# Arsenic in Latin America: Part I

**Marta I. Litter, María A. Armienta, Ruth E. Villanueva Estrada, Edda C. Villaamil Lepori, and Valentina Olmos**

**Abstract** A complete analysis on the occurrence of arsenic (As) in aquifers and several superficial water bodies in Latin America, identified in 13 countries, is presented. The Chaco-Pampean plain in Argentina is the largest area affected by groundwater As contamination. Research on the chemical and hydrogeological processes of release and mobilization of As has also been developed in Mexico, Chile, Bolivia, Peru, and Nicaragua. In most of the contaminated areas, As originates from geogenic sources, mainly volcanic rocks, hydrothermal fluids, and As-bearing minerals. However, anthropogenic sources are also present in certain zones, most of them coming from mining operations and, in some cases, related to agriculture. Mining is indeed the main As source in Brazil. The physicochemical characteristics of the water, such as pH and Eh, and the presence of other ions influence the mobilization of As. Hydrogeological conditions also determine the occurrence of As contamination. It has been found that the element is in the As(V) form in most locations. In all Latin American countries, more research has still to be conducted to determine As concentrations and speciation in water bodies used as drinking water source, to unravel its origin and mobilization processes.

Regarding analytical methods on As determination, 167 papers in scientific journals have been identified in the last 18 years in Latin America. The most widely

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M. I. Litter (✉)
Gerencia Química, Comisión Nacional de Energía Atómica-CONICET,
San Martín, Prov. de Buenos Aires, Argentina

Instituto de Investigación e Ingeniería Ambiental, Universidad Nacional de General San Martín, Campus Miguelete, San Martín, Prov. de Buenos Aires, Argentina

M. A. Armienta
Universidad Nacional Autónoma de México, Instituto de Geofísica, Circuito Exterior,
CU, Ciudad de México, México

R. E. Villanueva Estrada
Instituto de Geofísica, Unidad Michoacán, Universidad Nacional Autónoma de México,
Campus-Morelia, Morelia, Michoacán, México

E. C. Villaamil Lepori · V. Olmos
Facultad de Farmacia y Bioquímica, Cátedra de Toxicología y Química Legal, Universidad de Buenos Aires, Buenos Aires, Argentina

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analytical methodologies used for As determination are AAS (57%), specifically HG-AAS, and ICP (26%), mainly coupled with MS. Electrochemical methods have been applied in Chile, Brazil, and Argentina. UV-VIS spectrometry has been used mainly in Cuba and Mexico. XRF spectrometry, principally for solid samples, has been used in Mexico, Cuba, Brazil, Argentina, and Chile. Other used methodologies are INAA, the ARSOlux Biosensor and the SPRN technique.

**Keywords** Argentina · Arsenic · Brazil · Chile · HG-AAS · XRF spectrometry

## Abbreviations

| | |
|---|---|
| AAS | Atomic absorption spectrometry |
| AE | Anion exchange |
| AEC | Anion exchange chromatography |
| AES | Atomic emission spectrometry |
| AFS | Atomic fluorescence spectrometry |
| AS-SWV | Anodic stripping square-wave voltammetry |
| ASV | Anodic stripping voltammetry |
| ASV-(CAR-CPE) | Adsorptive stripping voltammetric carrageenan modified carbon paste electrode |
| BDES | Bi-directional electrostacking system |
| CPE | Cloud point extraction |
| CSV | Cathodic stripping voltammetry |
| CT | Cryotrapping gas |
| DPP | Differential pulse polarography |
| EcHG | Electrochemical hydride generation |
| ETAAS | Electrothermal atomic absorption spectrometry |
| ETV | Electrothermal vaporizer |
| EVA | Ethyl vinyl acetate |
| FI | Flow injection |
| GC-PFPD | Gas chromatography with pulsed flame photometric detection |
| GFAAS | Graphite furnace atomic absorption spectrometry |
| GFH | Granular ferric hydroxide |
| HG | Hydride generation |
| HPLC | High pressure liquid chromatography |
| HR-CS | High-resolution continuum source |
| HS-SPME | Headspace solid-phase micro-extraction |
| IC | Ionic chromatography |
| ICPAES | Inductively coupled plasma atomic emission spectroscopy |
| ICPMS | Inductively coupled plasma mass spectrometry |
| ICPOES | Inductively coupled plasma optical emission spectrometry |
| INAA | Instrumental neutron activation analysis |

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|---|---|
| IXED | Ion exchange/electrodialysis |
| LA | Laser ablation |
| LC | Liquid chromatography |
| MP | Microwave plasma |
| MS | Mass spectrometry |
| MSFIA | Multisyringe flow injection analysis |
| PA-NCu | Copper nanoparticles supported in polyamide pellets |
| SIA | Sequential injection analysis |
| SPE | Solid phase extraction |
| SPRN | Surface plasmon resonance nanosensor |
| SWCSV | Square wave cathodic stripping voltammetry |
| UV | Ultraviolet |
| XRFS | X-ray fluorescence spectrometry |

## 1 Situation of Arsenic in Latin America

The problem of arsenic (As) in drinking water is today very well-known due to the consequences on health all over the world. Arsenic (As) is a natural metalloid abundantly present in the earth's crust.[1] It is one of the most toxic pollutants, present mainly in groundwater by the release of As to soils and aquifers due to natural processes such as volcanic phenomena and rock disintegration, and it can be detected in a wide range of concentrations. Human activities such as industrial processes, metal smelting, pesticide production, and wood preservation increase the contamination of soils and aquifers. The exposure of humans to the element occurs through the consumption of contaminated water and food (International Agency for Research on Cancer (IARC) 2012; Argos et al. 2011; Arsénico en agua, informe Grupo Ad-Hoc Arsénico en agua 2018; Murcott 2012; McCarty et al. 2011; Bundschuh et al. 2008, 2010, 2012; Bhattacharya et al. 2006; Smedley et al. 2009; Gomez et al. 2009; Alarcón-Herrera et al. 2013; Nicolli et al. 2009; Mukherjee et al. 2014; Blanes et al. 2011; Zabala et al. 2016; World Health Organization (WHO) 2011; Nicolli et al. 2010; Sigrist et al. 2013; Vázquez et al. 2014; Farias et al. 2016; World Health Organization & International Programme on Chemical Safety 1996; Ormachea Muñoz et al. 2014).

The presence of As in water is a worldwide problem with high impact in the poorest regions, with more than 226 million exposed people (Murcott 2012; McCarty et al. 2011). Its presence has been identified in waters of many areas of Latin America since the twentieth century. Health effects from chronic exposure to As-enriched drinking water were first reported in Bell Ville, Argentina, in 1913 (Bundschuh et al. 2010). Since then, and mainly since the 1960 decade, As

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[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.

occurrence in aquifers and surface water has been found in other parts of Argentina and also in other Latin American countries (Bundschuh et al. 2008, 2012).

## 2 Distribution of Arsenic in Latin America

### *2.1 Generalities*

Arsenic concentrations and sources vary among sites, although, in most of them, it has a natural origin. The release of As to the water may involve complex geochemical processes that have been unraveled only in certain zones. In many of those sites, most or all drinking water comes from As-enriched aquifers, posing a health threat to the population. Here, an overview of As natural occurrence in Latin American water resources will be presented, including identified sources and geochemical processes involved in its release and mobilization, focusing on water bodies used as a drinking water sources.

### *2.2 Argentina*

A compilation of studies conducted in Argentina related to the As presence in water was recently reported (Bundschuh et al. 2012), being the Chaco-Pampean plain (about 1 million km$^2$) the largest area affected by groundwater As contamination in Latin America. In this study, the zones with As occurrence were divided in Chaco-Pampean plain, Andean highlands, sub-Andean valleys/Andean foothills, and Patagonia, each one with specific As concentration ranges. Main hydrogeochemical characteristics and geochemical processes influencing As occurrence and mobilization were summarized in this publication. The factors controlling As mobilization in the aquifers of the Río Dulce alluvial cone, where groundwater contains an average As concentration of 743 μg/L, have been identified (Bhattacharya et al. 2006). Arsenic release involves the influx from dissolution of volcanic glass, adsorption of As on Fe and Al mineral phases in relatively low pH zones, and high mobility of As in high pH zones. Processes of As water enrichment and mobility in the Quaternary loess aquifer at the Chaco-Pampean plain were defined (Smedley et al. 2009). Accumulation of As in the groundwater flow toward the depression and lack of flushing seem to be responsible for the high As concentrations, which reach 5300 μg/L. Sorption/desorption on Fe oxides and possibly on Mn oxides were considered as important controls on As mobility. In addition, a high correlation ($R^2 = 0.84$) between As and fluoride (F) contents in the groundwater of the phreatic aquifer of Coronel Moldes has been found (Gomez et al. 2009). Coexistence of As and F in groundwater of the Chaco-Pampean plain was also remarked (Alarcón-Herrera et al. 2013). It has been informed that groundwater flowing through Tertiary and Quaternary loess deposits at Tucumán province contains also high As concentrations (up to 1610 μg/L), with lower concentrations at large depth (Nicolli et al. 2009). Sorption was also considered as a control of As mobility in this study. The role of the tectonic setting in the As concentration increase of groundwater in the Chaco-Pampean plain was evaluated through flow path modeling (Mukherjee et al. 2014). This study included the chemical analysis of major, minor, and trace elements in water from 60 wells. The PHREEQC hydrogeochemical code was used to model reaction flow path for pairs of wells. The simulations considered chemical evolution through silicate weathering, dissolution of evaporites, reversible cation exchange reactions, and oxide phases. Arsenic concentration in water was as high as 7500 μg/L, with As(V) being the dominant species. Volcanic glass was considered to be the primary source of As in the Chaco-Pampean groundwater. In addition, mineralized, hydrothermal zones and hot springs are also a major geogenic source. The As origin may be tectonically controlled; As is transported to the surface aquifers by extrusive volcanism or hydrothermal fluids. Rhyolitic glass in volcanic ash beds and silicate rocks undergo hydrolytic dissolution releasing trace oxy-anions to groundwater that then undergo other geochemical processes in the groundwater flow. Arsenic concentrations and distribution in groundwater of the Central-West region of Chaco have been determined (Blanes et al. 2011). Approximately 88% of 86 groundwater samples collected in 2007 exceeded the WHO guideline value posing a risk to the population since this water is used for human and livestock consumption. Elevated As concentrations were associated to high pH and Na-$HCO_3$-type groundwater. The processes controlling As and F distribution in groundwater of the Pampeano aquifer and the Del Azul Creek basin, located southeast of the Chaco-Pampean plain, in Buenos Aires province, have been evaluated (Zabala et al. 2016). Concentrations above the present WHO safe drinking level (10 μg/L) (World Health Organization (WHO) 2011) were measured in 92% of 62 samples collected in the years 2011 and 2012. Hydrogeochemical, isotopic, and statistical interpretations within the hydrogeological framework allowed defining two main controls on As distribution. Hydrogeochemical processes control As distribution in low and moderately mineralized water of the middle and lower parts of the basin, while hydrogeological conditions control its distribution northeast and beyond the lower basin. Hydrogeochemical studies have also been performed in the Salí River basin part of the Tucumano-Santiagueña hydrogeological province, where 42 groundwater samples from shallow aquifers, 26 deep samples, and 17 from artesian aquifers were collected (Nicolli et al. 2010). Arsenic concentrations ranged from 11.4 to 1660 μg/L being 100% of the samples above the WHO guideline value. A strong positive correlation among As, F, and V was found in shallow groundwaters. Leaching from pyroclastic materials is favored by high pH and high bicarbonate waters. In another study, the distribution of inorganic arsenic (iAs) species in groundwater used for human consumption was determined in the Santa Fe province (Sigrist et al. 2013). Results showed a prevalence of As(V) and As contents above the WHO limit in all of the samples collected in 27 counties with concentrations up to 186.5 μg/L. Arsenic concentration in water, soils, human, and dog hair was determined at La Matanza District, 31 km away from Buenos Aires City (Vázquez et al. 2014). Average As concentration (measured by total reflection X-ray fluorescence, TXRF) in drinking groundwater was 57 μg/L, while As in human hair was below the reference level, and As in dog hair showed the occurrence of chronic As contamination. The presence of As in surface water and groundwater of the Argentine Altiplano (Puna) and sub-Andean valleys, which is consumed by 355,000 people, was also evaluated (Farias et al. 2016). The concentrations measured in 61% of the 62 samples collected in an area of 30,000 km$^2$ exceeded the WHO limit. Arsenic occurrence was ascribed to geogenic sources. Results showed that the daily As intake for the majority of the population from La Puna (561 μg/day average in summer and 280.5 μg/day in winter) was higher than the WHO reference value (146 μg/day) (World Health Organization & International Programme on Chemical Safety 1996).

## *2.3 Bolivia*

The presence of As has been identified in various areas of Bolivia, mainly related to mining activities, ore deposits, geothermal manifestations, and leaching of volcanic rocks. Its occurrence in various environmental compartments has been summarized in 2012 (Bundschuh et al. 2008). Many of the studies have focused on the Pilcomayo River basin and the Poopó Lake basin. The As concentration in the less developed area of the basin, where untreated surface water and groundwater are used as drinking water, has been determined (Ormachea Muñoz et al. 2014). General physicochemical characteristics were slightly alkaline with high electrical conductivity and predominance of sodium, chloride, and bicarbonate. Arsenic concentrations were above the WHO guideline value in 95% of the 41 sampled wells and 7 sites along 4 rivers, reaching 623 μg/L. The presence of As was related to water contact with alluvial material in lower terrains, besides arsenopyrite oxidation, and dissolution from volcanic rocks. Arsenic contamination in surface water, groundwater, and soils in the provinces of La Paz and Oruro of the Bolivian highland has been studied (Quintanilla et al. 2009). Groundwater average As concentration was 47 μg/L and ranged from below the detection limit (DL) to 200 μg/L in Kondo K, 245 μg/L in Santuario de Quillacas, 152 μg/L in the central region, and 187 μg/L in Pampa Aullagas. The Poopó lake contained the highest As concentrations of the sampled surface waters with 11,140 μg/L in the dry period. Geothermal processes are the main natural sources of As in the area; anthropogenic contamination is related to mine tailings located around San José, Huanuni, Poopó, Avicaya, Itos, and Llallagua. Arsenic presence in groundwater of the Poopó basin was ascribed to sulfide mineral oxidation. All the rivers that drain the mining area are enriched in As. The sources and geochemical processes controlling the mobilization of As and trace elements in shallow aquifers of the Antequera and Poopó sub-basins in the mining Oruro region have been evaluated (Ramos et al. 2014). In the Antequera sub-basin, As concentration was above the WHO limit in 89% of the samples, with a maximum value of

364 µg/L, while in the Poopó sub-basin, all samples were above that limit, reaching a maximum of 104.4 µg/L. Since high As concentrations were measured far from mining sites in the Antequera sub-basin, a natural origin related to the characteristics of the sediments was ascribed to the presence of the element. Statistical factor analysis showed that four processes could produce the mobilization of As and trace elements: desorption from hydrous ferric oxide surfaces, reductive dissolution of Fe and Mn hydrous oxides, increased trace element concentrations at acidic pH values, and oxidation of sulfide minerals.

## 2.4 Brazil

Mining has been an important As source in the Iron Quadrangle at the Minas Gerais state. This was assessed through an interdisciplinary project carried out from 1998 to 2007 (Matschullat et al. 2007). The main As source are primary ore deposits containing arsenopyrite and pyrite. Arsenic presence is related to natural leaching of rocks and soils as well as mining operations (Bundschuh et al. 2008). In the Ribeira Valley (southeastern Brazil), Pb and As have contaminated the Ribeira River as a result of Pb-Zn ore production and smelting. The Santana District in the Amazon region is also contaminated with As (up to 2.0 mg/L in some wells) produced from Mn ore benefit. However, low As exposure was identified in this latter area (Figueiredo et al. 2010). The occurrence of As in drinking waters at Paractu was also assessed (Bidone et al. 2014). The results showed that As concentrations in drinking water (surface water and groundwater) were below the WHO standard value in urban and rural communities and most of them below the instrumental DL. However, As reaches up to 40.10 µg/L in freshwater samples at Corrego Rico and Ribeirão Entre-Ribeiros watershed, due to the influence of a gold mining site and abandoned artisanal gold mining sites. In the Itapessoca catchment (northeast Brazil), As pollution due to a shrimp farm and fish ponds in surface waters, with concentrations up to 15.51 µg/L As, has been reported (Santos Pontes et al. 2014).

## 2.5 Chile

The area of Atacama Desert, northern Chile, is naturally enriched in As. People from the Arica zone have been affected by this metalloid for more than 4500 years (Figueiredo et al. 2010). Nevertheless, As-related health effects from As-rich drinking water pumped from the Loa river were identified only since 1962 at Antofagasta (Bundschuh et al. 2012). Arsenic concentrations up to 2000 µg/L were measured in the Loa river, as a result of high evaporation at alkaline pH and high salinity (Alarcón-Herrera et al. 2013). Arsenic is mainly released from volcanic rocks and sulfide ore deposits at the Andean chain and mobilized by snowmelts and rain to rivers and springs. At the Camarones Valley, about 100 km south of Arica City, drinking water from waterfalls and from the Camarones river contain 48.7 μg/L and 1252 μg/L of As, respectively, mostly as As(V) (Bundschuh et al. 2012). In the Tarapacá region, high As concentrations were determined in surface water and groundwater with a heterogeneous spatial distribution. Arsenic in drinking water of the rural area ranged from 0.1 μg/L in Guatacondo to 345.85 μg/L in Camiña, located at the north and south of the area, respectively. The highest As concentration in the sampled rivers was measured in Pachica. No correlation was found between As, boron (B), and salinity in the Tarapacá area. The occurrence of As was ascribed to the presence of volcanic sediments, salt lakes, thermal areas, predominance of closed basins, and anthropogenic sources like copper mining (Amaro et al. 2014). In the mining region of Antofagasta, high As concentrations were found in river waters (from 10 to 3000 μg/L). In addition, water used for human consumption ranged from 100 to 1900 μg/L. Nevertheless, As exposure has decreased, and As-related problems have been solved in most part of the country (Bundschuh et al. 2012; Figueiredo et al. 2010).

## *2.6 Colombia*

While Colombia geology indicates the presence of rocks containing As minerals, few studies have been developed to assess the actual concentrations in rocks or water. Arsenic was found in the Marmato river water in the Marmato mining district (Bundschuh et al. 2012). In 2010 and 2011, As concentrations were determined in 319 samples of drinking water in Bogotá DC (Patiño-Reyes and Duarte Portocarrero 2014). Concentrations were below the detection level in most of the samples (99.38%), and the rest was below the WHO guideline value. A review of the occurrence and sources of As in Colombia was reported in 2014 (Alonso et al. 2014). The presence of low As levels was determined in the Suratá river waters with concentrations up to 13 μg/L near the municipality of California. Arsenic occurrence was related to mining in the area (Alonso et al. 2014). Information reported in that review showed that As concentrations in surface water and groundwater exceeded national standards at some sites; its presence was ascribed to human activities, mainly to mining and agriculture. This last source of As (up to 255 μg/L) was detected in the phreatic water of several municipalities of the Bogotá savannah with intense irrigation of horticultural crops. Arsenic concentrations above the Colombian drinking water standard of 10 μg/L were also measured in the water near the Muña reservoir, which is used by people (41.8 μg/L average). Although concentrations are low at many of the studied sites, in several cases, the values exceed the national recommended levels for drinking, irrigation, livestock, and aquatic life. The authors of the review highlight the importance of performing more research to understand the occurrence, origin, and distribution of As in Colombia.

## *2.7 Cuba*

Arsenic concentrations have been reported at some sites in Cuba. Studies carried out at Isla de la Juventud, Manzanillo bay, Cienfuegos bay, and Santa Lucía mine have been informed (Bundschuh et al. 2012). At Isla de la Juventud, only one spring close to the Delita mine out of eight sampled points in the watershed was contaminated with 25–250 μg/L As (Toujague et al. 2003). Arsenic concentrations were above the WHO guideline value in wells at other watersheds, representing a risk for noncancerous diseases for children. Streams impacted by acid mine drainage (AMD) from the Santa Lucía mine showed decreasing As contents downstream ranging from 4 to 24 μg/L at around 1500–1700 m from the mine.

## *2.8 Ecuador*

Concentrations of As from 220 to 369 μg/L at the surface and from 289 to 351 μg/L at depth were measured in the water of the Papallacta lake (Cumbal et al. 2009). The authors identified discharges of geothermal waters (containing up to 7853 μg/L of As) to the Tambo river as the main As sources to the lake. Arsenic concentrations ranging from 9 to 126 μg/L were found in wells used as drinking water sources in Tumbaco and Guayabamaba towns in 2006; treatment options were then applied by the municipality (Bundschuh et al. 2012).

## *2.9 El Salvador*

Arsenic is present in the largest lakes of the country (Ilopango, Coatepeque, and Olomega), with the highest concentration (4210 μg/L) measured at the Olomega lake in 2000. While this water is not used for centralized supply, it has been reported to be used by people living in the watersheds (Bundschuh et al. 2012; López et al. 2012). High As contents (up to 770 μg/L) in the waters of the Ilopango lake are linked to hydrothermal fluid interaction with lake sediments. As and B concentrations (up to 8.6 mg/L) were correlated in the lake water with higher values to the south (López et al. 2009). Arsenic in springs and domestic wells of geothermal origin was determined in the Ahucahapán (from 20 to 210 μg/L) and Berlin (from 2 to 285 μg/L) geothermal fields. Arsenic was also found in Las Burras (164 μg/L) and Obrajuelo (16 to 330 μg/L) aquifers (Bundschuh et al. 2012). Water collected in the Bajo Lempa region in October 2012 and March 2013 showed a maximum of 12 μg/L As in surface water and 322 μg/L in groundwater. Arsenic presence is related to natural occurrence in rocks and geothermal fluid and probably to an anthropogenic source due to pesticides and fertilizers used in the area (López et al. 2014). The San Miguel aquifer was recognized to present a high risk due to As presence with up to 162 µg/L. Three rivers of the country (Paz, Sucio, and Jiboa) were identified to contain relatively high As concentrations with up to 123 µg/L in the Jiboa river (Bundschuh et al. 2012).

## *2.10 Guatemala*

In 2007, a concentration of 15 µg/L As, originated from leaching of volcanic rocks, was measured in the water of a well used as drinking water supply at Mexico (Bundschuh et al. 2012; Garrido Hoyos et al. 2007). Later, in the area of the Marlin mine (boundary between San Miguel Ixtahuacán and Sipacapa, San Marcos department, 300 km from Guatemala City), As concentration up to 261 µg/L was measured in wells downgradient from the tailings (Bundschuh et al. 2012).

## *2.11 Mexico*

Chronic As poisoning was first identified in Mexico in 1958 at the Comarca Lagunera, northern México (Cebrián et al. 1994). Since then, As has been detected in many areas of the country. Its presence is mainly related to geogenic sources, mineralization, geothermal systems, sorption and release from minerals, and salinization, but also to anthropogenic activities in some areas. An overview of the As presence in groundwater of Mexico and their possible sources was reported in 2008 (Armienta and Segovia 2008); areas identified with the presence of As and F have been also reported in 2013 (Alarcón-Herrera et al. 2013), and occurrence and mechanisms of As enrichment in geothermal zones were described (Birkle et al. 2010). Here, some of the As-rich areas resulting from diverse sources and recent studies in places where groundwater is used as drinking water are included.

Comarca Lagunera in Durango and Coahuila states has been one of the most studied areas with As concentrations up to 750 µg/L. The zones were where the former lagoons Mayrán and Viesca (currently dried up), in the northeastern part of the basin, are reported as the most As-enriched areas. Higher As concentrations have been determined for thousands of years in old waters with respect to recent infiltrated, young waters. Intensive groundwater abstraction, besides arrest of the Nazas river infiltration due to its canalization, has induced the pumping of deeper As-enriched old waters. As a result, As contents increased in 2010 compared to 1990, mainly in the northern part of the region. A correlation of As concentration with groundwater age, with older waters having higher As contents than the younger ones, has been identified (Boochs et al. 2014). From the interpretation of chemical and isotopic determinations and groundwater flow modeling, evaporation was postulated as the main process producing high As concentrations in the most southeastern part of this area (Ortega-Guerrero 2004). Release of As from sediments to the water due to pH increase was also proposed (Mejía-González et al. 2014). Recently, the geochemical influence of the aquitards on As enrichment at the edges of the Comarca Lagunera has been evaluated (Ortega-Guerrero 2017). Results of this study including geochemical modeling indicated that the advance of As-rich water to the main granular aquifer is due to a reversal of hydraulic gradients resulting from intensive groundwater exploitation and decrease of freshwater runoff from dam construction in the main rivers. Although various sources have been proposed as the origin of As, it was concluded that the most probable source is related to extinct hydrothermal activity and sedimentary process (Boochs et al. 2014). Increased groundwater abstraction and canalization of the Nazas river induced a drawdown of the groundwater level reaching about 100 m in the center of the area. Irrigation with As-rich water contributed also to As increase. Concentrations of As and F above the Mexican drinking water standards (i.e., 25 μg/L for As and 1.5 mg/L for F, Modificación a la Norma Oficial Mexicana 2000) have also been measured in the alluvial aquifer system of the Chihuahua state (Espino-Valdés et al. 2009; Reyes-Gómez et al. 2013). Interpretation of the distribution of concentrations within the hydrogeological and geological framework indicated a natural geogenic source related to the recharge flow coming from mountains presenting arsenopyrite deposits and from the contact of water with the aquifer sediments. Besides, at the Julimes municipality, geothermal water and high evaporation rate are also responsible of As contamination. A review including information from water, soils, and sediments reported natural (related to volcanic processes) and anthropogenic (related to mining and smelting) sources in the Chihuahua and Coahuila states (Mar Camacho et al. 2011). The co-occurrence of F and As in the central part of the Chihuahua state was studied (Reyes-Gómez et al. 2013). Petrographic analyses showed the presence of F as fluorapatite. Distribution maps depicted temporal (since 2003–2010) and spatial concentration variations of As and F. Measured values of pH and Eh indicated that As predominates as $HAsO_4^{2-}$ in groundwater. A geochemical conceptual model was proposed to reflect the mobility of As and F in groundwater. Highly fractured volcanic rocks and alluvial fans at the base of the *sierras* were identified as possible aquifer recharge zones. The alluvial fans contain rhyolites and shales with As and fluorapatite. Weathering releases these elements from the lithology of the area.

Arsenic contamination is related to natural and/or anthropogenic sources in mining zones. At Zimapán, Hidalgo state, two anthropogenic and one natural source were identified as the origin of As groundwater pollution in the aquifer system. Arsenic was determined in rocks, mining wastes, soils, and sediments (Fig. 1); chemical analyses of water included main ions determined by standard methods and isotopic analyses (δ18O, δ2H in water, and δ34S in dissolved sulfates). Interpretation of the results within the hydrogeological framework allowed to define the contamination degree and the As source and mobility. Water interaction with As-bearing minerals in the aquifer matrix releases As to the deep fractured limestone aquifer, while AMD from tailings and infiltration of As-enriched water from smelter stacks contaminated the shallow aquifer (Armienta et al. 2001; Sracek et al. 2010). At the Independencia basin, Guanajuato state, concentrations above drinking water

**Fig. 1** Mine tailings at Zimapán, Mexico. Mining residues are one of the main anthropogenic sources of As in water in Latin America

standards have been measured in groundwater. A study to determine the processes involved in the geochemical evolution and mineralization of the area by means of chemical and isotopic (δ18O, 13C, 3H) analyses of groundwater, mineralogical determinations of rocks from boreholes by XRD, geochemical modeling (PHREEQC), and multivariate statistical analysis has been developed (Mahlknecht et al. 2004). Interpretation of the results led to the conclusion that weathering of rhyolites and oxidation of As-bearing minerals produce the high As and F concentrations. The concentrations, distribution, and source of As and F in the same basin were also investigated (Ortega-Guerrero 2009). The study included chemical (major and trace elements) and isotopic (δ18O, δ2H, 13C/14C, 3H) determinations interpreted in the hydrogeological framework. Hydrogeochemical and isotopic results indicated that As originates from the dissolution of silicates, while F is related to the dissolution of fluorite and silicates, thermal water, and a longer residence time of the water. The hydrogeological and geothermal factors related to the origin of As and F in another area of the Guanajuato state, at the Juventino Rosas municipality, were also studied (Morales-Arredondo et al. 2016). Interpretation of the results within the geological and hydrogeological framework using hydrogeochemical plots and statistical methods allowed to relate the water type with concentration ranges and circulation patterns of the groundwater. Rhyolite units appeared to be the most probable source of As and F. At Los Altos de Jalisco, western Mexico, mean As concentration in drinking water varied from 14.7 to 101.9 µg/L, with the highest values in the city of Mexticacán (262.9 µg/L). While most of the surface water has low As contents, the concentrations reach values above the WHO standard value in all sampled wells in the Los Altos de Jalisco towns (Hurtado-Jiménez and Gardea-Torresdey 2006).

## 2.12 Nicaragua

In the southwestern part of the Sébaco Valley, drinking water has been contaminated by As from geogenic sources (mainly weathering of Tertiary volcanic rocks). The valley is located at the eastern region of the Central American graben and is characterized by intensive tectonic stress, fracturing, presence of active and inactive faults, and hydrothermal alteration. Concentrations range from 10 to 122 μg/L. The high polluted well at El Zapote (As concentration, 1320 μg/L) was closed in 1996; arsenicosis was detected in people consuming that water for 2 years. The aquifer is used by several communities as drinking water source. Changes in redox conditions increase the As mobility. A study developed in 2004 showed that the northern zone of the country presented the highest As contents. In 2005, the presence of geogenic As was identified at San Juan de Limay (Bundschuh et al. 2012; Altamirano Espinoza and Bundschuh 2009; Armienta et al. 2010).

## 2.13 Peru

The presence of As has been detected at several sites in Peru, mainly in the Andean region, released by weathering and mining operations. The Locumba river and its tributaries contain up to 1680 μg/L. Volcanic rocks and pyroclastic materials release As in the area of the Yucamane volcano to the Collazas and Salado rivers. In the area of Puno, Andean highland As concentrations ranged from 140 to 230 μg/L in river water, mostly present as As(V). East of Lima City, the Rimac river basin has been contaminated by mining activities, leaching of volcanic rocks, and ore deposits. Concentrations present high temporal variations and reached up to 1630 μg/L in 2000 in Puente Santa Rosa (Bundschuh et al. 2012).

## 2.14 Uruguay

The presence of As (between 25 and 50 μg/L) was reported in the Raigón aquifer, at the southwestern part of the country. Arsenic source was related with the continental sediments containing volcanic ash, also occurring in the Santa Fe province in Argentina (Bundschuh et al. 2012; Guérèquiz et al. 2009). Concentrations below 10 μg/L were only measured in 6 out of 37 samples collected in the Raigón aquifer system since 2007 (Mañay et al. 2014). The importance of a multidisciplinary approach to assess the status of As in health and the environment in Uruguay has been remarked in this study.

## 3 Analytical Determination of Arsenic in Latin America

Due to the problems that can provoke the presence of As in quantities that can be toxic to human health, the study of the presence of the element and its derivative compounds, together with their quantification, has a great relevance. Arsenic is present in different matrices that impact the different geochemical spheres, i.e., lithosphere (rocks), pedosphere (soils), biosphere (living organisms), atmosphere (air), hydrosphere (water), and anthroposphere (man's effect on the other spheres) (Hounslow 1995). The chemical behavior of As will depend on environmental conditions such as acidity conditions, oxidation-reduction state, presence of iron, organic matter or other ligands (e.g., sulfur), etc. Due to the low concentrations at which As may be present in an environment and its chemical behavior, the selection of an adequate analytical technique will greatly depend on the objectives of the study, the access to the adequate analytical methodology, the cost of the analyses, and the matrix to be studied. The analyst should take all these factors into account when selecting a technique, ensuring a high degree of precision and accuracy, as well as high sensitivity, which allow reaching concentrations below the μg/L range.

The presence of As in the environment has not been regulated until lethal diseases appeared (e.g., skin, lung, bladder cancers). For this reason, permissible limits of As content in water have been established by environmental agencies, and different maximum limits for As in drinking water can exist in each country. These limits are revised and lowered periodically to prevent the serious consequences on the human health.

In this chapter, different analytical methods for the determination of As in different matrices are presented, mainly focused on the studies conducted in Latin American countries. This study is based on a bibliographic research; 167 scientific manuscripts and articles of the last 18 years have been considered. Table 1 shows the different analytical methodologies used for the analysis of As (total or speciation) in different matrices. Classical methods (e.g., atomic flame absorption) and the most advanced methodologies such as the micro-X-ray synchrotron method or electrochemical methods are presented. It includes different matrices of interest such as water, food (e.g., wine, milk, and rice), human fluids (urine and human hair), rock, plants and marine organisms, and natural and synthetic materials.

Figure 2 shows the number of analytical methodologies reported in Latin America for As determination. The data indicate that the most widely analytical technique is AAS (57%), specifically with the method of sample introduction through hydride generation (HG-AAS) (Table 1). The DL using HG-AAS is about 0.1–0.6 μg/L (Arsénico en agua, informe Grupo Ad-Hoc Arsénico en agua 2018). This method has some advantages: the sensitivity and selectivity are improved, and the salinity of the sample does not influence the results (Arsénico en agua, informe Grupo Ad-Hoc Arsénico en agua 2018). Additionally, the methodology is simple and only requires relatively inexpensive and very versatile instrumentation, with excellent detection power for total and iAs (Litter et al. 2009). Figure 2 also shows that the second most used analytical technique is ICP (26%), with emphasis in

**Table 1** Methods applied for the determination of As in Latin American countries

| | Analytical methodology | Country | Application | References |
|---|---|---|---|---|
| Electrochemical | ASV-(CAR-CPE) | Chile | Water | Núñez et al. (2018) |
| | ASV | Ecuador and Venezuela | Water | Carrera et al. (2017) |
| | AS-SWV | Argentina | Water | Robles et al. (2017) |
| | ASV | Chile | Water | Núñez et al. (2016) |
| | CSV | Brazil | Food | Teixeira et al. (2014) |
| | DPP | Chile | Water | Gamboa et al. (2013) |
| | SWCSV | Chile | Carrots, beets, and irrigation water | Arancibia et al. (2006) |
| | SWCSV | Brazil | Water | Barra and Correia dos Santos (2001) |
| Atomic absorption spectrometry | HG-AAS | Mexico | Thermal spring | Morales-Arredondo et al. (2018) |
| | HG-AAS | Mexico | Natural zeolitic sorbents | Velázquez-Peña et al. (2019) |
| | AAS | Mexico | Endophyte-free plants, *Methylobacterium* sp.-colonized plants | Alcántara-Martínez et al. (2018) |
| | HG-AAS | Brazil | Seawater | Dos Santos et al. (2018) |
| | HG-AAS | Mexico | Groundwater | Sandoval et al. (2018) |
| | HR-CS-GFAAS | Brazil-UK | Agricultural soil | Schneider et al. (2018) |
| | AEC-ICP-MS/ETAAS | Argentina | Olive oils | Torres et al. (2018) |
| | FIAS-HG-AAS | Argentina | Soil and water | Yáñez et al. (2018) |
| | GFAAS | Brazil | Natural waters | Alves et al. (2017) |
| | HG-AAS | USA and Mexico | Urine | Kordas et al. (2017) |
| | HG-AAS | Mexico | Human urine | López Guzmán et al. (2017) |

(continued)

**Table 1** (continued)

| | Analytical methodology | Country | Application | References |
|---|---|---|---|---|
| | HG-AAS | Chile | Food | Muñoz et al. (2017) |
| | HG-AAS | Mexico | Groundwater | Navarro et al. (2017) |
| | IXED cell-HG-AAS | Mexico | Wastewater effluents and groundwater | Ortega et al. (2017) |
| | HG-AAS | Mexico | Soils | Rodríguez Garrido et al. (2017) |
| | FAAS | Mexico | Soils and plants | Salas-Luévano et al. (2017) |
| | HG-AAS | Mexico | Fungal biomass | Santos-Domínguez et al. (2017) |
| | HG-AAS | Mexico | Soils | Sariñana-Ruiz et al. (2017) |
| | HG-AAS | Mexico | Drinking and potable water, urine, and blood | Arcega-Cabrera and Fargher (2016) |
| | GFAAS | Mexico | Contaminated soils | Armienta et al. (2016) |
| | HPLC-HG-AFS | Argentina | Ionic liquids | Castro Grijalba et al. (2016) |
| | MSFIA-HG-AFS | Brazil | Peanuts | De Santana et al. (2016) |
| | GFAAS | Mexico-France | Arsenopyrite leachates | Lara René et al. (2016) |
| | HG-AAS | Brazil | Salmon fish | Oliveira et al. (2016) |
| | ETAAS | Argentina | Tap water | Peralta Ramos et al. (2016) |
| | HR-CS-GFAAS | Brazil-UK-Chile | Fish oil | Pereira et al. (2016) |
| | CPE-HG-AFS | Mexico-Spain | Corn and rice | Rosas-Castor et al. (2016) |
| | FI-HG-AAS | Argentina | Food samples | Sigrist et al. (2016) |
| | HPLC-HG-AAS | Mexico | Urine | Torres-Sánchez et al. (2016) |

(continued)

**Table 1** (continued)

| | Analytical methodology | Country | Application | References |
|---|---|---|---|---|
| | HG-AAS/<br>HPLC-HG-ICPMS | Uruguay | Human urine | Bühl et al. (2015) |
| | EcHG-AAS | Ecuador, Venezuela | Marine sediment | Caiminagua et al. (2015) |
| | MSFIA-HG-AFS | Mexico-Spain | Agricultural soil | Rosas-Castor et al. (2015) |
| | ETAAS | Argentina | Water | Castro Grijalba et al. (2015) |
| | AC-modified KR-ETAAS | Argentina | Medicinal herbs and tea infusions | Castro Grijalba et al. (2015) |
| | CPE-ETAAS | Brazil | Rice samples | Dos Santos Costa et al. (2015) |
| | HG-AAS | Mexico | Groundwater | Esteller et al. (2015) |
| | HG-AAS | Mexico | Groundwater | Morales et al. (2015) |
| | HG-AAS | Mexico | Water from shallow anddeep wells, irrigation canals and geothermalproduction wells | Armienta et al. (2014) |
| | HG-AAS | Mexico | Surface waters | Dótor Almazán et al. (2014) |
| | HG-AAS | Argentina | Human urine | Navoni et al. (2014) |
| | HG-AAS | Argentina | Water and human urine | De Pietri et al. (2014) |
| | HG-AFS/IC-HG-AFS | Mexico | Agricultural soil and maize crops | Rosas-Castor et al. (2014) |
| | Wagtech Arsenator field kit /HG-AAS | Mexico | Water | Avilés et al. (2013) |
| | HG-AAS | Ecuador | Milk | Ayala and Romero (2013) |
| | ETAAS | Argentina | Wine | Escudero et al. (2013) |
| | HG-AAS | Mexico | Soils | Hernández Ordáz et al. (2013) |
| | HG-AAS | Mexico | Mining acid leachates | Labastida et al. (2013) |

(continued)

**Table 1** (continued)

| | Analytical methodology | Country | Application | References |
|---|---|---|---|---|
| | AAS | Mexico | Rocks, sediments and groundwater | Reyes-Gómez et al. (2013) |
| | Total As: FI-HG-AAS. As speciation: SPE-FI-HG-AAS | Argentina | Water | Sigrist et al. (2013) |
| | ETAAS | Mexico | Sediment | Álvarez María and Carrillo (2012) |
| | HG-AAS | Mexico | Tailing deposit | Armienta et al. (2012) |
| | FI-HG-AAS | Chile and Spain | Algae | Díaz et al. (2012) |
| | HG-AAS | Mexico | River water | Méndez-Ramírez and Armienta Hernández (2012) |
| | HG-AAS | Uruguay | Water | Pistón et al. (2012) |
| | FIAS-HG-AAS | Mexico | Plants, soils, and mine tailings | Ruiz Huerta and Armienta (2012) |
| | SIA-HPLC-AFS | Brazil | Seafood | Jesus et al. (2011) |
| | IP-HPLC-HG-AFS | Argentina | Animal feed additives | Monasterio et al. (2011) |
| | HG-AAS | Mexico | Urine, blood, and bottled water | Rocha-Amador et al. (2011) |
| | SPE-FI-HG-AAS | Argentina | Groundwater | Sigrist et al. (2011) |
| | FIAS-HG-AAS | USA and Mexico | Urine | Roy et al. (2011) |
| | AAS | Mexico-Germany | Geothermal and petroleum reservoir fluids | Birkle et al. (2010) |
| | HG-CT-AAS | Mexico | Clays | Cervini-Silva et al. (2010) |
| | HG-AFS | Spain and Brazil | Vegetables, pulses, and cereals | Matos-Reyes et al. (2010) |
| | HG-AAS/ICPOES | Brazil | Humic acids | Menezes and Maia (2010) |

(continued)

**Table 1** (continued)

| | Analytical methodology | Country | Application | References |
|---|---|---|---|---|
| | ETAAS | Argentina | Natural waters | Monasterio and Wuilloud (2010) |
| | HG-AAS | Argentina | Urine | Navoni et al. (2010) |
| | HG-AAS | Mexico | Urine | Moreno et al. (2010) |
| | HG-AFS | Mexico | Urine and drinking water | Salgado-Bustamante et al. (2010) |
| | FI-HG-AAS | Argentina | Milk | Sigrist et al. (2010) |
| | FIAS-HG-AAS | USA and Mexico | Shallow wells and shallow river | Sracek et al. (2010) |
| | HG-AAS | Mexico | Surface sediments | Villalobos-Castañeda et al. (2010) |
| | AE-FI-HG-AAS/ IC-FI-HG-AAS | Peru | Water | Chávez (2009) |
| | GFAAS | Mexico | River sediments | Espinosa et al. (2009) |
| | HG-AAS | Brazil | Phosphate fertilizers and phosphate rocks | Macedo et al. (2009) |
| | HG-AAS | Mexico | Groundwater | Armienta and Segovia (2008) |
| | ETAAS | Chile | Marine food | Bruhn et al. (2007) |
| | BDES-FI-ETAAS | Brazil-Spain | Water | Coelho et al. (2007) |
| | FIAS-AAS | Brazil | Food | de Souza et al. (2007) |
| | FI-HG-AAS | Mexico | Water, urine | Valenzuela et al. (2007) |
| | HG-AAS | Chile | Human urine | Cáceres et al. (2005) |
| | HG-AAS | Argentina | Water | Martínez and Gazquez (2005) |
| | ETAAS | Brazil | Petroleum products | Reboucas et al. (2005) |
| | GFAAS-XRFS | Argentina | Deep and shallow groundwater | García et al. (2004) |

(continued)

**Table 1** (continued)

| | Analytical methodology | Country | Application | References |
|---|---|---|---|---|
| | HG-AAS | Mexico | Soil, stream sediment, surface water, and groundwater | Razo et al. (2004) |
| | HG-AAS | Mexico | Water | Rodríguez et al. (2004) |
| | LC-UV-HG-AFS | France-Chile | Certified reference fish tissue and sea food samples | Simona et al. (2004) |
| | GFAAS | Brazil | Environmental samples (sludges, soils, sediments, coal, ashes, and waters) | Lima et al. (2003) |
| | HG-AAS | Cuba | Water | Quevedo et al. (2003) |
| | HG-AAS | Brazil | Sediments, coal, and fly ash slurries | Antunes et al. (2002) |
| | ETAAS | Brazil | Petroleum refinery aqueous streams | Cassella et al. (2002) |
| | HG-AAS | Mexico | Cooked food and water | Del Razo et al. (2002) |
| | FI-HG-AAS | Venezuela | Water | Carrero et al. (2001) |
| | HG-AAS | Brazil | Hair | De Moraes et al. (2001) |
| | HG-AAS | Germany and Mexico | Groundwater | Planer-Friedich et al. (2001) |
| | FI-HG-AFS | Chile | Environmental solid reference materials | Vergara Gallardo et al. (2001) |
| X-ray fluorescence spectrometry | Microwave-assisted distillation-HG-AFS | Brazil | Soils | Barra et al. (2000) |
| | XRFS | Mexico | Plants | Gómez-Bernal et al. (2018) |
| | XRFS | Argentina | Water | Aranda et al. (2016) |
| | XRFS | Chile | Rock | Sepúlveda et al. (2015) |
| | XFRS | Mexico and UK | Plants and soils | Gómez-Bernal et al. (2014) |

(continued)

**Table 1** (continued)

| | Analytical methodology | Country | Application | References |
|---|---|---|---|---|
| | XRFS | Mexico-Bolivia-Spain | Tailings (mine wastes) | Martín et al. (2014) |
| | Synchrotron micro-X-ray | Mexico | Soil | López-Zepeda et al. (2008) |
| | XRFS | Brazil | Water | Zucchi et al. (2005) |
| | XRFS-CSV | Cuba | Water | Valcárcel et al. (2008) |
| Inductively coupled plasma spectrometry | ICPMS | Argentina | Soil, water, grapevine, and onion | Funes Pinter et al. (2018) |
| | LC-ICPMS | Mexico and USA | Urine | Quiller et al. (2018) |
| | HG-MP-AES | Mexico | Forest | Roque-Álvarez et al. (2018) |
| | HPLC-ICPMS | Brazil | Iron supplements | Araujo-Barbosa et al. (2017) |
| | ICPOES | Mexico | Soil, irrigation water, and maize samples | Ruíz Huerta et al. (2017) |
| | ICPMS | USA-Mexico | Urine and water | Cárdenas-González et al. (2016) |
| | HPLC-ICPMS | Mexico | Human urine | López-Carrillo et al. (2016) |
| | HG-ICPOES | Mexico | Tap water | Martínez-Acuña et al. (2016) |
| | ICPOES | Argentina | Tailings (mine wastes) | Nieva et al. (2016) |
| | LC-ICPMS | Chile and Spain | Carrots (*Daucus carota*), beets (*Beta vulgaris*), and quinoa (*Chenopodium*) | Pizarro et al. (2016) |
| | MPAES | Mexico | Pure arsenopyrite crystals | Ramírez-Aldaba et al. (2016) |
| | Total As: ICPMS; As speciation: HPLC-ICP-MS | Brazil | Rice samples | Segura et al. (2016) |

(continued)

**Table 1** (continued)

| | Analytical methodology | Country | Application | References |
|---|---|---|---|---|
| | ICPOES | Brazil-Mexico | Tropical peat | de Oliveira et al. (2015) |
| | ICPMS | Argentina | Biofilm | Rodríguez Castro et al. (2015) |
| | HPLC-ICPMS | Brazil | Plants | Amaral et al. (2014) |
| | ICPOES/HG-ICPMS | Chile-USA | Water from hydrothermal transect and sediments | Leiva et al. (2014) |
| | HPLC-ICPMS | Chile | Human urine | Muñoz et al. (2014) |
| | ICPOES | Bolivia | Superficial and underground water | Ormachea and Quintanilla (2014) |
| | ICPMS | México | Water | Martínez-Villegas et al. (2013) |
| | LC-ICPMS | Brazil | Tissues of bivalve mollusks | Santos et al. (2013) |
| | Arsenic in water samples was analyzed by ICPMS, and in rocks a sediment was determined by HG-AAS | Mexico | Hydrothermal manifestations, seawater, and sediments | Villanueva-Estrada et al. (2013) |
| | ICPAES | Mexico | As adsorption by anchor iron nanoparticles onto activated carbon from groundwater | Vitela-Rodriguez and Rangel-Mendez (2013) |
| | ICPAES | Mexico | Tailings and plants | Santos-Jallath et al. (2012) |
| | ETV-ICPMS | Brazil | Biological tissue samples | Tormen et al. (2012) |
| | ICPAES | Mexico | Wetlands | Zurita et al. (2012) |
| | HPLC-ICPMS | Brazil | Rice samples | Batista et al. (2011) |
| | LC-ICPMS | Brazil and Germany | Wine | Moreira et al. (2011) |
| | ICPAES | Mexico | Acid mine leachates | Romero et al. (2011) |

(continued)

**Table 1** (continued)

| | Analytical methodology | Country | Application | References |
|---|---|---|---|---|
| | LA-ICPMS | Chile | Hair | Arriaza et al. (2010) |
| | ICPOES | Brazil | Plants | Melo et al. (2010) |
| | ICPOES | Argentina | Algae | Pérez et al. (2010) |
| | ICPOES | Mexico and Cuba | Sulfide-rich waste rocks, surface water, and streambed sediments | Romero et al. (2010) |
| | ICPOES | Argentina | Groundwater and humic acids | Morgada et al. (2009) |
| | Total As; ICPOES, iAs: HG-AAS | Argentina and Spain | Macroalgae | Farías et al. (2007) |
| | EVA column/ HG-ICPOES | Argentina | Water | Gil et al. (2007) |
| | INAA/ICPOES | USA-Mexico | Soils | Ongley et al. (2007) |
| | ICPAES | Mexico | Tailings (mine wastes) | Romero et al. (2007) |
| | LC-ICPMS | USA and Argentina | Algae | Wuilloud et al. (2006) |
| | ICPMS | Bolivia | Hair, urine, and unfiltered water | Archer et al. (2005) |
| | HPLC-ICPMS | Brazil-Spain | Beverages (beer, soft drink, and juices) | Coelho et al. (2005) |
| | HPLC-HG-ICPMS | Chile and USA | Human hair | Yáñez et al. (2005) |
| | ICPMS | Mexico | Mine tailings | Armienta et al. (2003) |
| | HG-ICPOES | Argentina | Groundwater | Farías et al. (2003) |
| | HG-ICPMS | Brazil | Water and plants | Menegário and Gin (2000) |
| UV-VIS spectrometry | Colorimetry | Mexico | Groundwater | Saldaña-Robles et al. (2018) |
| | Colorimetry (digital arsenic test kit) | Mexico | Water | Contreras et al. (2017) |
| | UV-VIS spectrophotometry | Cuba | Water | Ramírez-González et al. (2017) |
| | Colorimetry | Mexico | Arsenic removal from irrigation water | Saldaña-Robles et al. (2017) |

(continued)

**Table 1** (continued)

| | Analytical methodology | Country | Application | References |
|---|---|---|---|---|
| | SIA-UV-VIS spectrophotometry | Mexico | Mine tailings | Ramírez Cordero and Cañizares-Macías (2009) |
| | UV-VIS spectrophotometry | Mexico | Water | Pérez Moreno et al. (2002) |
| | UV-VIS spectrophotometry | Mexico | Hair | Armienta et al. (1997) |
| | UV-VIS spectrophotometry | Mexico | Well water | Gómez-Arroyo et al. (1997) |
| Others | INAA | Chile | Hair | Echeverría et al. (2018) |
| | Surface plasmon resonance nanosensor | Colombia | Water | Salinas et al. (2014) |
| | ARSOlux Biosensor | Germany-Argentina | Groundwater | Siegfried et al. (2015) |

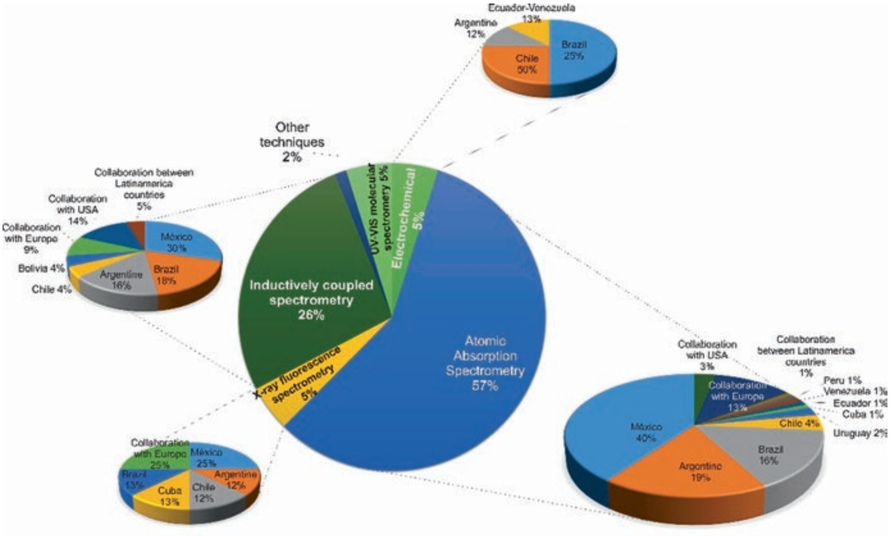

**Fig. 2** Analytical instrumentation reported in Latin America for As determination

ICPMS (Table 1). The DL reached by this methodology is 0.1 μg/L, and there is no need of preconcentrating the sample (Arsénico en agua, informe Grupo Ad-Hoc Arsénico en agua 2018). In general, ICP-MS and ICP-OES are robust and sensitive techniques, but they require very expensive equipment, special facilities, and a long and complex training of analysts (Litter et al. 2009). Figure 2 indicates that electrochemical analytical methods are the third most applied methodologies (5%). This method has a high analytical sensitivity, has a low cost, and is easy to use, with a concentration interval between 0.1 and 300 μg/L by anodic voltammetry (Arsénico en agua, informe Grupo Ad-Hoc Arsénico en agua 2018). Chile, Brazil, Argentine, Ecuador, and Venezuela reported the use of electrochemical methodologies for the determination of As mainly in water and food samples (Table 1). The fourth most used method (5%) is UV-VIS molecular spectroscopy. The methods based on this analytical methodology are simple and economical; however, although the sensitivity is high (10–50 μg/L), the accuracy is low (Arsénico en agua, informe Grupo Ad-Hoc Arsénico en agua 2018). Mexico and Cuba are the main countries that reported the use of this methodology for As determination in water and in samples of mine tailings (Table 1).

Regarding speciation, the two most widely methodologies used in Latin America are AAS and ICP spectroscopy combined with separation techniques (chromatography), which has led to the use of hyphenated methodologies (Table 1). These coupled techniques are the best options for the determination of arsenical species, due to their selectivity, their adequate precision, their high level of automation, and their relatively short response (Litter et al. 2009).

XRF spectrometry is mainly used for the identification and determination of As in solid samples. In quartziferous sands, the DL reaches 40 mg/kg (without interferences). Portable equipments can detect up to 60 mg/kg (Arsénico en agua, informe Grupo Ad-Hoc Arsénico en agua 2018). According to reference (Arsénico en agua, informe Grupo Ad-Hoc Arsénico en agua 2018), the future of this technique, regarding the determination of As in waters at the trace level, will be focused mainly through the development of preconcentration methodologies adaptable to laboratory equipment and to on-site determination.

Other methodologies are the instrumental neutron activation analysis (INAA) (Echeverría et al. 2018) and surface plasmon resonance nanosensor (SPRN) (Salinas et al. 2014). INAA is an accurate and sensitive methodology; it has been used for the determination of total As in biological samples (nail, hair, and other tissues), with a DL of 0.001 μg/g (Arsénico en agua, informe Grupo Ad-Hoc Arsénico en agua 2018). It is important to remark that SPRN is an autonomous sensor for mapping and monitoring As concentrations in water (Salinas et al. 2014). This system can be integrated to a portable suitcase, it is of low cost, and it is able to measure As concentrations below 5 μg/L. However, this method has been not yet applied to real cases. The ARSOlux sensor (Siegfried et al. 2015) is a novel method for field measurements of As in groundwater. This biosensor is a robust and accurate method for the detection of total bioavailable As concentrations and uses a lyophilizate containing a bioreporter bacteria strain.

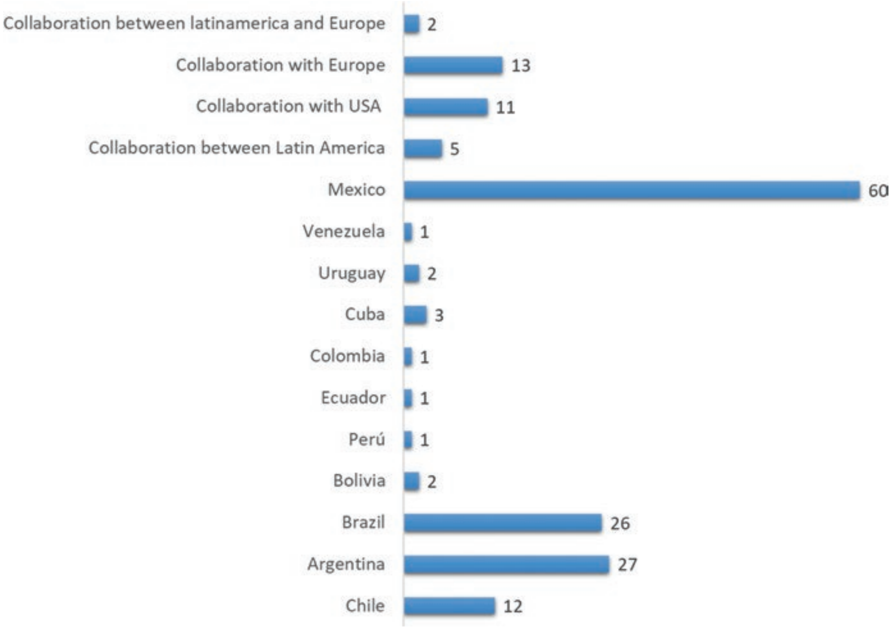

**Fig. 3** Number of scientific articles on As analytical methods published by country

Chemical speciation is an area of great importance for assessing the impact of As to evaluate its toxicity and bioavailability. In addition, the technological advance on development of analytical methods in the last two decades has allowed the application of chemical speciation. Chemical speciation is the qualitative and quantitative determination of the different chemical forms in which an element is present under environmental conditions. Some reviews are focused on the preparation of the sample for the chemical speciation of As analytical determination in terrestrial plants through different analytical methodologies (Amaral et al. 2013). A review on chemical analysis and speciation of traces of As in the environment, food, and industrial samples, mainly by the voltammetry technique, has been also published (Cavicchioli et al. 2004). An important review on the different techniques of extraction and derivatization for the chemical speciation of As can be found in the literature (Vieira et al. 2009).

Figure 3 shows the number of scientific articles related to analytical methods for As determination reported in Latin America. The data indicates that Mexico is the country reporting the largest number of studies (Table 1).

Several studies have been conducted in a joint collaborative way between Latin American and European countries (Spain, Germany, the UK, and France) focused on analytical aspects (Fig. 4).

Collaborative works between the United States and Latin American countries regarding analytical methods for As are also reflected in scientific articles (Fig. 5). Mexico, Chile, and Argentina are the main countries collaborating with the United States.

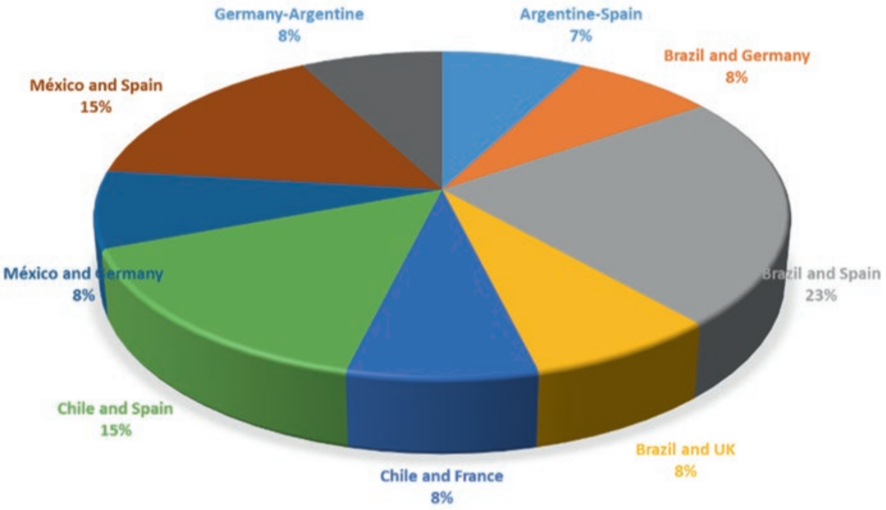

**Fig. 4** Collaborative works between Latin America and Europe on development and application of analytical methodologies for As determination

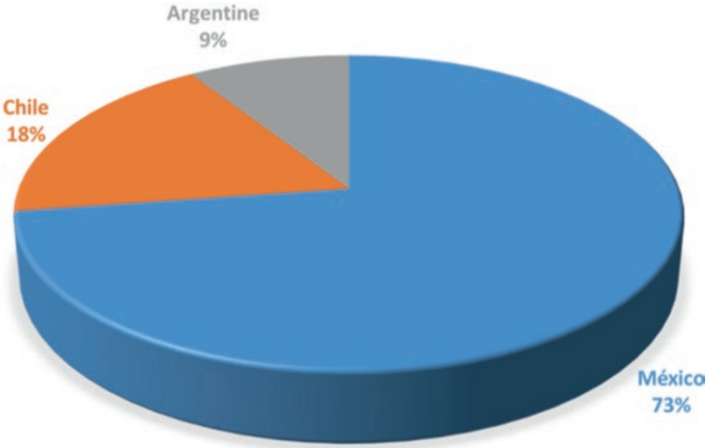

**Fig. 5** Collaborative works between Latin America and the United States on development and application of analytical methodologies for As determination

## 4 Conclusions

Arsenic is present in many aquifers and several superficial water bodies in most of the Latin American countries. Scientific publications related with As occurrence were identified in 13 out of the 19 countries considered in this review. This fact does not imply that concentrations of As above international or national drinking water standards are not present in the rest of the countries. The Chaco-Pampean plain in Argentina is the largest area affected by As contamination in groundwater. Occurrence, sources, geochemical, and mobilization processes of As, including hydrogeological influence, have been studied in diverse parts of this area. Research covering these aspects has also been developed in other countries such as Mexico, Chile, Bolivia, Peru, and Nicaragua. The origin of As in water has been identified in almost all the countries considered in this chapter. In most of the contaminated areas, As originates from geogenic sources, mainly volcanic rocks, hydrothermal fluids, and As-bearing minerals. However, anthropogenic sources are also present in certain zones, most of them as a result of mining operations and, in some cases, related with agriculture. Mining is indeed the main As source in Brazil. Physicochemical characteristics of the water, including pH and Eh, and presence of other ions influence the mobilization of As. Besides, hydrogeological conditions such as lack of flushing, evaporation, and flow-paths related with the tectonic setting also influence the occurrence of As contamination. Although As speciation has only been determined in some areas, it has been found to be mainly as As(V) in those locations. In all Latin American countries, more research has still to be conducted to determine As concentrations and speciation in all water bodies used as drinking water source and to unravel its origin and mobilization processes. This information is essential to develop adequate solutions to avoid the population exposure to this toxic element.

Regarding analytical methods on As determination in Latin American countries, 167 papers in scientific journals have been identified in the last 18 years. The most widely analytical methodology used for As determination is AAS (57%), specifically HG-AAS. The second most used analytical technique is ICP (26%), mainly coupled with MS. Regarding electrochemical methods, Chile, Brazil, and Argentina are the Latin American countries that have published on this topic. Although UV-VIS spectrometry is the least used methodology (5%), it has been employed mainly in Cuba and Mexico, with three reports in 2017 and one in 2018. XRF spectrometry is mainly used for the identification and determination of As in solid samples, and it has been mainly used in Mexico, Cuba, Brazil, Argentina, and Chile. The 2% of other techniques used are INAA and SPRN, with reported studies on As determination in hair and water by Chile in 2018 and Colombia in 2014, respectively. A third novel methodology, ARSOlux Biosensor, developed between Argentine and Germany, is useful for determination of total bioavailable As concentrations in groundwater. Meanwhile, the SPRN technique is at test stage and is used for solid samples.

With respect to scientific publications focused on the analysis of As, it can be concluded that:

- Mexico, Brazil, Argentina, and Chile are the countries presenting the largest number of scientific publications.
- The collaboration between Latin America and Europe is mainly with Spain, Germany, the UK, and France.
- Mexico, Chile, and Argentine are the main countries that have published in collaboration with the United States.

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