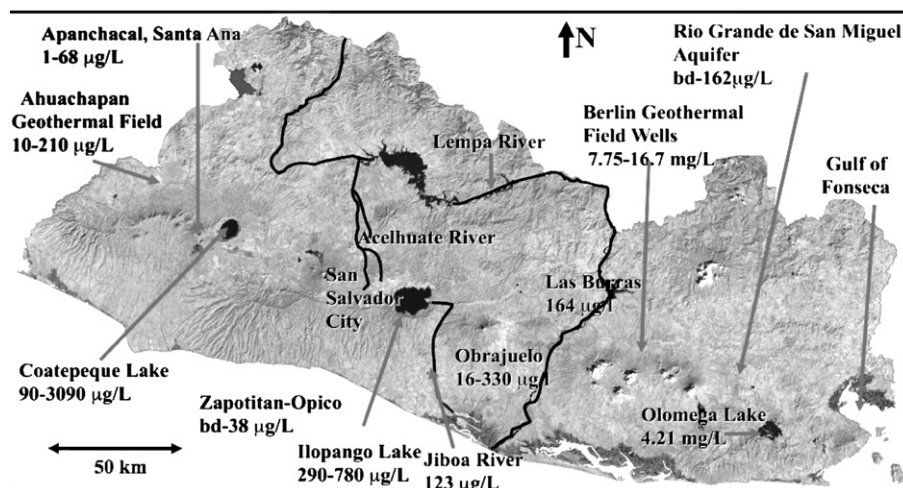


Fig. 7. Geomorphological setting and main arsenic sources in El Salvador. The satellite map is from <http://www.maplibrary.org/stacks/Central%20America/El%20Salvador/index.php>, taken on May 13, 2008.

reported for each one of these sites. The Honduran geothermal field with more information about the water chemistry is that of Platanares (Goff et al., 1986a; Janik et al., 1991). There, Arsenic was not detected in the cold waters; the mixed geothermal waters had As concentrations ranging from <50 to 7100 µg/L (mean ± SD: 940 ± 150 µg/L, for the 14 samples with detectable As), and, for geothermal well waters, concentrations ranged from 800 to 1260 µg/L (mean ± SD: 470 ± 200 µg/L).

With respect to contamination from gold mining, the San Martin gold mine in central Honduras has been operating since 1999. During many years, communities close to the mine in Siria Valley have complained about pollution problems in local rivers, forest destruction, and impacts on the local aquifers. A study done by Environmental Law Alliance Worldwide (ELAW; <http://www.elaw.org/node/1285> accessed 9/30/2010) found water quantity and quality problems associated with the mine and soil sediments of the San Martin mine. Data showed As levels exceeding limits set by the Honduran government and international organizations (>10 µg/L). According to ELAW, the government of Honduras imposed a US \$55,500 penalty on the mining company for polluting and damaging activities.

6.1.3. El Salvador

High concentrations of As have been detected in surface and ground waters in El Salvador (e.g. McCutcheon, 1998; López et al., 2009). In most cases, the origin of this As is from natural sources due to the tectonic setting of El Salvador at a subduction zone with numerous volcanoes and geothermal surface manifestations (fumaroles and hot springs) (e.g. López et al., 2004; Pérez et al., 2004; Birkle and Bundschuh, 2007a,b) (Figs. 1 and 7). Geothermal energy exploration in El Salvador started in the nineteen sixties and in 1976 exploitation begun with the Ahuachapán geothermal power plant, and later, in 1992 the Berlin geothermal power plant took up operation (Fig. 7). Investigations in these geothermal fields and other geothermal areas of the country produced evidence of the existence of geothermal groundwaters with high As concentrations (e.g. Raymond et al., 2005) and possible contamination of shallower aquifers. At Berlin geothermal field, As concentrations in the Na–Cl waters of the geothermal wells range from 7750 to 16,700 µg/L (mean: 11,710 µg/L, n = 5) (Raymond et al., 2005). However, Raymond et al. (2005) is the only reference in the peer-reviewed literature about As in geothermal wells of El Salvador. Data from geothermal wells are not public in El Salvador and are classified information that cannot be accessed and are handled by the national geothermal energy company (LaGeo). Arsenic of geothermal origin will be discussed in this issue in detail in the paper by López et al. (2012). Information in the ISOHIS data base of the International Atomic Energy Agency (IAEA) shows that water from springs and domestic wells located in the Ahuachapán geothermal field has concentrations of 20–210 µg/L, and at springs and domestic wells in the Berlin geothermal field of 2–285 µg/L. As concentrations in groundwater of Las Burras and Obrajuelo aquifers are 164 µg/L and 16–330 µg/L, respectively.

It is not known when the first As-rich waters were identified in El Salvador. However, other systems in El Salvador (in addition to geothermal reservoirs) present high concentrations of As, such as the three larger lakes in the country: Ilopango and Coatepeque, hosted in volcanic calderas (López et al., 2009; McCutcheon, 1998), and Olomega lake, in the eastern part of the country (Fig. 7). In Coatepeque lake, As concentrations in water ranged from 90 to 3090 µg/L (McCutcheon, 1998). In the waters of Ilopango lake, As concentrations ranged from 290 to 780 µg/L (Ransom, 2002; López et al., 2009). The Olomega lake water has an As concentration of 4210 µg/L and it is the highest As concentration determined in surface waters of El Salvador (analysis from early 2000; Vides and Castillo de Heskes, personal communication).

It is important to note that the three lakes mentioned above are the largest reservoirs of surface water in El Salvador but, due to its

high As concentration, they are not used for centralized water supply systems. However, they are used by the people living in the watersheds of these lakes for domestic purposes. It is estimated that around 200,000 people could be consuming waters high in As in the Ilopango area. However, it is difficult to estimate the number of people exposed for the other areas. These water resources are important because of the high population of El Salvador, more than 7 million inhabitants, in a small surface area (21,000 km²). This high population density has produced an overexploitation of groundwater resources and associated problems for the distribution of clean water to the population (US Army Corp of Engineers, 1998). Unfortunately, data of As concentrations in water supply systems is not public in El Salvador.

Arsenic contamination in Lempa river (the major river in the country) and its tributary Acelhuate (Fig. 7) was assessed by Monterrosa (2003). In this study, water samples were analyzed for As and heavy metals. The Acelhuate river is the anthropogenically most polluted river in El Salvador because it transports the waste waters from the capital city to the Lempa river. However, the highest concentration of As detected in these waters was only 26 µg/L at Acelhuate river. Similar results were obtained in a wide survey of different rivers in the country (Esquivel, 2007), where only three rivers were found with relatively high concentrations of As; they were: Paz river with up to 36 µg/L, Sucio river with up to 32 µg/L, and Jiboa river with up to 123 µg/L (Fig. 7). Waters from these rivers are used for irrigation and domestic uses. Ilopango lake discharges into Desagüe river, which is a tributary of Jiboa river (Fig. 7). Arsenic data (Esquivel, 2007) shows a clear attenuation of As concentration from 780 µg/L at Ilopango to 123 µg/L in Jiboa river, as the water runs away from the lake, suggesting sorption or co-precipitation processes that transfer the As from the water to the sediment or organic matter.

In 1998, the Hurricane Mitch hit Central America with devastating consequences for Honduras, Nicaragua, and El Salvador. The National Oceanic and Atmospheric Administration (NOAA) of the USA, in collaboration with local authorities, investigated waters, sediments and biota of the Gulf of Fonseca (Fig. 7) with the purpose of assessing contamination problems and the impact produced by the hurricane in this important body of water shared by the three countries (Matta et al., 2002). Arsenic in river waters discharging at the Gulf of Fonseca had an average (±SD) of 2 ± 2 µg/L (n = 18), (maximum value 7 µg/L). Sediments were also analyzed in this study, and an average value (±SD) of 1.280 ± 2.154 mg/kg (n = 18), (maximum value 6.360 mg/kg) was found. In addition, the As content of crabs and catfish was analyzed, and an average value (±SD) of 6.325 ± 12.343 mg/kg (n = 14), (maximum value 48.145 mg/kg) was found. These data suggest that As is preferentially retained in the sediments and incorporated from there into the food chain.

In 2008, the Ministry of the Environment in El Salvador carried out an investigation of contamination of three important aquifers (Hidrodesarrollo S.A. de C.V., 2008): Zapotitan–Opico, Apanchacal river aquifer in Santa Ana, and Río Grande de San Miguel river aquifer in San Miguel (Fig. 7). For these three aquifers, average values (±SD) for As are: 6 ± 8 µg/L (n = 29) (maximum value 38 µg/L); 4 ± 1 µg/L (n = 19) (maximum value 7 µg/L); and 11 ± 25 µg/L (n = 41) (maximum value 162 µg/L), respectively. These data show that the highest risk is for the people using the water from the San Miguel aquifer.

With respect to contamination of groundwater supply systems in El Salvador, samples are collected and analyzed by the National Administration of Aqueducts and Sewage (Administración Nacional de Acueductos y Alcantarillados, ANDA), the major government agency that exploits and sells potable water in El Salvador. It is widely known that there are As problems in groundwater of El Salvador and that ANDA has a special unit working in that kind of contamination. However, ANDA does not share the information about As in groundwater with the public. Water treatment for As removal has not been implemented in any water supply system in El Salvador.

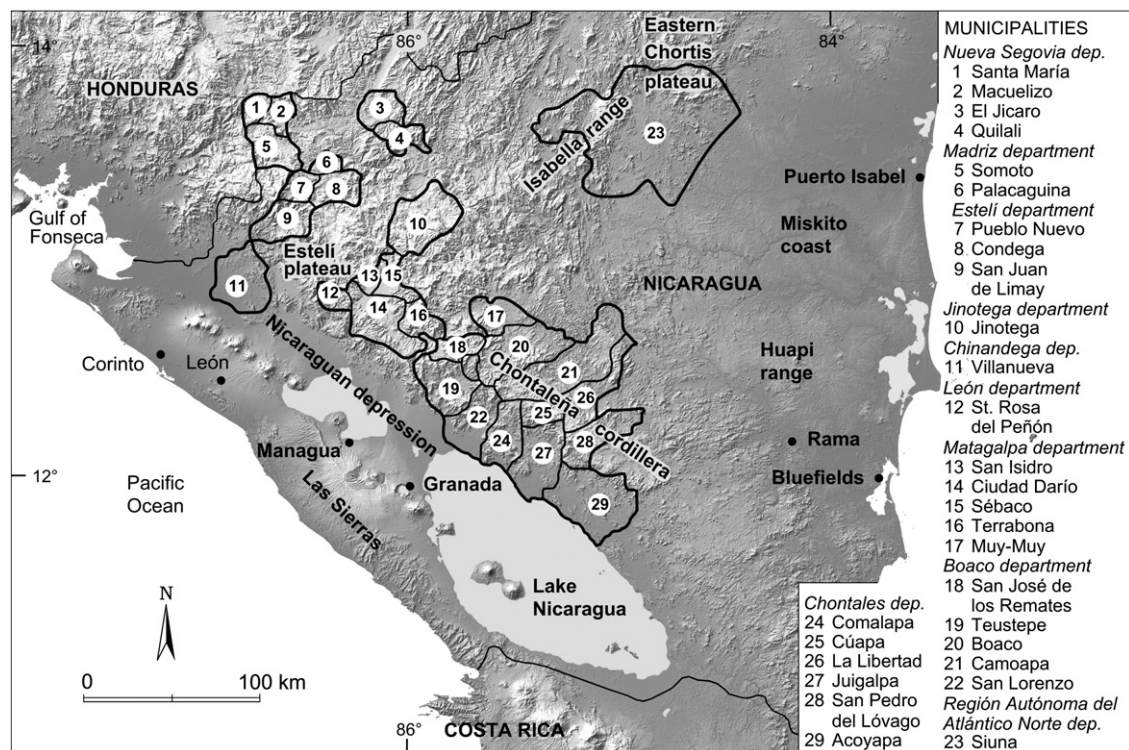


Fig. 8. Municipalities of Nicaragua with water sources whose arsenic concentration exceeds the national regulatory limit of arsenic in drinking water ($10 \mu\text{g/L}$) as known by the year 2011.

Because of other health, social and economic problems in El Salvador, the problem of As in water is not a priority within the government. Moreover, the public of El Salvador is not well informed of As contamination in their water supply because ANDA does not release this information. Only the As contamination of the three lakes mentioned above is widely known. The government has not put enough attention to the possible health effects of As contamination, and epidemiologic studies have not been done in the country yet.

6.1.4. Nicaragua

In Nicaragua, the contamination of groundwater with As was detected in May 1996 in water of an artesian well from the community El Zapote, in the Sébaco valley (municipality of San Isidro) (Figs. 1 and 8), which contained $1320 \mu\text{g As/L}$ (Aguilar et al., 2000). From then on, different institutions have performed studies that confirmed the extension of the problem into the neighboring communities and into other regions of the country (INAA, 1996; González et al., 1997; CARE, 2002; PIDMA-UNI, 2001; PIDMA-UNI-USAID, 2001; PIDMA-UNI, UNICEF, 2002; Barragne-Bigot, 2004; PAHO/WHO/UNICEF, 2005). Medical evaluations of the population exposed have been carried out in the communities of El Zapote (municipality of San Isidro), Kinuma (municipality of La Libertad), and in La Curva and Puertas del Paraíso (municipality of San Pedro del Lóvago) (Aguilar et al., 2000; Gómez, 2000, 2004, 2009; Gómez and Aguilar, 2000) (Figs. 1 and 8).

Between 1996 and 2001, a number of studies of As in water of springs, dug wells and tubewells at El Zapote and adjoining communities in the Sébaco valley have been performed by the Nicaraguan Institute of Aqueducts and Sewer Systems (*Instituto Nicaragüense de Acueductos y Alcantarillados*, INAA), the Center of Investigations and Studies on Health (*Centro de Investigaciones y Estudios de la Salud*, CIES), the University of Engineering (*Universidad de Ingeniería*, UNI) and the CARE International (NGO). They found that the As concentration of 32 from 98 samples (33%) exceeded the $10 \mu\text{g/L}$ national regulatory limit (INAA, 2001). The maximum value

detected was of $289.2 \mu\text{g/L}$ in a well drilled at El Zapote (INAA, 1996; González et al., 1997; PIDMA-UNI, 2001; CARE, 2002).

Though the Sébaco valley is one of the most fertile agricultural areas of Nicaragua, which produces a significant portion of vegetables consumed by the population of northwestern Nicaragua, the CIES study ruled out that the As contamination in water is by agrochemicals (González et al., 1997). Subsequently, the source of As was identified to be geogenic (Barragne-Bigot, 2004). The high As concentration in water was correlated with high As contents in rocks and soils (14.98 and $57.19 \mu\text{g/kg}$ respectively) (Altamirano Espinoza and Bundschuh, 2009).

During 2001, within the Research Program and Teaching in Environment (*Programa de Investigación y Docencia en Medio Ambiente*, PIDMA) – University of Engineering (*Universidad de Ingeniería*, UNI) – Environmental Health Program (EHP) of the USAID, 124 dug wells and tubewells were sampled outside of the Sébaco valley, in the north and northwest of Nicaragua (Departments of Madriz, Estelí, N. Segovia and Chinandega; Fig. 8). The study found that the water in 6 of the 124 wells (4.8%) had As concentrations exceeding $10 \mu\text{g/L}$ (PIDMA-UNI-USAID, 2001).

The population of El Zapote that was exposed from 1994 to 1996 to high As concentrations in drinking water ($1320 \mu\text{g/L}$) comprised 125 individuals (Gómez, 2009). In the other 15 communities of the Sébaco valley where As contamination was also detected in water resources, 3225 inhabitants are potentially at risk to As exposure. Studies on As-affected population of El Zapote and some communities of Chontales department (Fig. 8) confirmed the different level of damage that As caused on health of many persons (Gómez, 2000, 2004, 2009; Gómez and Aguilar, 2000). Health effects of As exposure in Nicaragua has been discussed in the paper by McClintock et al. (2012).

In 2002, PIDMA-UNI and UNICEF studied the groundwater quality in Nicaragua. Arsenic and heavy metals were analyzed in water samples collected from 106 dug wells, tubewells and springs located close to tectonic structures with hydrothermal mineralization that are

parallel to the tectonic depression of Nicaragua. In 5.7% of the samples, the As concentration exceeded 10 µg/L (PIDMA-UNI-UNICEF, 2002). The sites where the water samples exceeded 10 µg/L were resampled in a new, more ample study comprised 7 areas in western Nicaragua. The As concentrations in the 77 groundwater samples ranged from 0.4 to 106 µg/L (mean ± SD: 11.4 ± 20.8 µg/L, median: 3.65 µg/L); 22 water samples (28%) exceeded the national and WHO limit of 10 µg/L (Barragne-Bigot, 2004). Arsenate is the dominant As species, the percentage of the more toxic As(III) related to total As is 4.8–100% (mean ± SD: 27.8 ± 23.9%, median: 18.7 µg/L). Furthermore, it was observed that the As concentration did not depend on the hydro-chemical type of the groundwater; no correlation with the hydro-thermally mineralized structures was found (Barragne-Bigot, 2004). In the community of Kinuma (municipality of La Libertad, Chontales department; Figs. 1 and 8), where Barragne-Bigot (2004) found higher As(III) percentages of 8–97.1% (mean ± SD: 35.5 ± 31.1%, median: 28.9 µg/L), the population consumed As-contaminated water (54.4–255 µg/L) during 12 years (1992–2004); dermatological health effects are reported by Gómez (2004), which will be addressed in this special issue in the paper of McClintock et al. (2012).

The largest water quality study (1488 wells) was carried out by UNICEF and the Pan American Health Organization (PAHO) during 2004–2005. Eighteen of the 46 studied municipalities had water with As concentrations higher than 10 µg/L, most of them in the northern part, and the maximum As concentration (161 µg/L) was found in a tubewell of San Juan of Limay (department of Nueva Segovia, Fig. 8) (PAHO/WHO/UNICEF, 2005).

In the Jinotega municipality, *Empresa Nicaragüense de Acueductos y Alcantarillados* (ENACAL) and other institutions detected 33 of 44 dug wells (75%) had As > 10 µg/L in Llano La Tejera (semirural area at the periphery of Jinotega city; Figs. 1 and 8) in 2005 (ENACAL, 2005). The water of 13 of these wells had As concentrations > 100 µg/L (ENACAL, 2005). In Llano La Tejera, 714 people consumed water from 33 dug wells containing As in concentrations exceeding the national norms (Altamirano Espinoza and Bundschuh, 2009). Despite of the fact that the authorities have prohibited the consumption of water of the wells affected by As, the population still uses them because of the lack of alternative water sources.

Fig. 8 shows the 29 municipalities where groundwater resources with As concentrations exceeding the national limit for drinking water (10 µg/L) were found until present (2011). All of them are located in the western and central mountainous areas of Nicaragua (Chontaleña cordillera, Estelí plateau) where young volcanic rocks and their weathering rocks prevail as sources for As.

6.1.5. Costa Rica

From Costa Rica, only data on geothermal As were published and no effects on groundwater or surface water resources, used for drinking water purposes, have been reported. These occurrences will be discussed in the paper of López et al. (2012). Shallow groundwater was studied at several sites where geothermal activities and leaching from predominantly volcanic rocks and their weathering products did not caused significant As concentrations. Hammarlund and Piñones (2009) found low As concentrations of 5–6 µg/L in springs from shallow non-geothermal aquifers in the Miravalles and Rincón de la Vieja geothermal areas (Fig. 1).

6.2. Caribbean

6.2.1. Cuba

Arsenic in the environment has been studied in a few sites in Cuba. Information reported in three sites is presented in this section: Isla de la Juventud, Manzanillo Bay, and Cienfuegos Bay (Fig. 1).

6.2.1.1. Isla de Juventud. At the Isla de la Juventud, As is released from tailings of the gold mine Delita, which closed in 1997. The geology of

the mining area is predominantly mica schist rich in arsenopyrite, which releases As as it oxidizes in the near surface environment or in the tailing deposits. Toujague et al. (2003) studied the contamination (As, Fe, Cu, Zn, Cd, and Pb) of the surface waters in an area about 38 km² around the Delita mine and in nearby streams. The mining area is located on the watershed of the El Soldado river. Nine sampling points were located at wells and springs within this watershed and at the nearby watersheds of the Majagua, Itabo, and Los Indios rivers. The results of the study indicate that only the spring located close to the mine (La Mina spring) show high concentrations of As (25,250 µg/L), Fe (248.7 mg/L), and Zn (5.53 mg/L). These values are considerable higher than the WHO limits for drinking water (10 µg/L, 0.3 mg/L, and 3.0 mg/L, respectively). Previous studies (Bustamante et al., 1985) found similar results with 33 mg/L of Fe, and As ranging from 5000 to 7000 µg/L. Four stations had pH lower than the Cuban norm of 6.9 for the preservation of aquatic life (La Mina spring, Punto Jeep, Los Blanquitos and Malva wells). High Fe content which implied reducing conditions and low pH suggest that the dominant As species in the groundwater is As(III), that is probably transformed to As(V) at the surface. Note that the points that do not present As concentrations are located more than 1 km from La Mina spring. Attenuation processed throughout the conversion of As(III) to As(V), and further sorption on iron minerals could explain the lack of As in the farther points.

In order to identify previous exposure to As (over the years of activity at the mine), a preliminary survey of clinical data of the local population was performed in the Batey da La Mina community where 16 families live, about 3 km upstream of the mine (Toujague et al., 2006a). In this village, an increasing trend in the mortality rate due to cerebrovascular diseases was observed between 1994 and 1999, considerable greater than in the rest of the country (Robles and Morillo, 2001). The first cause of death in adults in the Isla de la Juventud during the period 1990–2000 was malignant tumors, especially lung cancer (2000–2001). Premature mortality also showed an increasing trend in this decade with respect to the rest of the country (Robles and Morillo, 2001).

The historical data of As in surface water and groundwater in the area of influence of Delita demarcates a stage of danger area of 72 km² in which the transport time and the return of those local waters of the mine is 13 years (Molerio, 2002). The first increase in stroke mortality was observed in 1994, just 13 years after the initial studies to evaluate the ore in Delita. In 1982, the surficial drainage from the mine to the sea stopped probably because it infiltrated the ground, suggesting some relationship between the contamination of the groundwater and the appearance of the illnesses 13 years later (Toujague et al., 2003).

To verify the actual exposure to As and heavy metals, a risk assessment study of As, Pb and Cd in the Delita gold region was carried out in the period 2006–2008 (Massahud, 2008), in order to apply for the first time in Cuba the “environmental inspection phase” of the methodology for risk assessment of the Pan American Health Organization (PAHO) (Díaz-Barriga, 1999). The study included the watersheds El Soldado, Pino, Majagua, Los Indios, Itabo and Río del Medio–Las Nuevas. The calculation of non-carcinogenic risk (target population: children aged 3–6 years) showed that there is risk of non-cancerous diseases suggested to be due to As for children who were supplied water of wells V-28 (Los Indios basin), S-7 (Itabo basin) and well drizzle Airport Siguanea, which showed risk quotients (RQ > 1) of 1.93, 3.05 and 20.8, respectively. The As concentrations in water of these points (11.6, 15 and 18.8 µg/L, respectively) in all cases exceeded the guideline value of WHO for As in drinking water (10 µg/L), and the maximum As value guide security (4.2 µg/L) for assessment of environmental media (EMEG). The three piles of mining waste arranged in the mine (R-1 R-2 and R-3) and soil (R-5), old mine tailings that fills the groundwater flow path to Playazo El Soldado, exceeded the permissible limit of As (75 mg/kg) and Pb

(840 mg/kg) (R-1 and R-3) for disposal of sewage sludge on soil (EPA, 1993), and should be removed from the site or treated to their proper destination. This is especially important for the soil (the path to Playazo El Soldado), where gastric bioaccessibility studies (protocols IVG) showed $40.5 \pm 1.95\%$ of bioaccessibility of As (Toujague et al. 2006b). For assessing cancer risk, future studies in the region should evaluate these tailings and consider the analysis of biological material of exposed populations in areas at risk from this study.

6.2.1.2. Manzanillo Bay. Increasing industrial growth around the city of Manzanillo (Fig. 1) has raised concern about increases in metal contamination in the bay and its impact on the marine ecosystem. Several studies have been carried out (Emilson and Tápanes, 1971; Suárez and Pergó, 1979; Arencibia and Perigó, 1985; Amat et al., 2002). The bay presents a temperature, salinity, and density profile characteristic of low salinity shallower layer produced by the input of river waters to the bay and deeper more marine water; the bottom sediments are characteristic of deltaic environment with coral and crystalline submerged rocks (Amat et al., 2002). In the last study, Amat et al. (2002) sampled seven stations for bottom sediments and macroinvertebrates. The large oyster specie *Crassostrea rhizophora*, a sediment filtration specie that lives in mangrove forest, was selected for sampling and metal analysis. Arsenic was below detection limits ($0.002 \mu\text{g/g}$) in the oysters. In the sediments, the As contents were in average 28.3 mg/kg (range $10\text{--}85 \text{ mg/kg}$, median 22.5 mg/kg). Arsenic was the element that presented the highest geoaccumulation index ($I_{\text{geo}} = \log 2(C_n/1.5B_n)$, where C_n is the actual content, and B_n is the background content in the sediments) for the seven sampling sites. The highest indices of urban contamination (sum of concentrations of Cu, Pb, and Zn) correspond to sites in the deltas of rivers Yara, Felipe, and Guá, which are also the sites with the highest As contents. The fact that a factory of batteries is discharging its wastewaters in Yara river suggests that this is the cause of the observed contamination (Amat, 2000; Ginarte, 1999).

6.2.1.3. Cienfuegos Bay. Cienfuegos Bay (Fig. 1) has a long history of heavy metal contamination due to industrial development around the bay. However, this situation got worse due to the spill of a high pH solution containing inorganic oxides of As in 2001, for which the *Empresa de Fertilizantes Nitrogenados de Cienfuegos*, a plant producing nitrogen-fertilizers, was responsible. Castellanos et al. (2005) determined the levels of As contamination in macroalgae living on the natural banks of the bay with the purpose of starting an effective bio-monitoring program. Only As is reported in this study. Results of this study showed levels of As between 0.044 mg/kg for *Enteromorpha flexuosa* and 11.834 mg/kg for *Gracilaria biddgettii*. Due to its high As bioaccumulation, this last specie was suggested as an excellent choice as bioindicator. The spatial distribution of the data indicates an accumulative effect of this metal in the algae, with the highest values close to the spill point.

6.2.1.4. Santa Lucía Mine. The chemical composition of the mine waste and the mine drainage of the inactive Zn–Pb mine of Santa Lucía, in western Cuba, was investigated, as well as the water quality of the streams impacted by this mine (Romero et al., 2010). The study found high total concentrations of potentially toxic elements Fe, Ba, Pb, Zn, As, and Cu in the solid waste of this mine, with an average value of 1724 mg/kg for As. Acid mine drainage is discharged from this mine due to the oxidation of sulfide minerals in the mine-waste dumps and in the open pit. The acidic waters have pH ranging from 2.5 to 2.6 and are enriched in dissolved sulfate (up to 6754 mg/L), Fe (up to 4620 mg/L) and Zn (up to 2090 mg/L). However, the concentration of the toxic elements Ba, Pb, and As decreased with distance from the mine. The concentration of As for the three samples taken from the mine effluent decreased from 0.293 mg/L for the point closest to the mine waste dump to 0.005 mg/L for a point only 300 m downstream.

In a similar way, the As concentration in four samples taken from impacted streams around 1500 m and 1700 m away from the mine ranged from 0.004 to 0.024 mg/L . In comparison, the concentration of two sediment samples in the same area was 327 and 320 mg/kg . The authors analyzed the mineralogy of the sediments and mine waste and found lead-bearing barite and beudantite as well as Fe-oxyhydroxides, jarosite, anglesite and plumbojarosite. They conclude that the low solubility of barite and beudantite under acidic conditions suggests that these minerals are controlling the mobility of As, Ba, and Pb, and that due to the relative high solubility of Fe-oxyhydroxides at the reported pH range, they cannot be responsible for the immobilization of these three elements.

6.3. South America

6.3.1. Colombia

The geology of Colombia indicates the existence of rocks with As minerals, specially in the mining areas (e.g. Bustos Rodriguez et al., 2007; Gaeta Tassinari et al., 2008). However, very few studies exist about As contents in rocks, soils, sediments, and water in Colombia. Prieto and Gonzalez (1998) studied the chemical composition of ore bodies, tailings, and waters of six gold mining districts located in Nariño, Antioquia, Bolivar, Valle de Cauca, and Caldas departments. They found that the presence of arsenopyrite is common in these deposits, but concentrations of As in water are not reported in this study. Similarly, the presence of arsenopyrite in El Diamante gold mine in the Nariño department (Fig. 1; Bustos Rodriguez et al., 2005; Bustos Rodriguez et al., 2007) and in the Mamarto mining district (Caldas department) (Fig. 1; Gaeta Tassinari et al., 2008) has been reported. However, the As contamination produced by the exploitation of these mines has not been reported. Alfaro-Valero (2005) investigated As and heavy metal contents in sixty hot springs of Cundinamarca department. Only the concentration of the hot spring with the highest As concentration is reported in this study. Hot springs with the highest salinity in Yacopi (Fig. 1) show the highest concentration of As and Sb, 37 and $4.8 \mu\text{g/L}$, respectively.

Only two studies have been reported in the referenced literature that contain data on As in water: i) heavy metal contents of estuarine waters of Barbacoas Bay (Mazo-Gray et al., 1997), and ii) heavy metals derived from gold-bearing minerals in the Marmato district (Gaeta Tassinari et al., 2008). The locations of these two sites are presented in Fig. 1. A summary of these two studies is presented next.

6.3.1.1. Arsenic and heavy metal content in the estuarine waters of Barbacoas Bay. Barbacoas Bay is located south of the city of Cartagena (Fig. 1) on the Atlantic coast of Colombia. The bay receives water from the Canal del Dique, a 117 km channel constructed by the Spaniards to connect the port of Cartagena with the Magdalena river. The Covado shrimp farms are adjacent to the bay. The purpose of the study was to evaluate if heavy metal contamination could be the cause of a 30% decrease in shrimp production. Sampling stations were located on the Canal del Dique (2), at points entering the shrimp farms (4), and at points exiting the farms (5). Water samples were taken at the surface and at 1 m depth. Total concentrations of As, Ti, Mn, Fe, Co, Ni, Cu, Zn, and Pb (soluble plus suspended metals) were analyzed. Iron was the metal found at the highest concentrations in the waters of the Canal del Dique ($1.5\text{--}11.0 \text{ mg/L}$), and the lowest for the water entering or exiting the shrimp farms, with a range of 0.8 to 2.9 mg/L (mean: 1.2 mg/L). According to the authors, the decrease in iron concentrations is due to flocculation and deposition processes produced by mixing of the river waters with the more saline bay waters. In comparison, As levels in the Canal del Dique waters were below the detection limit ($60 \mu\text{g/L}$) and the highest values were observed at the bay (range: $310\text{--}620 \mu\text{g/L}$, mean \pm SD: $500 \pm 120 \mu\text{g/L}$). Water entering the farms had the lowest As concentrations (range: $230\text{--}410 \mu\text{g/L}$, mean \pm SD: $310 \pm 80 \mu\text{g/L}$), and the waters exiting the farms had

intermediate values (range: 170–690 µg/L, mean ± SD: 460 ± 120 µg/L). Copper and zinc were also high in the bay and shrimp farm waters. Several possible sources are proposed for the contamination of the bay and shrimp farms: i) contaminated ballast water from old oil tankers arriving to the port of Cartagena, ii) contaminants picked up along the Central America coast and carried by the north-east currents of the Caribbean along the Colombian coast (Darién counter-current), iii) contaminants discharged from the Coveñas oil terminal about 65 km to the south of the bay, and iv) mine waters from the Cerramotoso nickel mine that are discharged into the Sinú river. This river discharges on the ocean about 80 km to the south of the bay. The discharge shows seasonal variations with a salinity decrease in the farm channels from December to March due to variations in precipitation.

6.3.1.2. Arsenic in the Marmato mining district. The Marmato mining district is located on the east side of the Western Cordillera, in western Colombia, northwest of Caldas department (Fig. 1). Metamorphic, igneous, and sedimentary rocks are present in this area with a Tertiary sequence of volcanic and pyroclastic rocks that have been intruded by porphyritic andesite bodies. Gold mineralization occurs in dacite-andesite porphyry rocks (Marmato stock) that outcrop in the area. The type of ore deposit is a gold–silver epithermal–mesothermal vein associated to sulfide minerals such as pyrite, iron-rich sphalerite, galena, arsenopyrite, chalcopyrite and pyrrhotite. The purpose of the study was to evaluate the contamination on the Marmato river and its tributaries as well as the Cauca river, where Marmato river discharges. Surface waters, river bed sediments, and suspended sediments were collected for analysis of major cations and anions and metals (As, Cu, Pb, Zn, Cd, Ag, Hg, Sb, and Cd). Samples were collected during the dry and the rainy season. Results of the study showed that the Marmato river waters carry high levels of metals, especially As, Zn, Cd, and Cu, as well as high levels of cyanide, making these waters unsuitable for irrigation, aquatic life, drinking, and other uses. Arsenic is enriched in the sediments of the Marmato river ranging from 10 to 850 mg/kg during the dry season sampling and from 440 to 1400 mg/kg during the wet season. Mixing of the Marmato water reduces As concentrations, with the Cauca river waters having As levels that range from 4 to 90 mg/kg in the rainy season, and 10–256 mg/kg in the wet season. Bioavailability of As is one of the lowest, with only Hg and Sb having lower bioavailability. Arsenic bioavailability ranges from 6 to 74 mg/kg in the dry season to 4–32 mg/kg in the wet season. Bioavailability of As in Cauca river is lower than the detection limit (2 mg/kg) at most sampling sites, with only 2 sites presenting detectable levels in the dry season and 1 site in the wet season. Active mines at Marmato district have sulfides that oxidate and produce acid mine drainage.

6.3.2. Ecuador

Gold mining in the south of Ecuador has brought about serious environmental problems. The main contaminants present in mines were cyanide, heavy metals and mercury. The sources of these contaminants are the aqueous effluents that are directly discharged into rivers and creeks and caused the extinction of superior life in some sectors of rivers (PRODEMINCA, 1998). Besides, the poor quality of the water of the rivers impairs its usage for irrigation, fisheries or as a source of drinking water (Cumbal et al., 2009a). Arsenic associated with mining activities has been rarely monitored and, as a consequence, no management or treatment program has ever been implemented. In 2003, As contamination on natural waters was found during the remediation of a crude oil spill in the Papallacta lake (Fig. 1), due to the rupture of the Transecuatorian pipeline. De la Torre et al. (2004) reported As concentrations between 39 and 10,560 µg/L in thermal waters and rivers in the lake watershed. This study also reported that As concentrations in the Papallacta lake were in the range of 390–670 µg/L. In 2006/07, Cumbal and other researchers performed a more detailed

study on the Papallacta lake basin. They found 62 to 698 µg/L of As along the Tambo river (Fig. 1), the main tributary of the lake. On the surface of the Papallacta lake, the distribution of As varied from 220 to 359 µg/L in summer, but, in winter, As values were lower and oscillated in the range of 86–177 µg/L. Besides, As levels found for geothermal waters at the Papallacta basin were in the range of 1090–7852 µg/L (Cumbal et al., 2009b). In 2007/08, Cumbal and his graduate students examined the As contamination in geothermal sources of the north-central Andean region of Ecuador. This region includes five provinces: El Carchi, Imbabura, Pichincha, Cotopaxi, and Tungurahua (Fig. 1). Geothermal springs in the Carchi province showed concentrations of As in the range of 2–684 µg/L. In the Imbabura province, As fluctuation on geothermal waters was even higher; it varied from 995 to 4969 µg/L. The concentration of As on the geothermal water of the Pichincha province were 11–405 µg/L, while in the Cotopaxi province, As concentrations were lower; they varied from 4 to 47 µg/L. In the southern province of this region (Tungurahua province), As ranged 6–114 µg/L. On the other hand, surface waters from El Angel river (El Carchi), Cachiycu Quebrada (Imbabura), San Pedro river and Ilalo Quebrada (Pichincha), which receive thermal waters, reached As concentrations up to 166 µg/L. Of these water bodies, San Pedro river showed the lowest As levels (2–23 µg/L) and the highest were found in the Cachiycu Quebrada (86–166 µg/L) (Cumbal et al., 2010). Although according to Ecuadorian regulations, water from Cachiycu Quebrada should not be used for irrigation as it exceeds the national regulatory limit of 100 µg/L total As (TULAS, 2003), it is used however for this purpose because it is the only water source for agricultural developments.

In 2006, wells used as drinking water sources serving Tumbaco and Guayllabamba towns (Fig. 1) were found contaminated with As. The concentration ranged from 9 to 126 µg/L (El Comercio, 2006). Under demands of the community of Tumbaco, the municipality named a special health committee to deal with the As problem. The committee collected hair samples taken from the residents of Tumbaco of different age and sex and sent them to a laboratory from Canada for As analysis. Results indicated that only 3% of the samples were above 1 µg/g, the As normal content in hair (Hindmarsh et al., 1999), thus As was not apparently being accumulated on Tumbaco residents; however, further research is needed to elucidate this issue. Next, the municipal enterprise for potable water installed As treatment plants for two wells of Tumbaco whose water has As concentrations exceeding the Ecuadorian (10 µg/L) (INEN, 2006). The treatment plants included an oxidation stage with chlorine, followed by a filtration unit loaded with ArsenX^{pp}, the As sorbent material manufactured by SolmeteX Inc. using the procedure developed at Lehigh University (SenGupta and Cumbal, 2005). Unfortunately, water matrixes were not properly characterized, and thus the treatment systems were not well designed, with very poor performances. Under this circumstance, the municipality decided to shut down the wells in 2007 and drinking water is being supplied now to Tumbaco from an As-free treatment plant through a long pipeline. In Guayllabamba, a low flow filter using a mixture of sand and ferric oxide as media was installed. No data on As concentrations of this drinking water have been reported yet.

6.3.3. Bolivia

In the Bolivian Highlands and the Eastern and Western Cordillera of the Andes, comprising the departments of La Paz, Oruro and Potosí (Fig. 3), As is naturally released into the environment by leaching from predominantly volcanic rocks, from geothermal surface manifestations such as geothermal springs and fumarolic activity, and by sporadic volcanic exhalations. Several mining areas, especially in the Eastern Cordillera, have been exploited intensively for five centuries, predominantly from sulfide ore deposits. Mine tailings, acid mine drainage and wastes, and atmospheric emissions from abandoned and active mining areas and metallurgical operations resulted in severe

contamination of water resources, soils, plants and animals by As and heavy metals, and entered the human food chain.

6.3.3.1. The Pilcomayo river basin. The Pilcomayo river and its tributaries, which rise in the Western Cordillera of the Andes mostly at heights of 4000–5300 m a.s.l., flow through the Cerro Rico de Potosí precious metal–polymetallic tin deposits and other mining areas in the Potosí department (southern Bolivia; Fig. 2). Historic intensive mining activities starting in the 15th century and present-day mining activities have caused contamination of the sediments and water of the Pilcomayo river for at least 200 km downstream of the mines (Miller et al., 2004).

From the Potosí area, the Pilcomayo river flows toward the SE reaching after about 700 km close to the town of Villa Montes (Fig. 2), the lowland of the Chaco–Pampean Plain. At Villa Montes, its average discharge is 80 m³/s in the dry season and 3600 m³/s during floods (Wilkinson and Mohler, 1995). Near its headwaters, the Pilcomayo river drains the large Cerro Rico de Potosí and other smaller mining area. There are several sources of metals from both historic and ongoing mining activities in the Potosí region to the headwaters of the Pilcomayo river (Hudson-Edwards et al., 2001; MMDEC, 1999). Most significant sources from present-day mining activities are the 30–40 ore mills that release As-rich flotation effluents and tailings into the Río de La Ribera river, which is a headwater tributary to the Pilcomayo river; effluents from the mills are 1300–1800 tons per day (Hudson-Edwards et al., 2001; Miller et al., 2004). The dark gray color of these effluents can be still observed 175 km downstream at the community of Sotomayor (Miller et al., 2004).

Hudson-Edwards et al. (2001) investigated the river channel sediments along the course of the Pilcomayo river starting from the Cerro Rico de Potosí mining area. The authors found that the channel sediments in Pilcomayo river between Potosí mining area and Icla, located 203 km downstream, contain high contents of sulfides (predominantly pyrite). The As concentration in river channel sediments declines from the mining area toward the lower Pilcomayo basin in different steps resulting from tributaries which are discharging along the course of the Pilcomayo river and partly dilute this water. Close to the mining area, effluents from the mines contain the following As concentrations: (i) in low-water channel sediments and tailings effluent: upstream of the Palaya river confluence (about 100 km upstream of Villa Montes) 210–7200 mg/kg (mean 2500 mg/kg, n=6), downstream of the Palaya river confluence 15–18 µg/kg (mean 16 mg/kg, n=2); (ii) in high water channel sediments: upstream of the Palaya river confluence 22–790 mg/kg (mean 160 mg/kg, n=11), downstream of the Palaya river confluence (Fig. 2) 5–37 mg/kg (mean 18 mg/kg, n=8). Arsenic concentrations in the river water are 42–100 µg/L in the Pilcomayo river upstream of the Palaya river confluence and 25–30 µg/L downstream of this confluence; all samples exceed the provisional WHO guideline value.

Together with water from other sources, river water is used by the communities along the Pilcomayo river for drinking and irrigation purposes as well as for animal husbandry. Miller et al., 2004 analyzed As concentrations (August to September 2001) from three communities in the upstream area of Pilcomayo river comprising Mondragón, Yocalla and Sotomayor (Fig. 2). Arsenic concentrations in the river water at these 3 communities were 13.5 µg/L at Yocalla (before the La Ribera river discharges into Pilcomayo river), 21.0 µg/L at Mondragón and 13.9 µg/L at Sotomayor (Miller et al., 2004).

Sotomayor is an example of an agricultural community in the Pilcomayo valley (Fig. 2), which uses river water for irrigation; this constitutes a potential risk to As exposure. Cadin (2006) studied As and heavy metals in water, soils and vegetable samples taken in September 2005 of the 260 ha covering agricultural land of this community. In soils, As contents range from 5.7 to 82.7 mg/kg (mean ± SD: 25.3 ± 21.6 mg/kg, median: 19.0 mg/kg, n=19). In the water sources, As concentration ranges from 50 to 70 µg/L in the Pilcomayo

river (57 µg/L) and in the irrigation channels (50 and 68 µg/L), with the exception of a secondary irrigation channel, whose water has 200 µg/L. That means that As contents are just at the allowed national limit of As concentrations in irrigation water (50 µg/L) or exceed this value. Water used for public water supply for drinking has 4 µg As/L and is therefore safe. In vegetables cultivated on the irrigated land, As contents are relative low. The As contents on dry weight base (dw) were in carrot 0.010–0.299 mg/kg (mean ± SD: 0.203 ± 0.076 mg/kg, median: 0.200 mg/kg, n=5), in beet 0.040–0.160 mg/kg (mean ± SD: 0.083 ± 0.067 mg/kg, median: 0.048 mg/kg, n=3) and in bean 0.040–0.060 µg/kg (n=3; two other samples were <0.025 mg/kg) (see also Bundschuh et al., 2012).

In the upper part of the Pilcomayo watershed, a series of mining accidents happened, causing momentaneous releases of large volumes of mining effluents and affect the Pilcomayo watershed; an example which received worldwide attention is that of the Porco mine in the upper part of the Pilaya river, a tributary to the Pilcomayo river (Fig. 1). Here, a breach of a tailings dam occurred on 29 August 1996 and until 1 September 235,000 m³ As-rich tailings were released together with fluid into Pilaya rivers tributaries. Macklin et al. (1996) found that As concentrations reduce rapidly in the first 200 km downstream from the spill site. On 9–10 November 2006, these authors took 35 samples of contemporary fine-grained (<2 mm) river sediment, material from floodplain, river terraces, and mine tailing ponds from 14 sites in the Pilaya and, for comparison, also from Pilcomayo catchment areas. In the contemporary river sediments, As contents decrease downstreams as follows. In Pilaya watershed, As contents were 2446, 1234, 642, and 225 and 100 mg/kg in 10, 15, 60, 130, and 200 km distance, respectively, from the Porco mine. In the Pilcomayo watershed, As contents in the same type of sediments were 17,127, 6806 and 62 mg/kg in distances of 0, 40 and 104 km, respectively, from the Potosí mining area. Arsenic contents in the main tailings were 2893–3260 and 5614 mg/kg in the Porco mine and the Potosí mines, respectively. As outcome of their investigations, the authors state that the Porco mine spill created serious contamination but that other mines that dump As-rich waste directly into rivers constitute a more serious long-term environmental threat in the Pilcomayo watershed.

Several studies were performed in the Pilcomayo river basin to study the As contents in fish, mainly in *sábalo* (*Prochilodus platensis*; synonym: *Prochilodus lineatus*), which is not only an important food for the local population, but also marketed within different other departments in Bolivia (e.g., Macklin et al., 1996; Quevillon et al., 1996; Stassen and van de Ven, 2007); some of their results are discussed in the paper of Bundschuh et al. (2012) together with the impact of As-rich irrigation water on vegetables and other edible plants.

Studies on human exposure to As were performed by Smolders et al. (2006) in the downstream area of the Pilcomayo river (Bolivian Chaco plain), which is not significantly contaminated by As, and by Archer et al. (2005) in the upstream areas of Pilcomayo in the Andes. Smolders et al. (2006) found, in 2003 and 2004, As concentrations in scalp hair of inhabitants of the village of Villa Montes (Fig. 2) and of both indigenous villages San Antonio and Tres Pozos, toward the southeast, (Fig. 2), whose principal diet are fish caught in the Pilcomayo river. As concentrations in samples from Villa Montes were 0.47 mg/kg (n=18), from Tres Pozos 0.70 mg/kg (n=34) and from San Antonio 0.45 mg/kg (n=25). For comparison, the value of the Potosí area is given (0.64 mg/kg, n=4) and, as reference, values from Sweden (0.09 mg/kg, n=112) and Canada (0.05 mg/kg, n=45). Archer et al. (2005) investigated As exposure in 5 riverside communities of Pilcomayo up to 150 km downstream of Potosí. Samples taken in 2003 (dry season) and 2004 (wet season) have As concentrations of 0.2–112, 0.6–329 and 0.9–12.8 µg/L in drinking, irrigation and river water, respectively. In hair and urine, the contents were 0.037–2.114 mg/kg and 11–891 µg/L, respectively. For discussion, see the paper of McClintock et al. (2012).

A holistic study of As was performed by researchers of the *Instituto de Tecnología de Alimentos (ITA, 2006)*, who sampled in October 2005 water, soil, river sediment, fish, vegetables, human blood, and animal blood from 12 sites in the Chuquisaca department (middle part of the Pilcomayo watershed). Arsenic concentration ranges were 2–101 µg/L (mean ± SD: 40 ± 34 µg/L, median: 36, n = 11) in water, 4.5–20.8 mg/kg (mean ± SD: 9.1 ± 4.5 mg/kg, median: 9.0 mg/kg, n = 11) in soil and 4.5–32.7 mg/kg (mean ± SD: 14.4 ± 10.1 mg/kg, median: 9.6 mg/kg) in river sediments. In muscles of edible fish As contents were based on fresh weight (ww) 0.14–18.3 mg/kg (mean ± SD: 2.70 ± 6.30 mg/kg, median: 0.59, n = 9). In vegetables, (onion, carrot, tomato, bean, lettuce, chard, cabbage, maize, beet) As contents (ww) 0.35–12.6 mg/kg (mean ± SD: 3.73 ± 3.27 mg/kg, median: 2.60 mg/kg, n = 21). As concentrations in human blood ranged from (ww) 50 to 1260 µg/L (mean ± SD: 828 ± 191 µg/L, median: 880 µg/L, n = 99: all based on ww). In animal blood (cow, goat, sheep, donkey, pig) As concentrations ranged from (ww) 20 to 3560 µg/L (mean ± SD: 1087 ± 569 µg/L, median: 950 µg/L, n = 76). This study will be discussed in more detail by *Bundschuh et al. (2012)*.

Stassen and van de Ven (2007) present data of As contents in water, suspended load, riverbed sediments and fishes from the upper (Andes) and middle part (Bolivian Chaco plain) of the Pilcomayo watershed. This report compiled data obtained from October 2005 to October 2006. In water of Pilcomayo, mean As concentrations from 3 sites were 14.6, 17.4 and 31.2 µg/L, whereas in the Chaco plain, values were significantly lower (3.9 µg/L at Villa Montes and Ibibobo sampling sites). In riverbed sediments, concentrations were 1.25, 2.41 and 9.74 mg/kg at the same sampling sites in the upstream area and 4.18 mg/kg and 14.03 at Villa Montes and D'Orbigny in the plain. At Villa Monte, As concentrations in river water (n = 300) ranged from 0.5 to 5 µg/L in filtered (mean 3.9 µg/L) and 1–20 µg/L in unfiltered samples (October 2005–October 2006), with short-term fluctuations but without any seasonal fluctuations, as such being observed for heavy metals such as Pb, Cu, Cd and Zn. The suspended load of the Pilcomayo river in this period ranged from 0.01 to 80 g/L (average 1 g/L); contents in the rainy season (October–April) are by factor 100 higher compared to the dry season (May–September). Arsenic contents in suspended load are 2.79–86.97 mg/kg (mean 32.23 mg/kg, median 24.70 mg/kg). In the dry season the contents are by factor 4 higher than in the rainy season. Using these data, it is possible to conclude that As transport by suspended load is about 10 times higher than by water. Unfortunately no corresponding river discharge data are available which would allow to determine As fluxes in river water and suspended load. Samples from 12 different fish species were obtained from Villa Montes (n = 100) and other parts (n = 20). In muscle the mean As contents varied in the different species from (dw) 0.02–0.54 mg/kg. The highest value corresponds to the species *Pimelodus clarias* (*Bagre amarillo*, n = 2) and the lowest in *Schizodon fasciatum* (salmon, n = 2). *P. lineatus* (*sábalo*, n = 29), as said the most consumed and marketed fish, had 0.13 mg/kg. However, it must be mentioned that only total As was determined and not the toxicity-relevant inorganic share, which would allow an appropriate evaluation of the human health risk. For more details on As in fish obtained in this study see *Bundschuh et al. (2012)*.

6.3.3.2. *Titicaca–Desaguadero–Poopó–Salt pans (TDPS) basin*. The endorheic Titicaca–Desaguadero–Poopó–Salt pans (TDPS) basin (Figs. 1 and 7) comprises the Titicaca lake in the north, which drains through the Desaguadero river and stretches 398 km over the Andean Highland plateau before splitting in two channels, one discharging directly into the Poopó lake (*Montes de Oca, 1997*) and the other one first into the Uru-Uru lake before reaching the Poopó lake (*PPO, 1996a*) (Fig. 3). During years with headwaters and consequently high water levels in Poopó lake, water from this lake drains to the south into Lacajahuira river and then into the Coipasa salt pan (Fig. 3). Additionally to the Desaguadero river, there are about 20 smaller rivers that rise mostly in the Eastern Cordillera (Fig. 7). Poopó and

Table 9

Arsenic concentrations in rivers of Poopó basin for the wet and dry season. With exception of the Lacajahuira River who drains Poopó Lake, all rivers are flowing into Poopó lake; for locations see Fig. 3). Modified from *Quintanilla et al., 2009*.

Sampling site	As (µg/L)		
	Dry period	Wet period	Intermediate period
Sora-Sora river	163	14	–
Poopó river	11,140	834–725	4666
Antequera river (Pazna)	60	212	203
Juancané river	<10	20	<10
Juchusuma river	5500	<10	<10
Huari river	807	<10	<10
Desaguadero river	<190	<190	993
Toledo bridge	–	–	2888
Caracilla river	–	–	700
Español bridge	–	5455	–
Cortadera river	1220	1783	–
Lacajahuira river	1850	2456	4040
Poopó lake	<10	31.8–34.7	<10

Uru-Uru lakes are shallow (0.5–2.5 m, average 1.4 m; *UNEP/OEA, 1996*). In the semiarid climate, this causes a strong evaporative concentration increase of dissolved chemical species including As. In TDPS, there are natural and anthropogenic As sources (*SERGEOMIN, 1999*). The principal natural sources are located in the Western Cordillera, Eastern Cordillera and the Andean Highlands, where As is released from leaching of predominantly volcanic rocks and their weathering products, and locally by geothermal manifestation (*SERGEOMIN, 1999; Banks et al., 2004*). Geothermal manifestations in the Western Cordillera are considered by *Banks et al. (2004)* (see also *López et al., 2012*) as principal As contributors to surface waters in streams feeding salt pans of Coipasa and Uyuni (Fig. 3) reaching their As concentrations up to 4600 µg/L. Arsenic is released into the environment in the Eastern Cordillera, from predominantly sulfidic ore deposits, other rocks, and main tailings. In the plain westwards of the Eastern Cordillera, there are located several metallurgical industries, which additionally contribute to As release into the atmosphere, pedosphere and hydrosphere (*SERGEOMIN, 1999; PPO, 1996b*).

The “Binational Autonomous Authority of the Titicaca Lake” (*Autoridad Binacional del Lago Titicaca, ALT*) “Alliance of the lake Titicaca” (*ALT, 1999*) performed a comprehensive evaluation of the mining activities on the environment in the entire watershed of the Titicaca lake. The general environmental conditions in the northwest of the Oruro province (including the Poopó lake) were studied from 1992 to 1996 in the project “Pilot Project Oruro” (*PPO, 1996a,b,c*). Several mining activities and related metallurgical industries such as foundries were found to be responsible together with natural processes (geothermal water and leaching from rocks contributing to release of As into the environment) for environmental contamination by As.

Quintanilla et al. (2009) performed a preliminary assessment of the status of As contamination in groundwater, surface water and soils in the departments of La Paz and Oruro of the Bolivian highland (Fig. 3), its relation to geology, present-day and historical mining, related metallurgical industrial activities, and implications on human health. In La Paz, in the suburb of Lima II (El Alto, where 18,000 people are living), three foundries (Calbol, Hormet and Bustos) and 3 more in the Vinto–Oruro area (Vinto 1, 2 and 3) (Fig. 3) contribute to atmospheric As contamination resulting in high As contents in soils. Details about production data and materials used can be found in *Quintanilla et al. (2009)*. In the Vinto–Oruro area (Fig. 3), soils contain, depending on the distance to the smelters, 39–793 mg/kg of As, which is about 5–90 times higher than the background (8.4–8.6 mg/kg) (*Quintanilla et al., 2009*). In the atmospheric dust of residential areas,

the highest As contents of 290 and 297 mg/kg were found in Vinto 1 and Vinto 2 (ranges 142–613 mg/kg, $n=6$ and 224–385 mg/kg, $n=4$), which is about 4 times higher than the natural background (71.5 mg/kg) (Quintanilla et al., 2009).

In the Poopó sub-basin, several studies of As concentrations in water resources were performed, most of them during the last 10 years. A first major environmental assessment study of the lake Poopó subbasin commenced in 1993 (Oruro Pilot Project; PPO, 1996a,b,c). The annual As influx into the Poopó basin has been estimated to be about 66 tones; 15% are estimated to be of anthropogenic release by mining activities (PPO, 1997). The most significant As influx into the Poopó lake comes from the Desaguadero river (Fig. 3), whose principal channel has As concentrations of 588–1180 $\mu\text{g/L}$ (average 740 $\mu\text{g/L}$); the respective As flux is $0.9\text{--}1.8 \times 10^5$ kg/year (PPO, 1996b). Additionally, mining effluents from San Juan de Sora Sora, Poopó and Antequera (or Pazña) (Fig. 3) and other river catchment areas, contribute to the As influx into Poopó lake (Table 9). The river water contains <170 $\mu\text{g/L}$ of As most of the time, but there are significant seasonal and short-term sporadically variations, the last due to operation activities in the mining installations and seasonal changes of water discharge. Thus, the As concentrations were 118 $\mu\text{g/L}$ in the dry season (July 2001) and decreased in the wet season to 14 $\mu\text{g/L}$, before increasing again in the next wet season to 163 $\mu\text{g/L}$ (August 2003) (Quintanilla et al., 2009). The As concentrations in different rivers of Poopó basin and seasonal variations are given in Table 9.

García Moreno (2006) and García and Bundschuh (2006) studied the control mechanisms of the seasonal variation of dissolved As in the surface waters of the Poopó subbasin, where surface waters from rivers and the Poopó lake have between 0.09 and 0.14 mg As/L in areas not affected by mining activities and up to 2.0 mg As/L in rivers influenced by mining activities. Sediments from rivers and lakes contain similar As concentrations in both the rainy and the dry season. In the Poopó lake, the highest As concentrations correspond to the dry season (210–220 $\mu\text{g/L}$ versus 20 $\mu\text{g/L}$ in the rainy season), whereas in most other rivers, maximum As values belong to the rainy season (10–380 $\mu\text{g/L}$ versus 10–50 $\mu\text{g/L}$ in the dry season). This different behavior can be explained by different dominating As-mobility controls in rivers and lakes. In the Poopó lake, evaporation and a possible uptake by biological sinks are the principal controls that explain the As maximum in dry season, whereas increased erosion and dissolution of weathered solids and transport into rivers explain the As maximum in the rivers in the rainy season.

Selander and Svan (2007) studied the As concentrations in water and sediments of the lake Poopó. These authors took 19 water and 19 sediment samples (the top 15 cm of the lake bottom) collected from 3 areas (El Choro at the northern end of the lake, Llapallapani in the southeast and Pampa Aullagas in the southwest (Fig. 3)) during two field trips in autumn 2006. Mean As concentrations (\pm SD) were 6.7 ± 4.3 $\mu\text{g/L}$ in the northern part of the Poopó lake ($2.4\text{--}13.8$ $\mu\text{g/L}$, $n=7$). They increased by factor 23.5 to 157.5 ± 27.7 $\mu\text{g/L}$ toward the sampling sites in the SE and SW of the lake ($89.8\text{--}202.3$ $\mu\text{g/L}$, $n=12$). The same trend could be observed for the sediment samples. The mean As value (\pm SD) in sediment was 1187.8 ± 348.7 mg/kg in northern part of the lake ($756.1\text{--}1673.3$ mg/kg, $n=7$) and increased by factor 1.8 to 2167.1 ± 304.9 at the sampling sites in the south ($1459.5\text{--}2662.2$ mg/kg, $n=12$). The ratio between mean As contents in sediment to As in water is highest in the north (177.3) and lowest (13.8) in the SE and SW area. This may be explained by an increasing mobilization of As, from north to south, from the sediments into the aqueous and at the same time occurring evaporative concentration increase; this contributes to generally higher As concentrations toward the south, whereas in the north the river is recharged permanently by inflowing water from the Desaguadero river.

Milikus (2008) used numerical modeling of chemical reactions to study the infiltration of river water through a groundwater system toward a well, and the transport of As(V) and As(III) species using field data taken from the rivers Poopó and Totoral (a tributary of the

Antequera river) (Fig. 3) with the aim of studying how As transport may vary in different geochemical environments. In the Poopó river, alkaline geothermal water infiltrates into the underground. Here, after a simulation of 4 years, 45% of As(III) and 60% of As(V) of the infiltrated As leave the system at the well; the rest remains adsorbed or otherwise bound in the underground, becoming there increasingly accumulated. In the case of the Totoral river, which is influenced by mine drainage influents, acidic water infiltrates into the underground; 50% of As(III) and 21% of As(V), which infiltrated from the river, leave the system in the well.

Ormachea et al. (2010) studied the occurrence of As in 16 geothermal springs (one sample each) located to the east of the Poopó lake (Fig. 3). The geothermal water is 40–75 °C warm water, moderately reducing (+106 to +204 mV, mean: +172 mV) and slightly acid to alkaline (6.3–8.3, mean: 7.0). It is commonly used for consumption, irrigation and recreation purposes. The geothermal springs discharge in rivers and the geothermal fluids reach finally the Poopó lake. Dissolved As concentration in the thermal springs ranged from 7.8 to 65.3 $\mu\text{g/L}$ (mean: 23.2 $\mu\text{g/L}$; 81% of them exceed the WHO 10 $\mu\text{g/L}$ limit). Arsenic (III) is the prevailing As species in most samples (9 samples, 56%); in two samples (13%) As(III) and As(V) are found in similar concentrations whereas in the rest (5 samples, 31%), As(V) was the dominant species (for details see López et al., 2012).

Rosenberg and Stålhammar (2010) studied the As concentrations in surface water and groundwater (22 sampling points) of the catchment areas of the Poopó and Antequera rivers (Fig. 3), which are part of the Poopó subbasin, to access the As input due to mining activities, natural weathering from rocks and geothermal springs. Sampling was performed in the dry season (September to November 2009). The Poopó river rises about 10 km upstream of the homonymous village in the Eastern Cordillera, and the Antequera river originates on the hillsides about 13 km north-east of the village Pazña (Fig. 3) and discharge into the Poopó lake; most of the tributaries are seasonal. Rosenberg and Stålhammar (2010) authors found that the As concentration in water from the Poopó river is mainly affected by geothermal water discharges. The As concentration in the upper part of the catchment area is low (<5.6 $\mu\text{g/L}$, detection limit). The discharge of a geothermal spring (As: 27 and 47 $\mu\text{g/L}$ in September and October, respectively) resulted in an increase of the As concentration in the river water just downstream of the confluence (22 $\mu\text{g/L}$ during both sampling series). Further downstream, the influx of mine tailing discharging mine drainage water with 43 $\mu\text{g/L}$ of As resulted in October 2009 to a further increase in the As concentration of the river water downstream of the mine drainage inlet (33 $\mu\text{g/L}$), whereas in September 2009, when the As concentration of mine drainage was less (17 $\mu\text{g/L}$), a decrease of the As concentration in the river water could be observed; this indicates that the influx of mine drainage occurs only occasionally. The maximum As concentration in the downstream parts of the Poopó river reached only 33 $\mu\text{g/L}$, which is in contrast to the findings of Lilja and Linde (2006), who reported extremely high As concentrations in the downstream part of the river (5000–12,000 $\mu\text{g/L}$). This could be explained by an occasional disturbance by mine water discharges. The same explains the high As concentrations in the Poopó river, which were reported by García Moreno (2006) and García and Bundschuh (2006). These last two studies found that As concentrations are higher in the dry season, when the share of the water from the geothermal spring is higher; the authors conclude that most of the As in the river comes from natural sources, weathering of rocks and input from the geothermal spring, in agreement with the previously mentioned results of Rosenberg and Stålhammar (2010) and Lilja and Linde (2006), who found that the Poopó river is influenced to some extent by mining activities, but most of As has natural origins. Groundwater samples taken by Rosenberg and Stålhammar (2010) at 8 sites in the Poopó catchment area in two depths (5 and 10 m) from the shallow groundwater, showed As concentrations varying $<5.6\text{--}119$ $\mu\text{g/L}$ (mean in September 2009: 35 $\mu\text{g/L}$, in October 2009: 27 $\mu\text{g/L}$); although there is no significant

correlation between As concentration and depth, there is however an increase of As concentrations in downstream direction.

The upper part of the Antequera river basin (Fig. 3), around the communities of Avicaya, Totoral and Bolívar, has evidence of As contamination from mining activity. Rosenberg and Stålhammar (2010) reported low As concentrations in river water (<5.6 µg/L, detection limit) from sampling sites upstream of a large mine tailings deposit. Mine drainages contained 14 (September 2009) and 7 µg/L (October 2009) of As. The As concentrations in the river downstream of the tailings deposit were 21 and 29 µg/L, respectively. However, it remains unclear whether the As concentration increase from the upstream to the downstream area of Antequera river is predominantly due to natural leaching from rocks/sediments or from mining effluents whose concentration may vary significantly in time. The As concentrations of shallow groundwater in Antequera basin sampled from 5 to 10 m deep piezometers are 6–32 µg/L (mean: 25 and 18 µg/L in September and October 2009, respectively). These findings are in agreement with previous studies by Quino Lima (2006) and López Cortés (2006). Quino Lima (2006) found a low As concentration of 14 µg/L in groundwater from a 5–8 deep wells close to the community of Pazña in the downstream area of Antequera river basin. López Cortés (2006) found, in surface waters, increasing contamination in downstream direction; although pH decreases from 7.35 to 2.8, As concentrations are low (1–13 µg/L). This author found two areas with As concentrations of up to 18 µg/L in groundwaters: (i) the area close to the community of Totoral, in the upstream part of the Antequera river basin, and (ii) the area around Bolívar mine, where water is drawn from a confined aquifer.

6.3.4. Brazil

Past and present mining activities and related metallurgical industries in the Iron Quadrangle (Minas Gerais state, Fig. 1), one of the most important long-term mineral resource regions of the world, have led to significant environmental impacts. Nova Lima, Santa Bárbara, and Ouro Preto/Mariana (Fig. 1) are the most important districts where large amounts of iron and gold have been mined from hydrothermal mineralizations since about 300 years. The impacts of As mobilization into different environments were assessed in a large interdisciplinary research project which ran from 1998 to 2007 (Matschullat et al., 2007). This research project forms a significant case study for assessing mining-related As problems in a holistic way. Intense studies have been performed on hydrosphere (water and sediments), pedosphere (soils), biosphere (plants and humans, human biomonitoring) as well as mitigation, which comprise remediation technologies and approaches such as environmental education, hygiene training, etc. The details of the project and its outcomes are published in the books by Deschamps and Matschullat (2007) in Portuguese, and an English version is in preparation (Deschamps and Matschullat, 2011). Individual results are given in several publications (e.g., Matschullat et al., 2000, 2007; Deschamps et al., 2009). Arsenic in air, soil, surface water, groundwater, suspended particulates, unconsolidated sediments, home-grown vegetables, home dust, human urine and hair, and private water supplies has been determined (Matschullat et al., 2007). In the following, only a short overview on As in geological environments and water resources will be given, whereas epidemiological aspects and As in the food chain will be addressed in this issue by McClintock et al. (2012) and Bundschuh et al. (2012).

In the Iron Quadrangle, the presence of As is associated with primary gold deposits where it is contained predominantly in sulfidic minerals such as arsenopyrite and pyrite (Borba et al., 2003). The ratio As/Au in the primary gold deposits varies from 300 to 3000 (Deschamps et al., 2002). The total gold production of the region exceeds 1300 tons, which translates into a mass of 390,000–3,900,000 tons of As. In soils, the lowest values are below 10 mg/kg, which can be considered as natural background value (Deschamps et al., 2002). However, values of up to

60 mg/kg have been reported as natural values and result from natural leaching of rocks and soils (Deschamps et al., 2011). Such values are in agreement with those reported by Campos et al. (2007) for non contaminated Brazilian oxisols (average 5.92 mg/kg; maximum 31.7 mg/kg). In areas close to gold mines, As contents in soil are 150–390 mg/kg, whereas close to old mining tailing deposits values exceed generally 1000 mg/kg (Deschamps et al., 2002). In the period 1900–1940, about 3×10^6 tones of tailings were deposited in valleys along the Cardoso creek, a tributary to the Rio das Velhas river (Nova Lima district, Fig. 1); after the deposits were full, the tailings were discharged directly into the local drainages, corresponding to an estimated As release of 390,000 tons of As (total as of the beginning of mining) (Borba et al., 2000). Extreme As concentrations in surface waters, in particular of Cardoso creek, show values of 260–1710 µg/L (Vasconcelos et al., 2011). Studies on surface water along the entire valley of the Rio das Velhas river were performed by the *Instituto Minero de Administración de Aguas* (IGAM). Highest As concentrations (450 µg/L) were found at the site where Cardoso creek discharges into the Rio das Velhas river. Here, the largest of six old tailing deposits is located (containing on average 14,500 mg/kg of As) (IGAM, 2005). In groundwater, influenced by the old tailing deposits, very high mean values of 7000 µg/L were found under reducing conditions (IGAM, 2005).

Studies of surface water and sediments of the Iron Quadrangle in areas close to the gold mineralizations reach up to 4500 mg/kg in the sediments and up to 350 µg/L in water (Borba et al., 2003). Water samples collected from subsurface mines and rock outcrops in the area of Ouro Preto and Mariana show As concentrations of 2–2.980 µg/L (1–86 µg/L as As(III)) (Borba et al., 2003). Out of the Iron Quadrangle but still in Minas Gerais state, Ono et al. (2010) have reported up to 2666 mg/kg of As in pond tailings from a gold mine area located close to the district of Paracatú, whereas natural concentrations found in a Private Natural Reserve (native Cerrado vegetation) inside the mine area ranged from 25 to 35 mg/kg. It is noteworthy to mention, however, that IVG protocols revealed that the bioaccessibility of As on such tailings was very small (close to 4%).

6.3.5. Uruguay

In the framework of the Guaraní Aquifer System Project (*Proyecto Sistema Acuifero Guaraní, PSAG*) to improve the water supply for agriculture and industry in different regions of Uruguay, financed by the Worldbank between 1998 and 2002, over 10,000 wells were drilled (depth: 30–80 m) without making any assessment of the water quality. Additionally, there exist other studies on the Guaraní and Raigón aquifers (IAEA, 2004); however, none of them considered the analysis of As and other trace elements. In the Raigón aquifer, about 3500 wells were drilled for agricultural purposes (irrigation and cattle watering), which has led to an overexploitation of the aquifer (Bundschuh et al., 2008).

In Uruguay, the presence of geogenic As in groundwater has been studied since 2005, and the first results have been reported from the south of the San José department in southwestern Uruguay (Guérèquiz et al., 2006, 2008, 2009; Fig. 1). In an area of 1800 km², which is predominantly used for agriculture and cattle breeding and where about 47,000 people are living, investigations by these authors found an average As content between 25 and 50 µg/L in groundwater, predominantly of sodium-bicarbonate type and very variable mineralization (TDS: <100 to >1500 mg/L). Guérèquiz et al. (2006) assume that the occurrence of As in the Raigón aquifer (located within the Formation of the same name) which has a maximum thickness of 45 m, is related to the same source: continental sediments containing volcanic ash, as in the nearby province of Santa Fe (Argentina) and the Puelche aquifer (Buenos Aires province). This assumption is supported by the positive correlations ($r > 0.90$) between the contents of arsenic, vanadium and other associated trace elements, which are typical

elements of this source (Guèrèquiz et al., 2009). At some sites, decimeter-thick volcanic ash layers are intercalated in the Raigón aquifer. The Raigón Formation is covered by deposits of the Libertad Formation, predominantly composed by clay, clayey silt and loess with carbonate concretions and, at some sites, with decimeter-thick intercalations of volcanic ash. The analysis of 22 groundwater samples from the Raigón aquifer gave a mean As concentration of 18 µg/L; at some localities, values of about 30 µg/L were found (Guèrèquiz et al., 2006).

Manganelli et al. (2007) presented data on As concentrations in groundwater from three aquifers in southwestern Uruguay, and evaluated the horizontal and vertical concentration variation. Elevated As concentrations were found in the Chuy (0.1–41.9 µg/L), Raigón (3.1–18.9 µg/L) and Mercedes (9.9–58 µg/L) aquifers. The Chuy aquifer is located in the Pleistocene Formation of the same name, composed by litoral clastic sediments from transgressive interglacial cycles. The Raigón aquifer comprises a sequence of fluvial and deltaic sediments of the homonymous Raigón Formation (Plio–Pleistocene). The Mercedes aquifer is located in the Mercedes Formation (Upper Cretaceous), composed by continental sediments (conglomerates, sandstones and pelites).

From the social point of view, the population seems not interested or concerned about the topic, since the waters of Uruguay are considered to be of good quality. However, recently the topic of human exposure to As from anthropogenic sources has received increased attention in Uruguay media (Guèrèquiz et al., 2006; *Diario El País*, 2007).

7. Conclusions

This review, based on a large number of accessible sources of information on As contamination in groundwater and surface water resources from the Latin American continent, suggests that both drinking and irrigation water sources contain As levels that affect a large number of people, especially in areas without central water supply systems.

At present, As problems have been described in 94 principal regions in 14 out of 20 countries comprising (in alphabetical order): Argentina, Bolivia, Brazil, Chile, Colombia, Cuba, Ecuador, El Salvador, Guatemala, Honduras, Mexico, Nicaragua, Peru, and Uruguay. The mitigation of the As-related problems is a huge challenge for this continent.

Arsenic sources are in most cases natural, and the release is largely from leaching of volcanic rocks, sulfidic ore bodies, hydrothermal alterations and their weathering products, and also from local geothermal fluids and volcanic exhalations. Furthermore, mining activities and related metallurgical industries are important local contributors to As in water resources and other environments.

The occurrence of high As concentrations in groundwater and surface water can be attributed to specific typical geological settings and climatic conditions. Therefore, it is possible to use certain geological settings and/or climatic conditions, which are known to have high As contamination, for exploring areas with potential As contamination in another country or region with similar geological and climate conditions. This approach can be useful to explore and delimit the potential high and low risk areas with As contamination. For example, in western Nicaragua, As is found in a few limited spots in groundwater of alluvial aquifers. The aquifer material is derived from weathering products of volcanic rocks and hydrothermal alterations. The similar geological conditions found in large parts of Nicaragua and in the neighboring countries make probable the finding of other As-impacted aquifers in these vast regions.

This approach is also valid if one focuses on the Argentine Chaco–Pampean plain and its extension into the neighboring countries of Bolivia, Paraguay and Uruguay. In the entire plain, sediments derived from the Andes are found. In Argentina, until today, aquifers with

elevated As concentrations have been found at many sites in 16 out of 23 provinces within the Chaco–Pampean plain and adjacent areas. Here, the similar geological conditions, for example the presence of loess deposits and intercalated or disperse distributed volcanic (the most important primary As source in this area), makes probable the detection at other sites of the Chaco–Pampean plain and the adjacent plains in Bolivia, Paraguay, and Uruguay. Therefore, it is not surprising that in 2005, nearly 100 years after the detection of the problem in Bell Ville, As was found in the groundwater of the San José department in SW Uruguay, which belongs to the same sedimentary basin.

Arsenic contamination of surface, groundwaters and soils in mining areas of various Latin American countries also present similarities. Solid waste deposits and acid drainage from sulfide ore processing have polluted sediments and waters in many areas of Bolivia, Brazil, Chile, Colombia, Ecuador, Guatemala, Honduras and Mexico. Natural and anthropogenic sources coexist in the same zones and have affected crops and human health. Specific remediation measures must be developed to remediate the anthropogenic polluted areas. This implies identification of the sources and environmental pathways of As.

Arsenic assessment must be a standard parameter for drinking and irrigation water, and uniform international guideline values should be adopted by all countries. Multidisciplinary research on As in Latin America has to be strengthened by national researchers and by international interdisciplinary cooperation, to build-up a robust Latin American network to investigate the occurrence and mobilization pathways of As release into the environment, and to create an on-line database, periodically updated, containing information regarding As-related topics to allow better access to information on regional and international base. These measures will allow to develop alternatives based on water treatment procedures or on the substitution of water sources to eradicate As exposure of Latin American inhabitants.

Acknowledgments

The authors thank the CYTED Project Red Temática 406RT0282 IBEROARSEN. J.B. and J.-S.J. thank the National Science Council of Taiwan for the financial support. L.C. greatly acknowledge support provided by the Convenio de Desempeño Universidad de Tarapacá (UTA-MINEDUC, 2008–2010). MIL thanks the financing of PICT512 Project of Agencia Nacional de la Promoción de la Ciencia y la Tecnología de Argentina.

References

- Adriano D. Trace elements in terrestrial environments: biogeochemistry, bioavailability, and risks of metals: chapter 7: arsenic. 2nd ed. Berlin, Germany: Springer; 2001. p. 220–56.
- Aguilar E, Parra M, Cantillo L, Gómez A. Chronic arsenic toxicity in El Zapote–Nicaragua, 1996. *Med Cután Iber Lat Am* 2000;28(4):168–73.
- Alarcón-Herrera MT, Flores-Montenegro I, Romero-Navar P, Martín-Domínguez IR, Trejo-Vázquez R. Contenido de arsénico en el agua potable del valle del Guadiana, México. *Hydraul Eng México* 2001;XV:63–70.
- Alfaro-Valero C. Geochemistry of hot spring at Cundinamarca Department, Colombia. *Proceedings World Geothermal Congress*. Antalya, Turkey: International Geothermal Association IGA; 2005. p. 1–8 [April 24–29].
- ALT. Macrozonificación ambiental del sistema TDPS. Autoridad Binacional Autónoma del Sistema Hídrico del Lago Titicaca, río Desaguadero, lago Poopó y Salar de Coipasa. La Paz-/Puno-Peru: The Binational Autonomous Authority of Lake Titicaca ALT-OIEA, 1999.
- Altamirano Espinoza M, Bundschuh J. Natural arsenic groundwater contamination of the sedimentary aquifers of southwestern Sébaco valley, Nicaragua. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB, editors. *Natural arsenic in groundwater of Latin America*. Leiden, The Netherlands: CRC Press/Balkema Publisher; 2009. p. 109–22.
- Amat, PD. Influencia de la contaminación por metales pesados en la Bahía de Manzanillo. Manzanillo, Cuba: MSc Thesis, Instituto Superior Minero Metalurgico de Moa (I.S.M.M.), 2000.
- Amat PD, Pierra A, Casals I. Estudio de la contaminación por metales pesados en sedimentos y ostones de la Bahía de Manzanillo, Cuba. *Rev Soc Quím México* 2002;46:357–61.

- Archer A, Elmore AC. Use of ceramic pot filters for drinking water disinfection in Guatemala. *Proceedings of the World Environmental and Water Resources Congress*; 2010. 2010 May 16–20, Providence, Rhode Island.
- Archer J, Hudson-Edwards KA, Preston D, Howarth RJ, Linge K. Aqueous exposure and uptake of arsenic by riverside communities affected by mining contamination in the Rio Pilcomayo basin, Bolivia. *Mineral Mag* 2005;69(5):719–36.
- Arencibia G, Perigó E. Estudio de la contaminación costera de la zona Santa Cruz del Sur hasta Niquero. *Rev Mar Pesca (Havana)* 1985;25:22–5.
- Armienta MA, Segovia N. Arsenic and fluoride in the groundwater of Mexico. *Environ Geochem Health* 2008;30:345–53.
- Armienta MA, Rodríguez R, Aguayo A, Cenicerio N, Villaseñor G, Cruz O. Arsenic contamination of groundwater at Zimapán, México. *Hydrogeol J* 1997;5:39–46.
- Armienta MA, Villaseñor G, Rodríguez R, Ongley LK, Mango H. The role of arsenic-bearing rocks in groundwater pollution at Zimapán Valley, México. *Environ Geol* 2001;40:571–81.
- Armienta MA, Amat PD, Larios T, López DL. América Central y México. In: Bundschuh J, Carrera AP, Litter M, editors. *Distribución del arsénico en las regiones Ibérica e Iberoamericana*. Buenos Aires, Argentina: Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo; 2008. p. 187–210.
- Arriaza B. Beyond death: the Chinchorro mummies of ancient Chile. Washington DC: Smithsonian Institution Press; 1995a.
- Arriaza B. Chinchorro bioarchaeology: chronology and mummy seriation. *Latin Am Antiquity* 1995b;6(1):35–55.
- Arriaza B, Standen V. Muerte, momias y ritos ancestrales. Santiago de Chile, Chile: Editorial Universitaria; 2008.
- Arriaza B, Amarasiriwardena D, Cornejo L, Standen V, Byrne S, Bartkus L, et al. Exploring chronic arsenic poisoning in pre-Columbian Chilean mummies. *J Archaeol Sci* 2010;37:1274–8.
- Arsênio antropogênico e natural. Um estudo em regiões do Quadrilátero Ferrífero. In: Deschamps E, Matschullat J, editors. *Belo Horizonte, Brazil: Fundacao Estadual do Meio Ambiente*; 2007.
- Astolfi EAN, Maccagno A, García-Fernández JC, Vaccaro R, Stimola R. Relation between arsenic in drinking water and skin cancer. *Biol Trace Elem Res* 1981;3:133–43.
- Astolfi EAN, Besuschio SC, García-Fernández JC, Guerra C, Maccagno A. *Hidroarsenicismo Crónico Regional Endémico*. Buenos Aires, Argentina: Edit. Coop. Gral. Belgrano; 1982.
- Ayerza A. Arsenicismo regional endémico (keratodermia y melanodermia combinadas). *Bol Acad Medicina* 1917a;2-3:11–24.
- Ayerza A. Arsenicismo regional endémico (keratodermia y melanodermia combinadas) (continuación). *Bol Acad Medicina* 1917b;2-3:41–55.
- Ayerza A. Arsenicismo regional endémico (keratodermia y melanodermia combinadas) (continuación). *Bol Acad Medicina* 1918:1–24.
- Banks D, Markland H, Smith PV, Mendez C, Rodriguez J, Huerta A, et al. Distribution, salinity and pH dependence of elements in surface waters of the catchment areas of the Salars of Coipasa and Uyuni, Bolivian Altiplano. *J Geochem Explor* 2004;84:141–66.
- Barragne-Bigot P. Contribución al estudio de cinco zonas contaminadas naturalmente por arsénico en Nicaragua. Managua, Nicaragua: UNICEF; 2004.
- Basu N, Hu H. Toxic metals and indigenous peoples near the Marlin mine in western Guatemala: potential exposures and impacts on health. Report for Physicians for Human Rights, Cambridge, MA; 2010.
- Bates MN, Rey OA, Biggs ML, Hopenhayn C, Moore LE, Kalman D, et al. Case-control study of bladder cancer and exposure to arsenic in Argentina. *Am J Epidemiol* 2004a;159(4):381–9.
- Bates M, Marshall G, Smith A. Arsenic-related cancer mortality in northern Chile, 1989–98. *Epidemiology* 2004b;15(4):S108–S.
- Bedregal P, Torres B, Olivera P, Ubillus M, Mendoza P, Creed-Kanashiro H, et al. Determination of trace elements and heavy metals in agricultural products cultivated at the river Rimac in the city of Lima. Lima, Peru: Peruvian Institute of Nuclear Energy (IPEN) Chemistry Department. Nutritional Research Institute (IIN); 2001. p. 1–18.
- Bejarano Sifuentes G, Nordberg E. Mobilisation of arsenic in the Rio Dulce alluvial Cone, Santiago del Estero Province, Argentina. MSc thesis. Stockholm, Sweden: Department of Land and Water Resources Engineering KTH, TRITA-LWR-EX-03-06; 2003.
- Bhattacharya P, Claesson M, Bundschuh J, Sracek O, Fagerberg J, Jacks G, et al. Distribution and mobility of arsenic in the Rio Dulce alluvial aquifers in Santiago del Estero Province, Argentina. *Sci Total Environ* 2006;358:97–120.
- Biagini RE, Salvador MA, de Querio RS, Torres-Soruco CA, Biagini MM, Diez-Barrantes A. Hidroarsenicismo crónico. Comentario de casos diagnosticados en el periodo 1972–1993. *Arch Arg Dermatol* 1995;45:47–52.
- Birkle P. Origin and environmental impact of Los Azufres geothermal water (original in German). *Wiss. Mitteilungen* 6, Institute for Geology, Technical University Freiberg, Germany; 1998.
- Birkle P, Bundschuh J. High and low geothermal resources and potentials. In: Bundschuh J, Alvarado GE, editors. *Central America – geology, resources and hazards*. Leiden, The Netherlands: Balkema; 2007a. p. 705–76.
- Birkle P, Bundschuh J. Hydrogeochemical and isotopic composition of geothermal fluids. In: Bundschuh J, Alvarado GE, editors. *Central America – geology, resources and hazards*. Leiden, The Netherlands: Balkema; 2007b. p. 777–838.
- Birkle P, Bundschuh J, Sracek O. Mechanisms of arsenic enrichment in geothermal and petroleum reservoirs fluids in Mexico. *Water Res* 2010;44(19):5605–17.
- Bittmann B. Revisión del problema Chinchorro. *Chungara* 1982;9:46–79.
- Blanco M del C, Amioti N, Aguilar Ruiz J. Reconstrucción paleoambiental de la evolución geo-pedogenética en una toposecuencia del sudoeste pampeano. *Cienc del Suelo* 2003;2(2):59–70.
- Blanes P, Giménez MC. Contaminación natural con arsénico y otros elementos traza en aguas subterráneas en la región central del Chaco. *Acta Toxicol Argent* 2004;4(Supl. 12).
- Blanes P, Herrera Aguad C, Giménez MC. Arsénico y otros oligoelementos asociados en aguas subterráneas de la prov. del Chaco: estudio preliminar. In: Litter M, editor. *Libro de resúmenes del taller de distribución del As en Iberoamérica*; 2006. p. 61–2. Buenos Aires, Argentina.
- Borba RP, Figueiredo BR, Rawlins BG, Matschullat J. Arsenic in water and sediment in the Iron Quadrangle, Minas Gerais state, Brazil. *Rev Bras Geocienc* 2000;20:554–7.
- Borba RP, Figueiredo BR, Matschullat J. Geochemical distribution of arsenic in waters, sediments and weathered gold mineralized rocks from Iron Quadrangle, Brazil. *Environ Geol* 2003;43:49–52.
- Borgoño JM, Greiber R. Epidemiological study of arsenism in the city of Antofagasta. *Trace Subst Environ Health* 1972;5:13–24.
- Borgoño JM, Vicent P, Venturino H, Infante A. Arsenic in the drinking water of the city of Antofagasta: epidemiological and clínica: study before and after the installation of a treatment plant. *Environ Health Perspect* 1977;19:103–5.
- Bundschuh J, Fariás B, Martín R, Stormiolo A, Bhattacharya P, Cortes J, et al. Groundwater arsenic in the Chaco-Pampean Plain, Argentina: case study from Robles county, Santiago del Estero Province. *Appl Geochem* 2004;19:231–43.
- Bundschuh J, Nicolli HB, Blanco M del C, Blarasin M, Fariás SS, Cumbal L, et al. Distribución de arsénico en la región sudamericana. In: Bundschuh J, Pérez-Carrera A, Litter MI, editors. *Distribución del arsénico en las regiones Ibérica e Iberoamericana*. Buenos Aires, Argentina: Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo; 2008. p. 137–86.
- Bundschuh J, García ME, Birkle P, Cumbal LH, Bhattacharya P, Matschullat J. Occurrence, health effects and remediation of arsenic in groundwaters of Latin America. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB, editors. *Natural arsenic in groundwater of Latin America*. Leiden, The Netherlands: CRC Press/Balkema Publisher; 2009. p. 3–15.
- Bundschuh J, Litter M, Ciminelli V, Morgada ME, Cornejo L, Garrido Hoyos S, et al. Emerging mitigation needs and sustainable options for solving the arsenic problems of rural and isolated urban areas in Iberoamerica – a critical analysis. *Water Res* 2010;44(19):5828–45.
- Bundschuh J, Liu C-W, Jean J-S, Armienta MA, Moreno López MV, Cornejo L, et al. Arsenic in the food chain of Latin America's population. *J Total Environ* 2012;429:2–35.
- Bustamante, et al. Propuesta de recuperación y estudio de las fuentes de agua minero medicinales del territorio de la Isla de la Juventud. Havana, Cuba: Oficina Nacional de Recursos Minerales (ONRM); 1985.
- Bustos Rodriguez H, Oyola Lozano D, Rojas Martínez YA, Pérez Alcázar GA, Balogh AG. Invisible gold in Colombian auriferous soils. *Hyperfine Interact* 2005;166:605–11.
- Bustos Rodriguez H, Oyola Lozano D, Rojas Martínez YA, Pérez Alcázar GA, Flege S, Balogh AG, et al. Mineralogical analysis of auriferous ores from the El Diamante mine, Colombia. *Hyperfine Interact* 2007;175:195–206.
- Byrne S, Amarasiriwardena D, Bandak B, Bartkus L, Kane J, Jones J, et al. Were Chinchorros exposed to arsenic? Arsenic determination in Chinchorro mummies' hair by laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS). *Microchem J* 2010;94:28–35.
- Caballero-Gutiérrez PU, Carrillo-Rodríguez JC, Gomez-Ugalde RM, Jerez-Salas MP. Presencia de arsénico en pozos y en cultivos en Oaxaca, México. *Agron Mesosamer* 2010;21(1):177–84.
- Cabrera A, Blarasin M, Matteoda E, Villalva G, Gómez ML. Composición química del agua subterránea en el sur de Córdoba: línea de base hidroquímica o fondo natural en referencia a arsénico y flúor. In: Blarasin M, Degiovanni S, Cabera A, Villegas M, editors. *Aguas superficiales y subterráneas en el sur de Córdoba: una perspectiva geoambiental*. Río Cuarto: Universidad Nacional de Río Cuarto; 2005. p. 81–90.
- Cáceres DD, Pino P, Montesinos N, Atalah E, Amigo H, Loomis D. Exposure to inorganic arsenic in drinking water and total urinary arsenic concentration in a Chilean population. *Environ Res* 2005;98(2):151–9.
- Cadin. Contaminación de aguas, suelos, y concentración de metales pesados en productos vegetales en la localidad de sotomayor, departamento de Chuquisaca. Sucre, Bolivia: Final technical report, Proyecto de Gestión Integrada y Plan Maestro de la Cuenca del Río Pilcomayo, Contract European Commission n.ASRIB7-3100/99/136, elaborated by Cadin S.R.L.; 2006.
- Calderon J, Navarro ME, Jimenez-Capdeville ME, Santos-Diaz MA, Golden A, Rodriguez-Leyva I, et al. Exposure to arsenic and lead and neuropsychological development in Mexican children. *Environ Res* 2001;85(2):69–76.
- Campos ML, Guilherme LRG, Lopes RS, Antunes AS, Marques JGSM, Curi N. Teor e capacidade máxima de adsorção de arsênio em Latossolos brasileiros. *Rev Bras Ciênc Solo* 2007;31:1311–8.
- Cano de los Ríos MP. Contaminación del agua por metales pesados en presas del municipio de Chihuahua. Chihuahua, Chih., Mexico: Bachelor Thesis, Facultad de Zootecnia y Ecología, Universidad Autónoma de Chihuahua; 2010.
- Cardoso S, Grajeda C, Argueta S, Garrido SE. Experiencia satisfactoria para la remoción de arsénico en Condado Naranjo, Mixco, Guatemala. In: Litter MI, Sancha AM, Ingallinella AM, editors. *Tecnologías económicas para el abatimiento de arsénico en aguas*. Buenos Aires, Argentina: Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo; 2010. p. 211–22.
- CARE Internacional, FUNDEC Matagalpa. Estudio hidrogeológico de trece comunidades de San Isidro; 2002.
- Carrillo-Chávez A, Drever JI, Martínez M. Arsenic content and groundwater geochemistry of the San Antonio-El Triunfo, Carrizal and Los Planes aquifers in southernmost Baja California, Mexico. *Environ Geol* 2000;39:1295–303.
- Carrillo-Chávez A, Morton-Bermea O, González-Partida E, Rivas-Solorzano H, Oeslerd G, García-Meza VE, et al. Environmental geochemistry of the Guanajuato Mining District, Mexico. *Ore Geol Rev* 2003;23:277–97.

- Castellanos ME, Sosa L, Moreira A, Maya H, Perez S, León AR, et al. Concentración de arsénico en macroalgas de la Bahía de Cienfuegos. *Rev Investig Mar* 2005;21–6. (Cuba).
- Castro ML. Evaluación de riesgos para la salud por el uso de las aguas residuales en agricultura: Aspectos toxicológicos. Lima, Peru: Centro Panamericano de Ingeniería Sanitaria y Ciencias del Ambiente (CEPIS); 1993.
- Castro de Esparza ML. Arsénico en el agua de bebida de la población de los valles de Lucumba y Chipe. OPS/CEPIS/02/IT-592; 2002. Lima, Peru.
- Castro de Esparza ML. The problem of arsenic in drinking water in Latin America. In: Murphy T, Guo J, editors. *Aquatic arsenic toxicity and treatment*. Leiden, The Netherlands: Backhuys Publishers; 2003. p. 67–76.
- Castro de Esparza ML. Removal of arsenic from drinking water and soil bioremediation. In: Bundschuh J, Armienta MA, Bhattacharya P, Matschullat J, Birkle P, Rodríguez R, editors. *Natural arsenic in groundwater of Latin America*; Abstract Volume, International Congress Mexico City, 20–24 June 2006; 2006. p. 16–7.
- Castro de Esparza ML. The presence of arsenic in drinking water in Latin America and its effect on public health. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB, editors. *Natural Arsenic in Groundwater of Latin America*. Leiden, The Netherlands: CRC Press/Balkema Publisher; 2009. p. 17–29.
- Castro de Esparza ML. Mejoramiento de la calidad del agua de pozos en zonas rurales de Puno, Perú. In: Litter MI, Sancha AM, Ingallinella AM, editors. *Tecnologías económicas para el abatimiento de arsénico en aguas*. Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo: Buenos Aires, Argentina; 2010. p. 243–56.
- Castro de Esparza ML, Noriega Pissani R, Wong Nonato M, Inamine Asato A. Estudio para el mejoramiento de la calidad del agua de pozos en zonas rurales de Puno. Lima, Peru: OPS-BJ; 2005.
- Castro-Larragoitia J, Krama U, Puchelt H. 200 years of mining activities at La Paz/San Luis Potosí/Mexico—consequences for environment and geochemical exploration. *J Geochem Explor* 1997;58:81–91.
- Cebrián ME, Albores A, García-Vargas G, Del Razo LM, Ostrosky-Wegman P. Chronic arsenic poisoning in humans: the case of Mexico. In: Nriagu JO, editor. *Arsenic in the environment, part II: human health and ecosystem effects*. New York: John Wiley & Sons, Inc.; 1994. p. 93–107.
- CEPIS. Estudio propuesto sobre los requisitos de tratamiento para el abastecimiento de agua potable. Lima, Peru: Technical report 165, Ministerio de Pesquería, Proyecto Meca Grande (Perú); 1975.
- Chávez A, Pérez C, Tovar E, Gramilla M. Estudios en una comunidad con arsenicismo crónico endémico. *Salud Publica Mex* 1964;6:421–33.
- Christian J, Hopenhayn CM. Is arsenic metabolism in exposed populations influenced by selenium? *Epidemiology* 2004;15(4):S107–S.
- Claesson M, Fagerberg J. Arsenic in groundwater of Santiago del Estero — Sources, mobility patterns and remediation with natural materials. Stockholm, Sweden: MSc Thesis, Dept. of Land and Wat. Res. Eng., KTH, TRITA-LWREX-03-05; 2003.
- Concha G, Nermell B, Vahter M. Metabolism of inorganic arsenic in children with chronic high arsenic exposure in northern Argentina. *Environ Health Persp* 1998a;106(6):355–9.
- Concha G, Vogler G, Lezcano D, Nermell B, Vahter M. Exposure to inorganic arsenic metabolites during early human development. *Toxicol Sci* 1998b;44(2):185–90.
- Corey G, Tomasini R, Pagura J. Estudio epidemiológico de la exposición al arsénico a través del consumo de agua. Provincia de Santa Fe, República Argentina; 2005. http://www.servtox.com.ar/img/item_full/CARATULA,%20PROLOGO,%20INDICE%20E%20INTRODUCCION.pdf. accessed September 2010.
- Cornejo L, Lienqueo H, Arenas M, Acarapi J, Mansilla H, Yañez J. Remoción de arsénico de aguas naturales del río de Camarones y su utilización para consumo humano, mediante la tecnología SORAS Modificada-Hierro Cero. In: Litter I, editor. *Final results of the OAS/AE/141 Project: research, development, validation and application of solar technologies for water potabilization in isolated rural zones of Latin America and the Caribbean*. La Plata, Chile, Buenos Aires, Argentina: Digital Grafic; 2006a. p. 149–57.
- Cornejo L, Lienqueo H, Arenas M, Acarapi J, Mansilla H, Yañez J. Transferencia de la metodología SORAS Modificada # Hierro Cero a los poblados que carecen de agua potable de la Comuna de Camarones, Arica, Chile. In: Litter I, editor. *Final results of the OAS/AE/141 Project: research, development, validation and application of solar technologies for water potabilization in isolated rural zones of Latin America and the Caribbean*. La Plata, Chile, Buenos Aires, Argentina: Digital Grafic; 2006b. p. 179–98.
- Cornejo L, Lienqueo H, Arenas M, Acarapi J, Yañez J, Mansilla H. In field arsenic removal from natural water by zero valent iron. *Environ Pollut* 2008;156(3):827–31.
- Cortina JL, Litter MI, Gibert O, Travesset M, Ingallinella AM, Fernández R, et al. Latin America experiences in arsenic removal from drinking water and mining effluents. *J Total Environ*, this issue.
- Cumbal L, Durán JC, Albuja L. Contaminación por mercurio de aguas y sedimentos de ríos que reciben efluentes de la minería de oro en los sectores de Nambija, Ponce Enriquez y Portovelo. *Rev Cienc* 2009a;12(2):166–79.
- Cumbal L, Durán JC, Albuja L. Contaminación por mercurio de aguas y sedimentos de ríos que reciben efluentes de la minería de oro en los sectores de Nambija, Ponce Enriquez y Portovelo. *Rev Cienc* 2009b;12(2):166–79.
- Cumbal L, Vallejo P, Rodríguez B, López D. Arsenic in geothermal sources at the North-Central Andean Region of Ecuador: concentrations and mechanisms of mobility. *Environ Earth Sci* 2010;61(2):299–310.
- Daesslé L, Lugo-Ibarra K, Tobschall H, Melo M, Gutiérrez-Galindo E, García-Hernández J, et al. Accumulation of As, Pb, and Cu associated with the recent sedimentary processes in the Colorado Delta, South of the United States–Mexico Boundary. *Arch Environ Contam Toxicol* 2009;56:680–92.
- Davies JA, Kent DB. Surface complexation modeling in aqueous geochemistry. In: Hochella MF, White AF, editors. *Mineral–water interface geochemistry*. Rev Mineral/Mineral Society of America; 1990. p. 177–260.
- De la Torre E, Guevara A, Muñoz G, Criollo E. Estudio de aguas superficiales y sedimentos de la cuenca de los ríos Sucus, Tambo y Papallacta. Quito, Ecuador: Unpublished report for the Ecuadorian Congress; 2004.
- Del Razo LM, Arellano MA, Cebrián ME. The oxidation states of arsenic in well water from a chronic arsenicism area of northern Mexico. *Environ Pollut* 1990;80:91–4.
- Deschamps E, Mello J, Matschullat J. Soils and sediments. In: Deschamps E, Matschullat J, editors. *Arsenic: Natural and Anthropogenic*. In: Bundschuh J, Bhattacharya P, series editors. *Arsenic in the Environment, Volume 4*. Leiden, The Netherlands, CRC Press/Balkema Publisher; 2011. p. 127–39.
- Deschamps E, Matschullat J, editors. *Arsenic: natural and anthropogenic*. Bundschuh J, Bhattacharya P, editors. *Arsenic in the environment* Leiden, The Netherlands: CRC Press/Balkema Publisher; 2011.
- Deschamps E, Ciminel VST, Frank LFT, Matschullat J, Raue B, Schmidt H. Soil and sediment geochemistry of the Iron Quadrangle, Brazil: the case of arsenic. *J Soils Sediments* 2002;2:216–22.
- Deschamps E, Oberdád SM, Matschullat J, Silva NOC, Vasconcelos OR. Mitigation actions respond to arsenic exposure in Brazil. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB, editors. *Natural arsenic in groundwater of Latin America*. Leiden, The Netherlands: CRC Press/Balkema Publisher; 2009. p. 699–704.
- Diario El País (Uruguay). Reunión por UTE y arsénico en Durazno. Montevideo, Uruguay, 27/02/2007. http://www.elpais.com.uy/07/02/27/pciuda_266402.asp. accessed September 2007.
- Díaz-Barriga F. Metodología de identificación y evaluación de riesgos para la salud en sitios contaminados. Pan American Health Organisation and World Health Organization; 1999. <http://www.bvsde.ops-oms.org/tutorial3/e/bienvenida.html>. accessed September 2010.
- Dymas. Contribución al conocimiento geohidrológico del sudoeste bonaerense: región de vertiente pampeana. La Plata, Argentina: Ministerio Obras Publicas provincia Buenos Aires; 1975.
- Dzombak DA, Morel FM. *Surface complexation modeling*. New York: John Wiley & Sons; 1990.
- El Comercio. Redacción Quito. La EMAAP-Q pide más tiempo para depurar el arsénico; 2006. Quito, Ecuador; October 3rd.
- Elmore AC, Miller GR, Parker B. Water quality in Lemoa, Guatemala. *Environ Geol* 2005;48:901–7.
- Emilson FM, Tápanes J. Contribución a la Hidrología de la plataforma sur oriental de Cuba. *Rev Mar Pesca (Havana)* 1971;6:15–8.
- ENACAL, MINSA, MEDC, CEPIS, UNICEF. Proyecto Agua y Ambiente Saludable. Registro de análisis de arsénico realizados a muestras de agua potable de sistemas de abastecimiento rural. Managua, Nicaragua; 2005.
- EPA. Federal register: part 503. Standards for the Use or Disposal of Sewage Sludge, 58. Washington DC: Environmental Protection Agency; 1993. p. 9387–404(32).
- Esquivel AO. Diagnostico nacional de calidad Sanitaria de las aguas superficiales de El Salvador. San Salvador, El Salvador: Programa de Descontaminación de Areas Criticas, Ministerio del Medio Ambiente y Recursos Naturales de El Salvador, Contrato de Prestamo BIS-MARN No 1209/OC-ES; 2007.
- E-Tech International. Evaluation of predicted and actual water quality conditions at the Marlin Mine, Guatemala. Report presented to Oxfam America; 2010. http://www.etechnical.org/082010guatemala/MarlinReport_Final_English.pdf. accessed October 2010.
- Farfán Torres EM, Naranjo PM, Boemo A, Lomniczi I, Lorenzo L. Distribution of arsenic in groundwater in the Chaco Salteño, Argentina. In: Litter MI, editor. *Workshop on As distribution in Ibero-America*. Buenos Aires, Argentina: CyTED IBEROARSEN Abstract book; 2006. p. 57–60.
- Fariás SS, Casa VA, Vazquez C, Ferpozzi L, Pucci GN, Cohen IM. Natural contamination with arsenic and other trace elements in ground waters of Argentine Pampean plain. *Sci Total Environ* 2003;309(1–3):187–99.
- Fariás SS, Bianco de Salas G, Servant RE, Bovi Mitre G, Escalante J, Ponce RI, et al. Survey of arsenic in drinking water and assessment of the intake of arsenic from water in Argentine Puna. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB, editors. *Natural arsenic in groundwater of Latin America*. Leiden, The Netherlands: CRC Press/Balkema Publisher; 2009. p. 397–407.
- Fernández RG, Ingallinella AM. Experiencia argentina en la remoción de arsénico por diversas tecnologías. In: *Tecnologías económicas para el abatimiento de arsénico en aguas*. In: Litter MI, Sancha AM, Ingallinella AM, editors. *Tecnologías económicas para el abatimiento de arsénico en aguas*. Buenos Aires, Argentina: Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo; 2010. p. 155–67.
- Fernández RG, Ingallinella AM, Stecca LM. Arsenic removal from groundwater by coagulation with polyaluminum chloride and double filtration. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB, editors. *Arsenic in the environment, Volume 1*. Leiden, The Netherlands: CRC Press Balkema; 2009. p. 665–79.
- Ferreccio C, González C, Milosavljevic V, Marshall G, Sancha AM, Smith AH. Lung cancer and arsenic concentrations in drinking water in Chile. *Epidemiology* 2000;11(6):673–9.
- Fiorentino C, Sequeira M, Paoloni D, Echeverría N. Detección y distribución de arsénico, flúor y boro en aguas subterráneas regionales. *Proceedings of the Congreso Nacional del Agua Santa Fe, Argentina: Mapas de Riesgo*; 1998. p. 71–9.
- Flores Y. Análisis químico toxicológico y determinación del arsénico en aguas de consumo directo en la provincia de Huaytará, Departamento de Huancavelica. Lima, Peru: Lic. Thesis, School of Pharmacy and Biochemistry, UNMSM; 1999.
- Fuller CC, Davis JA, Waychunas GA. Surface chemistry of ferrihydrite: Part 2. Kinetics of arsenate adsorption and coprecipitation. *Geochim Cosmochim Acta* 1993;57:2271–82.

- Gaeta Tassinari CC, Diaz Pinzon F, Buena Ventura J. Age and sources of gold mineralization in the Marmato mining district, NW Colombia: a Miocene–Pliocene epizonal gold deposit. *Ore Geol Rev* 2008;33:505–18.
- Galindo G, Sainato C, Dapeña C, Fernández Turiel JL, Gimeno D, Pomposiello MC, et al. Surface and groundwater quality in the northeastern region of Buenos Aires Province, Argentina. *J South Am Earth Sci* 2007;23:336–45.
- García Moreno ME. Transport of arsenic and heavy metals to Lake Poopó–Bolivia. Natural leakage and anthropogenic effects. Lund, Sweden: PhD Thesis, Department of Water Resources Engineering, Lund Institute of Technology, Lund University; 2006.
- García ME, Bundschuh J. Control mechanisms of seasonal variation of dissolved arsenic and heavy metal concentrations in surface waters of Lake Poopó basin, Bolivia. Geological Society of America Annual Meeting, Philadelphia. *Geol Soc Amer Abstracts with Programs* 2006; 2006. p. 320.. 22–25 Oct.
- García A, Armienta MA, Cruz O. Sources, distribution and fate of arsenic along the Toliman river, Zimapán, México. In: Acreman MC, editor. Hydro-ecology: linking hydrology and aquatic ecology. 266. IAHS publ; 2001. p. 57–64.
- García MG, Moreno C, Galindo MC, del V. Hidalgo M, Fernández DS, Sracek O. Intermediate to high levels of arsenic and fluoride in deep geothermal aquifers from the northwestern Chaco–Pampean plain, Argentina. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB, editors. Natural arsenic in groundwater of Latin America. Leiden, The Netherlands: CRC Press/Balkema Publisher; 2009. p. 69–79.
- García-Meza JV, Ramos E, Carrillo-Chávez A, Duran-de-Bazúa C. Mineralogical and chemical characterization of historical mine tailings from the Valenciana mine, Guanajuato, Mexico: Environmental implications. *Bull Environ Contam Toxicol* 2004;72:170–7.
- García-Meza JV, Carrillo-Chávez A, Morton-Bermea O. Sequential extractions on mine tailings samples after and before bioassays: implications on the speciation of metals during microbial re-colonization. *Environ Geol* 2006;49:437–48.
- Garrido Hoyos SE, Avilés Flores M. Análisis de la información técnica y evaluación del funcionamiento de la planta para remoción de arsénico, Mixco Guatemala. Final report TC0811.3. Jutepec, Mexico: Instituto Mexicano de Tecnología del Agua; 2008.
- Garrido Hoyos SE, Avilés Flores M, Rivera Huerta ML, Nájera Flores MC. Diagnóstico de la presencia de arsénico en agua de pozo. Mixco, Guatemala. Final report TC-0711.3. Jutepec, Mexico: Instituto Mexicano de Tecnología del Agua; 2007.
- Ginarte Z. Estudio de la contaminación por metales pesados en el entorno de la fábrica de acumuladores de Manzanillo. Manzanillo, Cuba: MSc Thesis, Instituto Superior Minero Metalúrgico de Moa (I.S.M.M.) ; 1999
- Goff F, Shevenell L, Truesdell AH, Janik CJ, Grigsby CO, Paredes R. Hydrogeochemistry and preliminary reservoir model of the Platanares geothermal system, Honduras, Central America. Los Alamos National Laboratory Report LA-UR-86-1404/1986; 1986a.
- Goff F, Grigsby CO, Shevenell LA, Gutierrez JW. Geochemistry at Honduras Geothermal Sites. Los Alamos Sci Fall 1986b:90–3.
- Gómez A. Arsenic and cancer in S and SW communities of the valley of Sebaco, Nicaragua 1999. Proceedings of the XXII Central America Congress of Dermatology; 2000.. Nov. 21–26; Panama City.
- Gómez A. Evaluación de daños causados por la ingesta prolongada de arsénico en las comunidades de Kinuma, La Curva y Las Puertas de Paris, municipios de La Libertad y San Pedro del Lóvago, departamento de Chontales. Managua, Nicaragua: UNICEF; 2004.
- Gómez A. Chronic arsenicosis and respiratory effects in El Zapote, Nicaragua. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB, editors. Natural arsenic in groundwater of Latin America. Leiden, The Netherlands: CRC Press/Balkema Publisher; 2009. p. 409–18.
- Gómez A, Aguilar E. Case of hydroarsenicosis and cutaneous cancer. El Carrizo, valley of Sebaco–Nicaragua 1952–2000. Proceedings of Summer Meeting American Academy of Dermatology; 2000.. July 31–August 4; New York.
- González M, Provedor E, Reyes M, López N, López A, Lara K. Arsenic exposition in rural communities of San Isidro, Matagalpa. Health Studies and Research Center (CIES), Pan American Health Organization /WHO PLAGSALUD-MASICA; 1997.
- González D, Ferrúa N, Cid J, Sansone G, Jiménez I. Arsénico en aguas de San Luis (Argentina). Uso de un equipo alternativo Al De Gutzeit modificado. *Acta Toxicol Argent* 2003;11(1):3–6.
- González DM, Ferrúa NH, Sansone MG, Ferrari S, Cid JA. Arsénico en agua de consumo humano en poblaciones de las provincias de San Luis y Buenos Aires. *Acta Toxicol Argent* 2004;12:7.
- González-Hita L, Sánchez L, Mata I. Estudio hidrogeoquímico e isotópico del acuífero granular de la Comarca Lagunera. Jutepec, Mor., Mexico: Instituto Mexicano de Tecnología del Agua; 1991.
- Goyenechea M. Sobre la nueva enfermedad descubierta en Bell-Ville. *Rev Med Rosario* 1917;7:485.
- Guéréquizar AR, Mañay N, Goso Aguilar C, Bundschuh J. Evaluación de riesgo ambiental por presencia de arsénico en el sector oeste del acuífero Raigón, Departamento de San José, Uruguay. Presentación del proyecto. In: Litter M, editor. Libro de actas del taller de distribución del arsénico en Iberoamérica. Buenos Aires, Argentina: Red Temática 406RT0282 IBEROARSEN, Centro Atómico Constituyentes; 2006.
- Guéréquizar R, Mañay N, Goso C, Fernandez J, García M. Environmental risk assessment of arsenic in the Raigón Aquifer, Uruguay: Research Advancements. PA23. Abstract volume II International Congress: Arsenic in the Environment: From Nature to Humans; 2008.. May 21–23; Valencia, Spain.
- Guéréquizar R, Mañay N, Goso-Aguilar C, Fernández-Turiel JL, García-Valles M. Environmental risk assessment of arsenic in the Raigón aquifer, Uruguay. *Biologist (Lima)* 2009;7(1–2). Special Issue, C0130.
- Guillén SE. Chinchorro culture: Mummies and crania in the reconstruction of preceramic coastal adaptation in the south central Andes. PhD Thesis, University of Michigan, 1992.
- Guillimette N, Williams-Jones AE. Genesis of the Sb-W-Au deposits at Ixtahuacan, Guatemala: Evidence from fluid inclusions and stable isotopes. *Mineralium Deposita* 1993;23:167–80.
- Gutiérrez M, Carreón E. Contenido de As, Ba, y Cu en sedimentos y su asociación con depósitos minerales en el noreste de Chihuahua. *Medio Ambiente Desarrollo Sustentable* 2008;11:108–17.
- Gutierrez S. Caracterización química de las patinas negras utilizadas en la momificación de las momias negras de la cultura Chinchorro. Arica, Chile: Thesis, Universidad de Tarapacá; 2007.
- Gutierrez-Ojeda C. Determining the origin of arsenic in the Lagunera region aquifer, Mexico using geochemical modeling. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB, editors. Natural arsenic in groundwater of Latin America. Leiden, The Netherlands: CRC Press/Balkema Publisher; 2009. p. 163–70.
- Gutiérrez-Ruiz M, Romero FM, González-Hernández G. Suelos y sedimentos afectados por la dispersión de jales inactivos de sulfuros metálicos en la zona minera de Santa Bárbara, Chihuahua, México. *Rev Mex Cienc Geol* 2007;24:170–84.
- Hammarlund L, Piñones J. Arsenic in geothermal waters of Costa Rica—A minor field study. Stockholm, Sweden: MSc Thesis, Department of Land and Water Resources Engineering, Royal Institute of Technology, TRITA-LWR LWR-EX-09-02; 2009.
- Hernández García Y. Metales pesados y arsénico en agua y sedimento de embalses artificiales del estado de Chihuahua, México. Chihuahua, Chih., Mexico: MSc Thesis, Facultad de Zootecnia y Ecología. Universidad Autónoma de Chihuahua; 2007.
- Hernández-García Y, Sosa-Cerecedo M, Moreno M, Alcalá J, Puga SR. Evaluación de la contaminación por metales pesados y arsénico en el sedimento en embalses del estado de Chihuahua, México (Assessment of the contamination by heavy metals and arsenic in reservoir sediments from Chihuahua, Mexico). *Rev Latinoam Recursos Nat* 2008;8:89–94.
- Hidrodesarrollo SA de CV. Primer Informe de Avance del proyecto “Diagnostico de la calidad de aguas subterráneas, modelo de flujo y evaluación del riesgo a la contaminación, en tres zonas prioritarias: A) Zapotitan–Opico, B) Subcuenca Río Apanchacal (Santa Ana), y C) Subcuenca Río Grande de de San Miguel (Acuífero San Miguel). San Salvador, El Salvador. Report presented to Ministerio del Medio Ambiente y Recursos Naturales de El Salvador, Contrato MARN-BID120G-OC-ES No. 03/2008; 2008.
- Hindmarsh JT, Dekerkhove D, Grime G, Powell JO. Hair arsenic as an index of toxicity. In: Chappell WR, Abernathy CO, Calderon RL, editors. Arsenic exposure and health effects. 1st ed. Oxford, UK: Elsevier; 1999.
- Hopenhayn-Rich C, Biggs ML, Fuchs A, Bergoglio R, Tello EE, Nicolli H, et al. Bladder cancer mortality associated with arsenic in drinking water in Argentina. *Epidemiology* 1996;7(2):117–24.
- Hopenhayn-Rich C, Biggs ML, Smith AH. Lung and kidney cancer mortality associated with arsenic in drinking water in Cordoba, Argentina. *Int J Epidemiol* 1998;27(4):561–9.
- Hopenhayn-Rich C, Browning SR, Hertz-Picciotto I, Ferreccio C, Peralta C, Gibb H. Chronic arsenic exposure and risk of infant mortality in two areas of Chile. *Environ Health Persp* 2000;108(7):667–73.
- Hudson-Edwards KA, Macklin MG, Miller JR, Lechler PJ. Sources, distribution and storage of heavy metals in the Río Pilcomayo, Bolivia. *J Geochem Explor* 2001;72: 229–50.
- Hurtado-Jiménez R, Gardea-Torresdey J. Contamination of drinking water supply with geothermal arsenic. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB, editors. Natural arsenic in groundwater of Latin America. Leiden, The Netherlands: CRC Press/Balkema Publisher; 2009. p. 179–90.
- IAEA RLA/8/031. Proyecto regional de cooperación técnica. Manejo integrado y sostenible de aguas subterráneas. América Latina: Gestión sostenible del acuífero Raigón, Uruguay. Vienna, Austria: Technical report; 2004.
- IGAM. Relatório de monitoramento das águas superficiais na bacia do rio São Francisco, subbacia do rio das Velhas. Projeto Qualidade das Águas superficiais no Estado de Minas em 2004. Belo Horizonte, Brazil: Instituto Mineiro de Gestão das Águas; 2005.
- INAA. Informe de los resultados de muestreo de As en comunidades rurales del municipio de San Isidro. Managua, Nicaragua: Instituto Nicaragüense de Acueductos y Alcantarillados; 1996.
- INAA. Normas Técnicas para el Diseño de Abastecimiento y Potabilización del Agua (NTON 09003–99). Managua, Nicaragua: Instituto Nicaragüense de Acueductos y Alcantarillados; 2001.
- INEN (Instituto Ecuatoriano de Normalización). Norma 1108: Sobre requisitos del agua potable. Registro Oficial N° 231, 17 de marzo, Quito, Ecuador; 2006.
- Infante Fernández LM, Sosa Palomino SJ. Cuantificación espectrofotométrica de arsénico en aguas de consumo humano en la vertiente del río Rimac. Lima, Peru: Lic. Thesis, School of Pharmacy and Biochemistry, UNMSM; 1994.
- ITA. Muestreo de aguas, suelos, vegetales, sangre humana y animales, peces y sedimentos en puntos seleccionados en la Cuenca del Río Pilcomayo en Chuquisaca. Sucre, Chuquisaca department, Bolivia. Final report, Fundación Instituto de Tecnología de Alimentos I.T.A. Universidad Mayor Real y Pontificia de San Francisco Xavier de Chuquisaca; 2006.
- Janik CJ, Truesdell AH, Goff F, Shevenell L, Stallard ML, Trujillo PE, et al. A geochemical model of the Platanares geothermal system, Honduras. *J Volcanol Geotherm Res* 1991;45:125–46.
- Jara-Marini ME, García-Rico L. Distribution of arsenic in three geochemical fractions of surface sediments from coastal sites of Sonora, Gulf of California, Mexico. *Bull Environ Contam Toxicol* 2006;76:677–83.
- Jorge C, Venero J, Diaz J, Carpio E, Zúñiga P, Maúrtua D, et al. The Peruvian experience with water disinfection and decontamination using solar energy. In: Litter M, editor. Final results of the OAS/AE/141 project: research, development, validation and application of solar technologies for water potabilization in isolated rural zones

- of Latin America and the Caribbean. Buenos Aires, Argentina: Digital Grafic, La Plata, Chile; 2006. p. 307–34.
- Juárez Soto HS. Contaminación del Río Rímac por metales pesados efecto en la agricultura en el cono este de Lima metropolitana. Lima, Peru: Reporte final de investigación para Agropolis — Programa Internacional de becas de investigación en Agricultura Urbana. Maestría en Ciencias Ambientales, Universidad Nacional Agraria la Molina; 2006.
- Karcher S, Cáceres L, Jekel M, Contreras R. Arsenic removal from water supplies in northern Chile using ferric chloride coagulation. *J Chart Inst Water Environ Manag* 1999;13(3):164–9.
- Kirchmer CJ, Castro ML. Tratamiento para la remoción de arsénico en aguas con alto contenido de magnesio: Río Locumba, Perú. Bogotá, Colombia: ACODAL, Organo Oficial de la Asociación Colombiana de Acueductos y Alcantarillados, 89; 1979. p. 11–30.
- Klohn W. Boro y arsénico en aguas del norte de Chile. *Internat. Symp. on Hydrology of Volcanic Rocks*. Lanzarote, Spain; 1974. p. 579–92.
- Landrum JT, Bennett PC, Engel AS, Alsina MA, Pastén PA, Milliken K. Partitioning geochemistry of arsenic and antimony, El Tatio Geyser Field, Chile. *Appl Geochem* 2009;24:664–76.
- Lara F, Cornejo L, Yáñez J, Freer J, Mansilla H. Solar-light assisted arsenic removal from natural waters: the effect of iron and citrate concentrations. *J Chem Technol Biotechnol* 2006;81:1282–7.
- Leal-Ascencio MT, Gelover-Santiago S. Evaluación de acuíferos de la mesa del norte. *Proceedings V Congreso Internacional y XI Congreso Nacional de Ciencias Ambientales*; 2006. June 7; Oaxtepec, Morelos, Mexico.
- Lilja A, Linde G. Occurrence and distribution of heavy metals in three rivers on the Bolivian high plateau. Lund, Sweden: MSc Thesis, Department of Water Resources Engineering, Lund University, TVRL 2006;12: 2006
- Lillo J. Peligros geoquímicos: arsénico de origen natural en las aguas. Madrid, Spain: University Rey Juan Carlos; 2003.
- Lindbäck K, Sjölin AM. Arsenic in groundwater in the southwestern part of the Río Dulce alluvial cone, Santiago del Estero Province, Argentina. Stockholm, Sweden: MSc Thesis, Dept. of Land and Wat. Res. Eng., KTH, TRITA-LWREX-06-26; 2006.
- Litter ME, Morgada ME, Bundschuh J. Possible treatments for arsenic removal in Latin American waters for human consumption. *Environ Pollut* 2010a;158:1105–18.
- Litter MI, Sancha AM, Ingallinella AM, editors. *Tecnologías económicas para el abatimiento de arsénico en aguas*. Buenos Aires, Argentina: Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo; 2010b.
- Litter MI, Alarcón-Herrera MT, Arenas MJ, Armienta MA, Avilés M, Cáceres RE, et al. Small-scale and household methods to remove arsenic from water for drinking purposes in Latin America. *J Total Environ* 2012;429:106–21.
- López Cortés P. Diagnóstico hidrológico hidrogeológico de la subcuenca Antequera. Potosí, Bolivia: Universidad Autónoma Tomás Frías, Empresa Minera Sinchiwayra SRL; 2006.
- López D, Ramson L, Monterrosa J, Soriano T, Barahona J, Bundschuh J. Volcanic arsenic and boron pollution of Ilopango lake, El Salvador. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB, editors. *Natural arsenic in groundwater of Latin America*. Leiden, The Netherlands: CRC Press/Balkema Publisher; 2009. p. 129–43.
- López DL, Birkle P, Bundschuh J, Sracek O, Armienta MA, Cornejo L, et al. Arsenic in geothermal fluids of Latin America. *J Total Environ* 2012;429:56–74.
- López DL, Padron E, Magaña MI, Gómez L, Barrios LA, Pérez NM, et al. Structural control on thermal anomalies and diffuse surficial degassing at Berlín Geothermal Field, El Salvador. *Geother Resour Council Trans* 2004;28:477–83.
- Macklin MG, Payne I, Preston D, Sedwick C. Review of the Porco mine tailings dam burst and associated mining waste problems, Pilcomayo basin, Bolivia. Report to the UK Overseas Development Agency; 1996.
- Madiec H, Cepero E, Mozzionaccai D. Treatment of arsenic by filter coagulation: a South American advanced technology. *Water Supply* 2000;18(1):613–8.
- Mahlknecht J, Steinich B, Navarro de León I. Groundwater chemistry and mass transfers in the Independence aquifer, central Mexico, by using multivariate statistics and mass-balance models. *Environ Geol* 2004;45:781–95.
- Mahlknecht J, Horst A, Hernández-Limón G, Aravena R. Groundwater geochemistry of the Chihuahua City region in the Río Conchos Basin (Northern Mexico) and implications for water resources management. *Hydrol Processes* 2008;22:4736–51.
- Manganelli A, Gosso C, Gêrêquiz R, Fernández Turiel JL, García Vallés M, Gimeno D. Estudio preliminar del contenido de arsénico de las aguas subterráneas del suroeste de Uruguay. *Geogaceta* 2007;41:3–6.
- Manz M, Castro J. The environmental hazard caused by smelter slags from the Sta. Maria de la Paz mining district in Mexico. *Environ Pollut* 1997;98:7–13.
- Marshall G, Ferreccio C, Yuan Y, Bates MN, Steinmaus C, Selvin S, et al. Fifty-year study of lung and bladder cancer mortality in Chile related to arsenic in drinking water. *J Natl Cancer Inst* 2007;99(12):920–8.
- Martínez SE, Carrillo-Rivera JJ. Socio-economic constraints of groundwater in Capital La Rioja, Argentina. *Environ Geol* 2006;49:875–86.
- Martínez P, García M. Distribución de iones mayores y metales en el agua subterránea de la subcuenca del Río Turbio, estados de Guanajuato y Jalisco. *Rev Geocienc* 2007;1:37–54.
- Massahud RTR. Avaliação de risco a arsênio, chumbo e cádmio na região aurífera Delita, Cuba. PhD Thesis. Lavras, Minas Gerais, Brazil: Universidade Federal de Lavras; 2008.
- Matschullat J, Perobelli Borba R, Deschamps E, Ribeiro Figueiredo B, Gabrio T, Schwenk M. Human and environmental contamination in the Iron Quadrangle, Brazil. *Appl Geochem* 2000;15:181–90.
- Matschullat J, Birmann K, Borba RP, Ciminelli V, Deschamps EM, Figueiredo BR, et al. Long-term environmental impact of arsenic-dispersion in Minas Gerais, Brazil. Trace metals and other contaminants in the environment, Volume 9. Elsevier; 2007. p. 355–72.
- Matta MB, McKinnie D, Barraza E, Sericano J. Hurricane Mitch — reconstruction/Gulf of Fonseca contaminant survey and assessment. Seattle: Office of Response and Restoration, NOAA Ocean Service; 2002.
- Matteoda E, Blarasin M, Damilano G, Cabrera A. Valores característicos del fondo natural de flúor y arsénico en aguas subterráneas en la cuenca del arroyo El Barreal, Córdoba. In: Galindo G, Nicolli H, editors. *El Taller sobre arsénico en aguas: hacia una integración de las investigaciones*. III Seminario Hispano-Latinoamericano sobre Temas Actuales de Hidrología Subterránea and V Congreso Hidrogeológico Argentino. Paraná: Universidad Nacional de Entre Ríos, Facultad de Ciencias Agropecuarias; 2007. p. 31–42.
- Mazo-Gray V, Sbriz L, Alvarez M. Determination of traces of heavy metals in estuarine waters of Barbaças Bay, Colombia, by X-ray fluorescence spectrometry. *X-Ray Spectrom* 1997;26:57–64.
- McClintock TR, Chen Y, Bundschuh J, Oliver JT, Navoni J, Olmos V, et al. Arsenic exposure in Latin America: Biomarkers, risk assessments and related health effects. *J Total Environ* 2012;429:75–90.
- McCutcheon M., 1998. Anthropogenic and volcanic pollution at Coatepeque Lake, El Salvador. Ohio: BSc Thesis, Ohio University; 2002.
- Medina ML, Merino LA, Miranda O, Gorodner JO. Hidroarsenicismo Crónico Regional Endémico (H.A.C.R.E.) y patologías gingivoperiodontales en pobladores del Chaco (Argentina). *Web Odontológica*; 2004. <http://webodontologica.com/index.asp> (accessed September 2010).
- Medus M, Mariño E, Schulz C. Variación temporal de los contenidos de arsénico en la batería de pozos que abastece a General Pico, La Pampa, Argentina. In: Galindo G, Fernández Turiel JL, Parada MA, Gimeno Torrente D, editors. *Arsénico en aguas: origen, movilidad y tratamiento*. IV Cong. Hidrogeológico Argentino, Río Cuarto, Argentina; 2005. p. 73–82.
- Mejía JA, Rodríguez R, Armienta, Mata E, Fiorucci A. Acuífer vulnerability zoning, an indicator of atmospheric pollutants input? Vanadium in the Salamanca aquifer, Mexico. *Water Air Soil Pollut* 2007;185:95–100.
- Mella U. Caracterización química de las patinas negras presentes en el casco y mascarilla de las momias rojas de la cultura Chinchorro. Arica, Chile: Thesis, Universidad de Tarapacá; 2007.
- Mellano MF, Ramirez AE. Groundwater arsenic in the area around Maria Elena in Santiago del Estero Province, Northwestern Argentina. Stockholm, Sweden: Department of Land and Water Resources Engineering KTH, TRITA-LWR1336 EX-04-40; 2004.
- MEM-DGAA. Evaluación ambiental territorial de la cuenca del Río Rímac. Lima, Peru: Ministerio de Energía y Minas; 1997 (Dirección General de Asuntos Ambientales).
- Méndez W. Contaminación de Rímac River basin, Peru, due to mining tailings. Stockholm, Sweden: MSc Thesis, Dept. of Land and Wat. Res. Eng., KTH, TRITA-LWR-EX-05-23; 2005.
- Méndez M, Armienta MA. Arsenic phase distribution in Zimapán Mine Tailings, Mexico. *Geofísica Int* 2003;42:131–40.
- Mendoza Amézquita E, Armienta MA, Ayora C, Soler A, Ramos-Ramírez E. Potencial lixiviación de Elementos Traza en Jales de la Mina “La Asunción” y Jales de la Mina “Las Torres”, en el Distrito Minero de Guanajuato, México. *Rev Mex Cienc Geol* 2006;23:75–83.
- Milkus B. Hydrodynamic and geochemical modelling of arsenic in the shallow aquifer of the Bolivian Altiplano. Stockholm, Sweden: MSc Thesis, Department of Land and Water Resources Engineering, Royal Institute of Technology (KTH), TRITS LWR-EX-08-11; 2008.
- Miller JR, Hudson-Edwards KA, Lechler PJ, Preston D, Macklin MG. Heavy metal contamination of water, soil and produce within riverine communities of the Río Pilcomayo basin, Bolivia. *Sci Total Environ* 2004;320:189–209.
- Ministerio de Salud. Epidemiología del hidroarsenicismo crónico regional endémico de la Argentina: Estudio colaborativo multicéntrico. Buenos Aires, Argentina: Ministerio de Salud; 2005 http://www.ambiente.gov.ar/archivos/web/UniDA/File/libro_hidroarsenicismo_completo.pdf (accessed June 2009).
- MMDEC. The study on evaluation of environmental impact of mining sector in Potosí Prefecture of the Republic of Bolivia. Mitsui Mineral Development Engineering Co.Ltd. and Unico International Corporation Final Report; 1999.
- Molerio LL. Factores de control y variabilidad de la contaminación por arsénico en las aguas terrestres de la mina Delita y su área de influencia. Havana, Cuba: Report, Institute of Geophysics and Astronomy; 2002.
- Molina MA. Estudio hidrogeoquímico en la Comarca Lagunera, México. Mexico City: MSc Thesis, Posgrado en Ciencias de la Tierra, National Autonomous University of Mexico, UNAM; 2004.
- Monterrosa AJ. Estudio sobre la contaminación del Río Lempa y sus afluentes en El Salvador. Consulting Report presented to El Salvador Government. Project “Concientización y educación ambiental integral en el ámbito local y cuencas seleccionadas en El Salvador”, PROCEDAM06. PRRAC/S/SE/01/032. Convenio de financiación Comunidad Europea No ACR/B7-3130/IB/99/0302; 2003.
- Montes de Oca I. Geografía y Recursos Naturales de Bolivia. EDOBOL, 3rd ed. La Paz, Bolivia; 1997.
- Naranjo-Pulido A, Romero-Schmidt H, Mendez-Rodríguez L, Acosta-Vargas B, Ortega-Rubio A. Soil arsenic contamination in the Cape Region, B.C.S., Mexico. *J Environ Biol* 2002;23(4):347–52.
- Nicolli HB, Suriano JM, Gómez Peral MA, Ferpozzi LH, Baleani OM: groundwater contamination with arsenic and other trace elements in an area of the Pampa, Province of Córdoba, Argentina. *Environ Geol Water Sci* 1989;14(1): 3–16.
- Nicolli HB, O'Connor TE, Suriano JM, Koukharsky ML, Gómez-Peral MA, Bertini LM, et al. Geoquímica del arsénico y de otros oligoelementos en aguas subterráneas de la llanura sudoriental de la Provincia de Córdoba. *Miscelánea* 1985;71:1–112. (Academia Nacional de Ciencias, Córdoba).

- Nicolli HB, Tineo A, García JW, Falcón CM, Merino MH. Trace-element quality problems in groundwater from Tucumán, Argentina. In: Cidu R, editor. Water–rock interaction 2. Balkema, Lisse; The Netherlands; 2001a. p. 993–6.
- Nicolli HB, Tineo A, Falcón CM, Merino MH. Movilidad del arsénico y de otros oligoelementos asociados en aguas subterráneas de la cuenca de Burruyacú, provincia de Tucumán, República Argentina. In: Medina A, Carrera J, Vives L, editores. Congreso Las Caras del Agua Subterránea I. Instituto Geológico y Minero de España, Madrid; Spain; 2001b. p. 27–33.
- Nicolli HB, Tineo A, García JW, Falcón CM, Merino MH, Etchichury MC, et al. The role of loess in groundwater pollution at Salí River basin, Argentina. In: Wany RB, Seals II RR, editors. Water–rock interaction 2. Leiden: Balkema; 2004. p. 1591–5.
- Nicolli HB, Tineo A, Falcón CM, García JW, Merino MH, Etchichury MC, et al. Arsenic hydrogeochemistry in groundwater from the Burruyacú basin, Tucumán province, Argentina. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB, editors. Natural arsenic in groundwater of Latin America. Leiden, The Netherlands: CRC Press/Balkema Publisher; 2009a. p. 47–59.
- Nicolli HB, Tujchneider OC, Paris M del C, Blanco M del C, Barros AJ. Movilidad del arsénico y oligoelementos asociados en aguas subterráneas del centro-norte de la provincia de Santa Fe, Argentina. In: Galindo G, Fernández Turiel J, Storniolo A, editores. Presencia de flúor y arsénico en aguas subterráneas, VI Cong. Hidrogeológico Argentino, Santa Rosa, La Pampa, Argentina; 2009b. p. 81–90.
- Nicolli HB, Bundschuh J, García JW, Falcón CM, Jean J-S. Sources and controls for the mobility of arsenic in oxidizing groundwaters from loess-type sediments in arid/semi-arid dry climates – evidence from the Chaco–Pampean plain (Argentina). *Water Res* 2010;44(19):5589–604.
- Nicolli HB, Bundschuh J, Blanco MdC, Panarello HO, Dapeña C, Jean J-S. Arsenic and associated trace elements in groundwater from the Chaco-Pampean plain, Argentina: Results from 100 years of research. *J Total Environ* 2012;429:36–55.
- Nordstrom DK, Alpers CN. Geochemistry of acid mine waters. In: Plumlee GS, Logsdon MJ, editors. The environmental geochemistry of mineral deposits, part a: processes, methods and health issues. Reviews in Economic Geology/Littleton, CO: Soc. Econ. Geol.; 1999. p. 133–60.
- Nordstrom DK, Southam G. Geomicrobiology of sulfide mineral oxidation. Chap. 11. In: Banfield JF, Nealson KH, editors. Interactions between microbes and minerals. Reviews in mineralogy/Washington, DC: Min. Soc. Am.; 1997. p. 361–90.
- Ongley LK, Sherman L, Armienta A, Concilio A, Ferguson-Salinas C. Arsenic in the soils of Zimapán, Mexico. *Environ Pollut* 2007;145:793–9.
- Ono FB, Guilherme LRG, Penido ES, Carvalho GS, Hale B. Bioaccessibility of arsenic in a gold mining area in Brazil In: 15th International Conference on Heavy Metals in the Environment, 2010, Gdansk. Proceedings of 15th International Conference on Heavy Metals in the Environment (ICHMET). Gdansk: Department of Analytical Chemistry - Gdansk University of Technology, 2010. p.1014–1014.
- Ormachea M, Blanco E, Ramos O, García ME, Bhattacharya P, Thunvik R, et al. Arsenic occurrence in thermal springs of the Central Bolivian Altiplano. In: Jean J-S, Bundschuh J, Bhattacharya P, editors. Arsenic in geosphere and human diseases. Proceedings AS 2010 3rd International Congress Arsenic in the Environment. Leiden, The Netherlands: Balkema/CRC Press; 2010. p. 520–2.. 2010 May 17–21; Tainan, Taiwan.
- Ortega-Guerrero A. Origin and geochemical evolution of groundwater in a closed-basin clayey aquifer, Northern Mexico. *J Hydrol* 2003;284:26–44.
- Ortega-Guerrero MA. Presencia, distribución, hidrogeoquímica y origen de arsénico, fluoruro y otros elementos traza disueltos en agua subterránea, a escala de cuenca hidrológica tributaria de Lerma–Chapala, México. *Rev Mex Cienc Geol* 2009;26(1):143–61.
- Osicka RM, Agulló NS, Herrera Aguad CE, Jiménez MC. Evaluación de las concentraciones de fluoruro y arsénico en las aguas subterráneas del Domo Central de la Prov. del Chaco. Ciencia y Técnica, Comunicaciones Científicas y Tecnológicas. Corrientes, Argentina: Universidad Nacional del Noroeste; 2002 <http://www.unne.edu.ar/Web/cyt/cyt/2002/cyt.htm> (accessed 2007).
- Oyarzun R, Lillo J, Higuera P, Oyarzú J, Maturana H. Strong arsenic enrichment in sediments from the Elqui watershed, Northern Chile: industrial (gold mining at El Indio–Tambo district) vs. geologic processes. *J Geochem Explor* 2004;84:53–64.
- PAHO/WHO/UNICEF. Evaluación rápida de la calidad del agua de bebida Nicaragua. Informe Final, Managua, Nicaragua; 2005. www.bvsde.paho.org (accessed September 2010).
- Pantuzzo FL, Ciminelli VST. Arsenic association and stability in long-term disposed arsenic residues. *Water Res* 2010;44(19):5631–40.
- Parra C. Caracterización química de arcillas utilizadas en la momificación en la cultura Chinchorro. Arica, Chile: Thesis, Universidad de Tarapacá; 2007.
- Pérez Carrera A, Fernández Cirelli A. Niveles de arsénico y flúor en agua de bebida animal en establecimientos de producción lechera (Bell Ville, Pcia de Córdoba). *Rev Invest Vet (INVET)* 2004;6(1):51–9.
- Pérez Carrera A, Fernández Cirelli A. Problemática del arsénico en la llanura sudeste de la provincia de Córdoba: Biotransferencia a leche bovina. *In Vet* 2007;9(1):123–35.
- Pérez Carrera A, Salomón M, Abraham E, Fernández Cirelli A. Calidad de agua en sistemas de cría de cabras en el Departamento de Lavalle, provincia de Mendoza. *Rev Arg de Prod Anim* 2008;28(1):1–112.
- Perez Vargas MR. Contaminación del sedimento de presas del municipio de Chihuahua. Chihuahua, Chih., Mexico: Bachelor Thesis, Facultad de Zootecnia y Ecología, Universidad Autónoma de Chihuahua; 2010.
- Pérez NM, Salazar JML, Hernández PA, Olmos R, Barahona F, Cartagena R, et al. Diffuse CO₂ and ²²²Rn degassing from San Salvador volcano, El Salvador, Central America. In: Rose WI, Bommer JJ, López DL, Carr MJ, Major JJ, editors. Natural hazards in El Salvador, 375. Geological Society of America Special Paper; 2004. p. 227–36.
- PIDMA-UNI. Calidad del agua en 20 pozos del triángulo La Cruz de la India, Darío y San Isidro, Nicaragua, con énfasis en la presencia de Arsénico, Managua Nicaragua: Programa de Investigación y Docencia en Medio Ambiente (PIDMA) and Universidad de Ingeniería (UNI); 2001.
- PIDMA-UNI, UNICEF. Evaluación rápida de la contaminación por Arsénico y metales pesados de las aguas subterráneas de Nicaragua. Managua, Nicaragua: Programa de Investigación y Docencia en Medio Ambiente (PIDMA), Universidad de Ingeniería (UNI) and UNICEF; 2002.
- PIDMA-UNI-USAID. Calidad físico-química del agua para consumo humano de 124 pozos en la región noroccidental de Nicaragua con énfasis en la presencia de Arsénico. Managua, Nicaragua: Programa de Investigación y Docencia en Medio Ambiente (PIDMA), Universidad de Ingeniería (UNI) and Proyecto de Salud Ambiental (EHP) de la USAID; 2001.
- Pizarro G, Balabanoff L. Estudio de eliminación del arsénico en el agua de Antofagasta. *Bol Soc Chil Quím* 1973;12:1–8.
- Planer-Friedrich B, Armienta MA, Merkel BJ. Origin of arsenic in the groundwater of the Rioverde basin, Mexico. *Environ Geol* 2001;40:1290–8.
- PPO. Ministerio de Desarrollo Sostenible y Medio Ambiente Secretaría Nacional de Minería & Swedish Geological AB; Proyecto Piloto Oruro – Mineral Waste Deposits in the Poopó Area, La Paz, Bolivia; 1996a.
- PPO. Impacto de la minera y el procesamiento de minerales en cursos de aguas y lagos. Proyecto Piloto Oruro, R-BO-E-9.45-9703-PPO 9612, La Paz, Bolivia; 1996b.
- PPO. Impacto de la contaminación minera en industrial sobre aguas subterráneas. Proyecto Piloto Oruro, R-BO-E-9.45-9702-PPO 9616, La Paz, Bolivia; 1996c.
- PPO. Ministerio de Desarrollo Sostenible y Medio Ambiente & Swedish Geological AB, Proyecto Piloto Oruro – Final report: findings, recommendations and the environmental management plan. PPO-9701 La Paz, Bolivia; 1997.
- Prieto GR, Gonzalez ML. Diagnosis of environmental problems related to vein gold mining in Colombia. *Environmental Geochemistry in the Tropics. Lect Notes Earth Sci* 1998;72:185–91.
- PRODEMINCA. Monitoreo Ambiental de las Áreas Mineras del Sur del Ecuador, MEM. Quito, Ecuador: Subsecretaría de Minas; 1998.
- PSAG. Proyecto para la protección ambiental y el desarrollo sostenible del sistema acuífero Guarani. <http://www.sg-guarani.org>. (accessed August 2010).
- Puga F, Olivos P, Greyber R, González I, Heras E, Barrera S, et al. Hidroarsenicismo crónico: Intoxicación arsenical crónica en Antofagasta: Estudio epidemiológico y clínico. *Rev Chil Pediatr* 1973;44(3):215–23.
- Quevillon M, Gibb C, Dogterom J. The Río Pilcomayo: an assessment of metal contamination in the fish *Prochilodus platensis* (sábalo), a primary food staple of the Guarani, Itika, Guasu. Kingston, Ontario, Canada: Report to the Queen's Project on International Development (QPID), Centro de Estudios Regionales para el Desarrollo de Tarija (CER-DET) and Fondo de Intercambio Ambiental (FIA); 1996.
- Quino Lima I. Determinación de la calidad físico-química de las aguas subterráneas en la región norte y este del lago Poopó. La Paz, Bolivia: Lic. Thesis, Universidad Mayor de San Andrés; 2006.
- Quintanilla J, Ramos O, Ormachea M, García ME, Medina H, Thunvik R, et al. Arsenic contamination, speciation and environmental consequences in the Bolivian plateau. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB, editors. Natural arsenic in groundwater of Latin America. Leiden, The Netherlands: CRC Press/Balkema Publisher; 2009. p. 91–9.
- Quinto A, Santoyo E, Torres V, González E, Castillo D. Estudio geoquímico-ambiental de los efluentes naturales producidos en la zona geotérmica de Acoculco, Puebla. *Hydraul Eng México* 1995;X:21–7.
- Ramos-Arroyo YR, Siebe C. Weathering of sulphide minerals and trace element speciation in tailings of various ages in the Guanajuato mining district, Mexico. *CATENA* 2007;71:497–506.
- Ransom L. Volcanic diffuse soil degassing and lake chemistry of the Ilopango Caldera system, El Salvador, Central America. Athens (OH): MSc Thesis, Ohio University; 2002.
- Raymond J, Williams-Jones AE, Clark JR. Mineralization associated with scale and altered rock and pipe fragments from the Berlin geothermal field, El Salvador; implications for metal transport in natural systems. *J Volcanol Geotherm Res* 2005;145:81–96.
- Razo I, Carrizales L, Castro J, Díaz-Barriga F, Monroy M. Arsenic and heavy metal pollution of soil, water and sediments in a semi-arid climate mining area in Mexico. *Water Air Soil Pollut* 2004a;152:129–52.
- Razo I, Téllez J, Monroy M, Carrizales L, Díaz-Barriga F, Castro J. As and Pb bioaccessibility in polluted soils from a mining site under semiarid climate in Mexico. *Proceedings Tailings and Mine Waste'04*. London: Taylor & Francis Group; 2004b. p. 173–82.
- Reichert F, Trelles R. Yodo y arsénico en las aguas subterráneas. *Anal Asoc Quim Argent* 1921;9:89–95.
- Reyes-Cortés IA, Vázquez-Balderas JF, Ledesma-Ruiz R. As en el sistema hidrogeológico del valle de Delicias, Chihuahua, Mexico. *Geos* 2006;26:40.
- Rivadeneira M, Santoro C, Marquet P. Reconstructing the history of human impacts on coastal biodiversity in Chile: constraints and opportunities. *Aquatic Conserv: Mar Freshw Ecosyst* 2010;20:74–82.
- Rivara M, Cebrían M, Corey G, Hernandez M, Romieu I. Cancer risk in an arsenic contaminated area of Chile. *Toxicol Ind Health* 1997;13(2–3):321–38.
- Robles JA, Morillo S. Mortalidad por enfermedad cerebrovascular en la Isla de la Juventud, período 1990–2000. Cuba: Informe de Salud; 2001.
- Rocha-Amador D, Navarro ME, Carrizales L, Morales R, Calderon J. Decreased intelligence in children and exposure to fluoride and arsenic in drinking water. *Cad Saude Publica* 2007;23(Suppl 4):S579–87.
- Rodríguez de Sastre MS, Salmoral G, Varillas A, Courtade T, Aguilera N. Estudio Cuantitativo de Arsénico en Aguas de la Provincia de Salta, Argentina: Final Technical Internal Report, Research Council, Universidad Nacional de Salta; 1993.
- Rodríguez R, Armienta MA, Mejía Gómez JA. Arsenic contamination of the Salamanca aquifer system in Mexico: a risk analysis. In: Bundschuh J, Bhattacharya P, Chandrasekharan D, editors. Natural arsenic in groundwater: occurrence, remediation and management. London: Taylor & Francis Group; 2005. p. 77–83.

- Rodríguez R, Armienta A, Morales P, Silva T, Hernández H. Evaluación de vulnerabilidad acuifera del valle de Irapuato Gto. JAPAMI, CONCYTEG, IGF UNAM. Technical report il; 2006.
- Romero L, Alonso H, Campano P, Fanfani L, Cidu R, Dadea C, et al. Arsenic enrichment in waters and sediments of the Rio Loa (Second Region, Chile). *Appl Geochem* 2003;18:1399–416.
- Romero FM, Armienta MA, Villaseñor G, González JL. Mineralogical constraints on the mobility of arsenic in tailings from Zimapán, Hidalgo, Mexico. *Int J Environ Pollut* 2006;26:23–40.
- Romero FM, Armienta MA, Gutiérrez ME, Villaseñor G. Factores geológicos y climáticos que determinan la peligrosidad y el impacto ambiental de jales mineros. *Reva Int Contam Ambiental* 2008;24:43–54.
- Romero FM, Prol-Ledesma RM, Canet C, Núñez Alvares L, Pérez-Vázquez R. Acid drainage at the inactive Santa Lucía mine, western Cuba: natural attenuation of arsenic, barium and lead, and geochemical behavior of rare earth elements. *Appl Geochem* 2010;25:716–27.
- Rosas I, Belmont R, Armienta A, Baez A. Arsenic concentrations in water, soil, milk and forage in Comarca Lagunera, Mexico. *Water Air Soil Pollut* 1999;112:133–49.
- Rosenberg M, Ståhlhammar K. Evaluation of heavy metals in waters influenced by mining in the Poopó and Antequera river basins, Oruro–Bolivia. Lund, Sweden: MSc Thesis, Environmental Technology Lund University, Division of Water Resources Engineering, TVVR-10/5001; 2010.
- Sancha AM. Removing arsenic from drinking water: a brief review of some lessons learned and gaps arisen in Chilean water utilities. In: Chappell WR, Abernathy CO, Calderon RL, Thomas DJ, editors. Arsenic exposure and health effects. Amsterdam, The Netherlands: Elsevier; 2003. p. 471–81.
- Sancha AM, Castro de Esparza ML. Arsenic status and handling in Latin America. Lima, Peru: AIDIS/DIAGUA, CEPIS/OPS; 2000.
- Sancha AM, Frenz P. Estimate of the current exposure of the urban population of northern Chile to arsenic. Interdisciplinary perspectives on drinking water risk assessment and management, 260. IAHS Publ.; 2000. p. 3–8.
- Sancha AM, O’Ryan R, Pérez O. The removal of arsenic from drinking water and associated costs: the Chilean case. Interdisciplinary Perspectives on Drinking Water Risk Assessment and Management, 260. IAHS Publ.; 2000. p. 17–25.
- Sandali G, Diez E. Determinación del contenido de arsénico en agua de consumo humano en la provincia del Chubut. *Acta Toxicol Argent* 2004(Supl. 12):1–46.
- Schiappacasse V, Niemeyer H. Descripción y análisis interpretativo de un sitio arcaico temprano en la Quebrada de Camarones. Santiago de Chile: Publicación Ocasional N° 41 Museo Nacional de Historia Natural; 1984.
- SEDAPAL. Memoria Anual 2004. Lima, Peru: Servicio de Agua Potable y Alcantarillado de Lima; 2004.
- Selander L, Svan P. Occurrence and distribution of heavy in lake Poopó, Bolivia. Lund, Sweden: MSc Thesis, Department of Chemical and Water Resources Engineering, Lund University, TWR 07/5010; 2007.
- SenGupta, AK, Cumbal, LH, US Patent Appl. 156136 (07/21/05), 2005.
- SERGEOMIN. Inventariación de recursos naturales renovables (hídricos) y no renovables (minerales e hidrocarburos) del departamento de Oruro. *Bol Serv Nac Geol Min* 1999;24.
- Shumilin E, Paez-Osuna F, Green-Ruiz C, Sapochnikov D, Rodríguez-Meza GD, Godínez-Orta L. Arsenic, antimony, selenium and other trace elements in sediments of the La Paz lagoon, Peninsula of Baja California Mexico. *Mar Pollut Bull* 2001;42:174–8.
- Sigg L, Stumm W. The interaction of anions and weak acids with the hydrous goethite (α -FeOOH) surface. *Colloids Surf* 1981;2:101–17.
- Sigrist M, Beldoménno H, Repetti MR. Evaluation of the influence of arsenic levels in cow’s raw milk from Argentinean dairy farms. *Food Chem* 2010;121:487–91.
- Siveroni M. Eliminación de arsénico del Río Locumba, para uso doméstico e industrial de la ciudad de Locumba. Proceedings IV Congreso de Ingeniería Sanitaria y Ambiental; 1989. Lima, Peru.
- Smedley PL, Kinniburgh DG. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl Geochem* 2002;17:517–68.
- Smedley PL, Nicolli HB, Macdonald DMJ, Barros AJ, Tullio JO. Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina. *Appl Geochem* 2002;17(3):259–84.
- Smedley PL, Kinniburgh DG, Macdonald DMJ, Nicolli HB, Barros AJ, Tullio JO. Arsenic associations in sediments from the loess aquifer of La Pampa, Argentina. *Appl Geochem* 2005;20:989–1016.
- Smith AH, Goycolea M, Haque R, Biggs ML. Marked increase in bladder and lung cancer mortality in a region of Northern Chile due to arsenic in drinking water. *Am J Epidemiol* 1998;147(7):660–9.
- Smith AH, Arroyo AP, Mazumder DNG, Kosnett MJ, Hernandez AL, Beeris M, et al. Arsenic-induced skin lesions among Atacameño people in northern Chile despite good nutrition and centuries of exposure. *Environ Health Persp* 2000;108(7):617–20.
- Smith AH, Marshall G, Yuan Y, Ferreccio C, Liaw J, von Ehrenstein O, et al. Increased mortality from lung cancer and bronchiectasis in young adults after exposure to arsenic in utero and in early childhood. *Environ Health Perspect* 2006;114(8):1293–6.
- Smolders A, Archer J, Stassen M, Llanos Cavero JC, Hudson-Edwards K. Concentraciones metálicas en cabellos de habitantes de las orillas de la cuenca baja del río Pilcomayo. *Rev Bol Ecol* 2006;19:13–22.
- Sraccok O, Armienta MA, Rodríguez R, Villaseñor G. Discrimination between diffuse and point sources of arsenic at Zimapán, Hidalgo state, Mexico. *J Environ Monit* 2010;12:329–37.
- Standen VG. El Cementerio Morro-1: Nuevas evidencias de la tradición funeraria Chinchorro (periodo Arcaico, norte de Chile). Lima, Peru: MCs Thesis, Pontificia Universidad Católica del Perú, 1991.
- Standen VG. Temprana complejidad funeraria de la Cultura Chinchorro (Norte de Chile). *Latin Am Antiquity* 1997;8(2):134–56.
- Stassen MJM, van de Ven MWPM. Calidad ambiental de la cuenca alta y media del río Pilcomayo 2005–2006. Villa Montes, Dep. Tarija, Bolivia and Nijmegen, The Netherlands: Fundación Los Amigos del Pilcomayo (LAMP) for the Proyecto de Gestión y Plan Maestro de la cuenca del río Pilcomayo; 2007.
- Steinmaus C, Yuan Y, Kalman D, Rey OA, Skibola CF, Dauphine D, et al. Individual differences in arsenic metabolism and lung cancer in a case–control study in Cordoba, Argentina. *Toxicol Appl Pharmacol* 2010;247(2):138–45.
- Suárez G, Pergó E. Estudios sobre contaminación en las aguas de la plataforma sur oriental de Cuba. *Rev Mar Pesca Havana* 1979;23:22–5.
- Talavera MO, Yta M, Moreno TR, Dótor AA, Flores MN, Duarte GC. Mineralogy and geochemistry of sulfide-bearing tailings from silver mines in the Taxco, Mexico area to evaluate their potential environmental impact. *Geofísica Int* 2005;44(1):49–64.
- Talavera MO, Armienta HMA, García AJ, Flores MN. Geochemistry of leachates from the El Fraile sulfide tailings piles in Taxco, Guerrero, southern Mexico. *Environ Geochem Health* 2006;28:243–55.
- Tello EE. Hidroarsenismo Crónico Regional Endémico (HACRE), sus manifestaciones clínicas. Córdoba, Argentina: Imprenta de la Universidad Nacional de Córdoba; 1951.
- Tello EE. Arsenicosis hídricas: Que es el hidroarsenismo crónico regional endémico argentino (HACREA)? *Arc Argent Dermat* 1986;4:197–214. XXXVI.
- Tello EE. Carcinomas of internal organs and their relationship to arsenical drinking water in the Republic of Argentina. *Med Cutan Ibero Lat Am* 1988;16:497–501.
- Toujague RT, Leonarte A, Reyes Verdecia BL, Miravet RM. Arsenio y metales pesados en aguas del área Delita, Isla de la Juventud. *Cienc Tierra Espacio Cuba* 2003;4:5–8.
- Toujague R, Pacheco P, Vera A, Ramirez RML, Acosta F, Jaimez E. Relatório final do projecto: Estimación preliminar del riesgo en la salud humana por exposición a arsénico y plomo en la Mina Delita y sus alrededores, Isla de la Juventud, Cuba. Havana, Cuba: Instituto de Geofísica e Astronomía; 2006a.
- Toujague R, et al. Estimación preliminar del riesgo en la salud humana por exposición a arsénico y plomo en la Mina Delita y sus alrededores, Isla de la Juventud. Informe Final del Proyecto. Instituto de Geofísica e Astronomía-IGA. Ministerio de Ciencia, Tecnología y Medio Ambiente de Cuba (CITMA); 2006b. 54 p.
- Trejo-Vázquez R, Bonilla-Petriciolet A. Cuantificación de arsénico en el agua subterránea de la ciudad de Aguascalientes, México, y evaluación de riesgos entre la población. *Rev Ingen Hidrául Méx* 2002;17:79–88.
- Trelles R, Larghi A, Paez JP. El problema sanitario de las aguas destinadas a la bebida humana, con contenidos elevados de arsénico, vanadio y flúor, 4. Buenos Aires, Argentina: Universidad de Buenos Aires, Facultad de Ingeniería, Instituto de Ingeniería Sanitaria, Publ.; 1970.
- TULAS (Texto Unificado de Legislación Ambiental Secundaria del Ecuador). Libro VI: Anexo I. Quito, Ecuador; 2003.
- Uhle M. Museo de Etnología y Antropología N° 14 y N°. Los Aborígenes de Arica, 15 Publicaciones del Museo de Etnología y Antropología; 1917. p. 151–76.
- Uhle M La. Arqueología de Arica y Tacna. *Bol Soc Ecuator Estudios Histó* Am 1919;3(7–8): 1–48.
- UNEP/OEA. Diagnostico ambiental del sistema hídrico del lago Titicaca, río Desaguadero, lago Poopó y Salar de Coipasa (TDPS) Bolivia–Perú. Washington DC: Departamento de Desarrollo Regional y Medio Ambiente. Secretaria General de la OEA; 1996.
- US Army Corp of Engineers Mobile District and Topographic Engineering Center. Water resources assessment of El Salvador. Report prepared by the Mobile District and Topographic Engineering Center; 1998.
- Vasconcelos O, Palmieri H, Matschullat J, Deschamps E. Arsenic in edible and bioaccumulating plants. In: Deschamps E, Matschullat J, editors. Arsenic: Natural and Anthropogenic. In: Bundschuh J, Bhattacharya P, editors. Arsenic in the Environment, Volume 4. Leiden, The Netherlands: CRC Press/Balkema Publisher; 2011. p. 141–51.
- Warren C. Hydrogeology and groundwater quality of Los Pereyres, Tucuman, Argentina. London, UK: MSc Thesis, University College London; 2001.
- WHO. Arsenic in drinking-water. Background document for preparation of WHO Guidelines for drinking-water quality. Geneva, Switzerland: World Health Organization; 2003 [WHO/SDE/WSH/03.04/75].
- Wilkinson M, Mohler RRJ. Colmatation of the Pilcomayo river as observed from space shuttle photography. *GSA Progr Abstr* 1995;27(6):116.
- Wyatt CJ, Fimbres C, Romo L, Méndez RO, Grijalva M. Incidence of heavy metal contamination in water supplies in Northern Mexico. *Environ Res A* 1998;76:114–9.
- Yan X, Kerrich R, Hendry M. Distribution of arsenic(III), arsenic(V) and total inorganic arsenic in pore-waters from a thick till and clay-rich aquitard sequence, Saskatchewan, Canada. *Geochim Cosmochim Acta* 2000;64:2637–48.
- Yáñez L, García-Nieto E, Rojas E, Carrizales L, Mejía J, Calderón J, et al. DNA damage in blood cells from children exposed to arsenic and lead in a mining area. *Environ Res* 2003;93:231–40.
- Yáñez J, Fierro V, Mansilla H, Figueroa L, Cornejo L, Barnes RM. Arsenic speciation in human hair: a new perspective for epidemiological assessment in chronic arsenicosis. *J Environ Monit* 2005;7:1335–41.
- Yuan Y, Marshall G, Ferreccio C, Steinmaus C, Selvin S, Liaw J, et al. Acute myocardial infarction mortality in comparison with lung and bladder cancer mortality in arsenic-exposed region II of Chile from 1950 to 2000. *Am J Epidemiol* 2007;166(12):1381–91.
- Yuan Y, Marshall G, Ferreccio C, Steinmaus C, Liaw J, Bates M, et al. Kidney cancer mortality: fifty-year latency patterns related to arsenic exposure. *Epidemiology* 2010;21(1):103–8.
- Zenitagoya Y, Torres R, Jorge C, Rodríguez J, Estrada W. Monitoreo de arsénico total en aguas superficiales y de consumo humano: Poblado de Yauli y humedales del lago Junín. Lima, Peru: Internal report UNI; 2004.