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Towards a comprehensive understanding of the "Origin, distribution, and biogeochemistry of arsenic in the Altiplano-Puna plateau of South America" with the IGCP-707 project

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Arsenic (As) is one of the most prevalent geogenic trace elements in the groundwater environment that presents a worldwide health concern. In South America, the "Altiplano-Puna" plateau exhibits high As concentrations in water that could be affecting 3 million inhabitants from Argentina, Bolivia, Chile, and Perú. In this As-rich environment with limited water resources, there exists a lack of knowledge regarding the basic geochemistry of As, water quality characterization, and affected population and biodiversity. Between 2020-2022 we performed interdisciplinary research to understand (i) the origin of As, (ii) its geochemistry and mobility, (iii) its distribution in the environment, and (iv) its effects in the local community and unique biodiversity. Our research provides new scientific insights into the biogeochemical cycle of As in the environment and its effect on human health and biodiversity. Our dissemination activities increased the visibility of the As issue for the region that had historically received little attention from the scientific community and local authorities. This project led to additional funding and the creation of a solid research network between the South and North hemispheres, fostering the participation of young researchers, students, and women. An extension of the project was obtained to continue our work during 2023.

Introduction

Arsenic (As) is one of the most prevalent geogenic trace elements in the groundwater environment that presents a worldwide health concern (Bowell et al., 2014; Nordstrom, 2002). Inorganic As is carcinogenic, mutagenic, and teratogenic for humans and the risks of developing several types of severe diseases from chronic exposure are well documented (IRIS, 1991). According to the World Health Organization (2022), approximately 140 million people from 50 countries are exposed to drinking water containing arsenic levels higher than the recommended limit (> 10 μg/L). In Latin America at least 20 countries are affected by high As concentrations in waters (Bundschuh et al., 2020). In 2019, a revision about the "Origin, distribution, and geochemistry of arsenic in the Altiplano-Puna plateau of Argentina, Bolivia, Chile, and Perú" was made by the leaders of this IGCP-707 project (Tapia et al., 2019). We found out that in the Altiplano-Puna plateau As concentrations in water could be affecting 3 million inhabitants mainly through the consumption of untreated drinking water that contains naturally elevated As concentrations that in some cases can be enhanced by the presence of acid mine waters (Tapia et al., 2019). The high Altiplano-Puna plateau of South America, situated in the Central Andes region is the second highest plateau in the Earth after Tibet and comprises areas of Argentina, Bolivia, Chile, and Perú. Its high altitude (> 3500 m.a.s.l.) and breadth (≈ 400 km) produces distinctive meteorological conditions making it one of the highest arid to semi-arid regions on Earth (Gregory-Wodzicki, 2000). Water is a scarce resource in the plateau and it is naturally enriched in As with concentrations that are often above the limit recommended for human consumption (Argentina: 50 μg/L; R 34/19, 2019; Bolivia, Chile, and Peru: 10 μg/L; Gobierno de Bolivia, 2005; Peru, Ministerio de Salud, 2011; NCH 409, 2006).

In this extreme region, Cenozoic volcanism and closed basin hydrology are the most important geological and hydrogeological features. Drainages are not connected to the ocean and converge in large lakes and salt flats at the center of the basins. Arsenic is found in all water types of the plateau over a wide range of concentrations ranging from 10 μg/L to more than 10,000 μg/L (Tapia et al., 2019). In terms of water treatment to remove As, centralized treatment systems can be found mainly for towns in which capture of surface waters (generally with low As concentrations) is used (as observed in Argentina). However, population living in rural areas generally rely on groundwaters for cooking and drinking (with generally high As concentrations) lacking remediation strategies. Some alternative low-cost methods (i.e., zero- valent iron method combined with citrate and solar light, and sunlight-assisted As removal) have been successful applied to remove As from waters in small towns of Chile and Bolivia nearby the Altiplano-Puna plateau that should be considered where communities are at risk of exposure to this metalloid (Tapia et al., 2019).

Despite the health risks of living in this As-rich and water scarce environment, not all of the Altiplano-Puna is properly characterized and there is a lack of information regarding the basic As geochemistry in the region (Tapia et al., 2019). Therefore, the aim of the IGCP-707 project is to determine: (i) the origin of As; (ii) its geochemistry and mobility; (iii) its distribution in the environment; and (iv) its effects in the local community and unique biodiversity. We aim to improve human health by facilitating As remediation and capacity building in the local communities, and increase scientific knowledge that could be transferred to other sites in the world with high As concentrations. With a multidisciplinary approach, the studies were carried out in selected sites located within the different countries of the plateau (Table 1 and Fig. 1). In this report we summarize the activities achieved by the IGCP-707 project from 2020 to 2022.

Main Activities of the Project

Webinar Lecture Series

The IGCP-707 project started on March 2020 and at the same time we faced the coronavirus pandemic. Therefore, our planned activities such as trips for meetings, conferences, and field work suffered restrictions, especially during the first year of the project. In this framework, we created a cycle of webinar series to provide an environment in which not only the IGCP-707 project members were able to meet and discuss, but also for the scientific community, students, and stakeholders. The main topics of the webinars were related to the origin, geochemistry, and geomicrobiology of arsenic, its effects on human health, and remediation technologies. The study cases presented were not only focused on the Altiplano-Puna regions but also in other sites of the world in which As is an issue. In total, 15 webinars (Appendix 1) with lecturers from different countries (Argentina, Chile, Bolivia, El Salvador, Germany, Mexico, Sweden, Switzerland, United States, and Uruguay) were organized. More than 500 participants from different countries were actively attending with a strong presence of students from Latin America. The streamed lectures are available at present for further views in the YouTube Channel (@IGCPUNESCO707) created for this activity as well as on the web site of the project https://ibigeo.conicet.gov.ar/unesco/. These webinars provided strong international visibility of the As issue of the region that had historically received little attention from the scientific community and local authorities.

Field Work

Field work was performed during 2021 and 2022 in Argentina, Bolivia, and Chile. The project leaders, research collaborators, and students were actively participating on field work in areas strategically selected to achieve our objectives (Table 1 and Fig. 1). Samples were taken from different inorganic and organic matrices (river waters, lagoon waters, thermal waters, fluvial sediments, soils, vegetation, and plankton) to characterize the biogeochemical cycle of As in the region. Moreover, blood, urine, and stool samples were taken in inhabitants from selected towns in Bolivia to address the impact of As on human health.

Waters and sediments in Lauca River basin (Chile-Bolivia)

The Lauca River was selected because it is a binational river which originates in the Chilean Altiplano and crosses the border to Bolivia discharging its waters in the Copaisa Lake. The river has a length of 250 km and different lagoons, thermal waters, and several tributaries contribute to its geochemistry. High As concentrations are known for the Lauca River, and its waters are mainly used for irrigation and drinking water. Since the pandemic-imposed border restrictions, the field studies were executed separately in the Chilean and Bolivian side by the leaders and students from each country, respectively. The main objective of IGCP-707 is to achieve a better understanding of the origin, mobility, and spatial variation of As concentration along the basin with a binational perspective. For that, water and fluvial sediment samples for physicochemical analysis and As concentration and speciation were taken in Lauca River and some of its tributaries (Fig. 2).

Table 1. List of sites where fieldwork was conducted during the IGCP-707 project

Site	Country	Type of sample for arsenic analyses	Code in Map (Fig. 1D)
Lauca river basin	Bolivia-Chile	River water; fluvial sediments; vegetation and soils	7 and 9
Cerro Galán caldera	Argentina	Thermal waters	19
Sajama National Park	Bolivia	Thermal waters; vegetation and soils	9
Los Pozuelos basin	Argentina	Lagoon water; river water; plankton; vegetation and soils	13
Uru Chimpaya Nation	Bolivia	Drinking water; blood; urine and stool	D
Uyuni salt flat	Bolivia	Brine waters	E
Sol de Mañana	Bolivia	Thermal mud	11
Milluni mine	Bolivia	Acid mine drainage; secondary minerals; tailings sediments	5

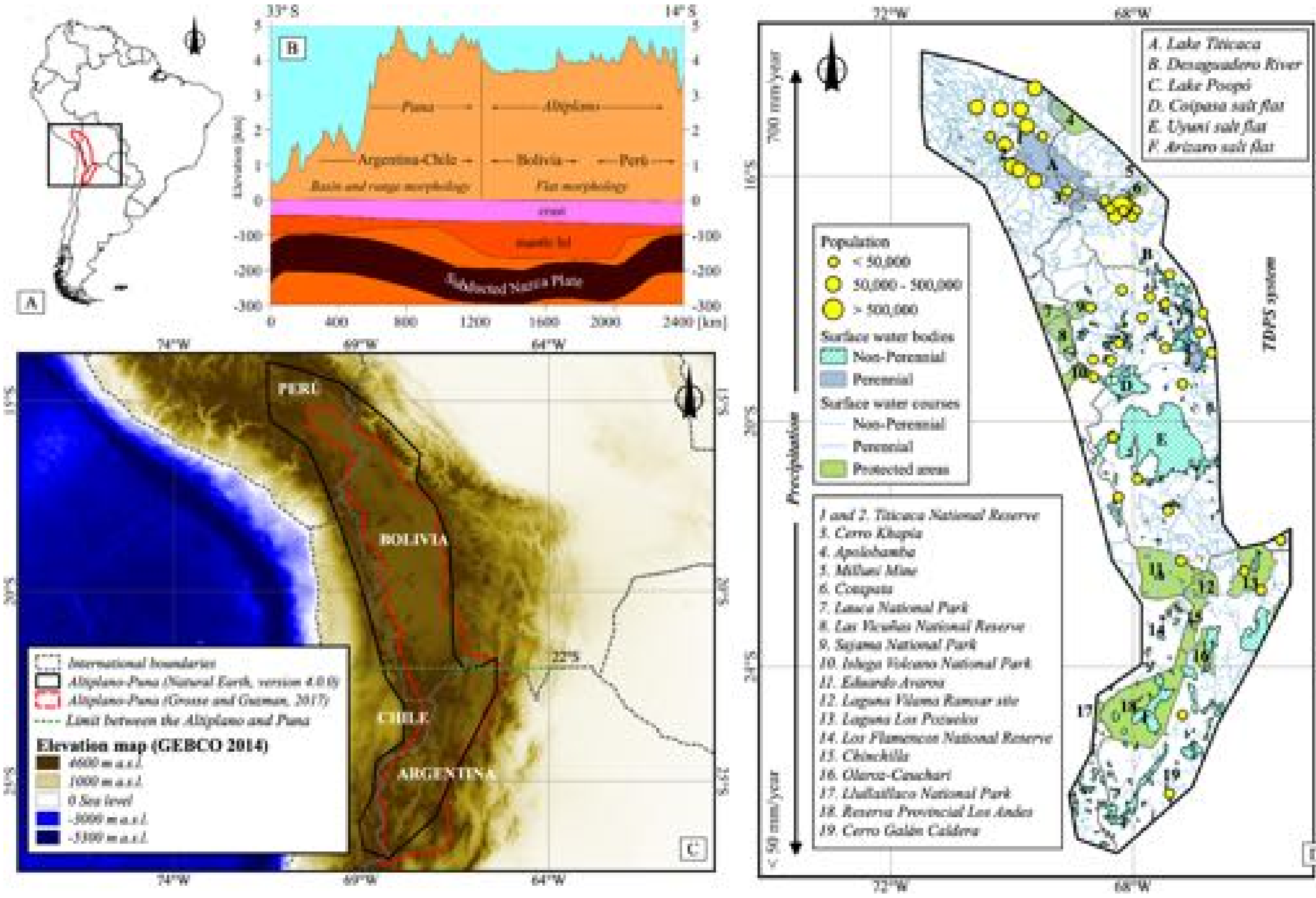

Figure 1. (A) Altiplano-Puna region in South America. (B) Topography and tectonic profile. (C) Borders of the Altiplano-Puna and countries. (D) The study sites referenced in Table 1. Tapia et al. (2019).

Thermal springs in Cerro Galán volcanic caldera (Argentina) and Sajama National Park (Bolivia)

Cerro Galán volcanic caldera is situated in the Southern Puna of Argentina at > 4000 m.a.s.l. (Fig. 1) and constitutes one of the largest calderas in the region (30 km long and 20 km wide). Different water types are present in the area such as thermal springs and fumaroles that reach temperatures of up to 85 ℃, river waters from snow melting, and the brines belonging to the Diamante lagoon. This is a hypersaline lagoon situated inside the caldera receiving the discharge of thermal waters with high As concentrations. In this extreme environment microorganisms have adapted to tolerate the presence of As and benefit from it as a source of energy for their growth. This mechanism is considered as an analog to As cycling on early Earth that may have driven microbial life (Sancho-Tomás et al., 2020). Despite the relevance of As as a metabolic energy source, a study on its origin in these waters has not been addressed. During the field work, water samples for chemical analysis, As speciation, and secondary mineralogy characterization were collected to better understand the origin and mobility of As in the caldera (Fig. 3). This research work was performed in collaboration with a project funded in parallel with "*Estimation of the geothermal potential of the Caldera Cerro Galán through the study of diffuse CO_2 emissions and fluid geochemistry (Southern Puna)*" granted by MINCyT-Argentina and led by researchers of IGCP-707, IBIGEO-CONICET-University of Salta, and GESVA – IDEAN-National University of Buenos Aires.

Sajama National Park (SNP) in Bolivia is the first national park created in 1939 to protect queñua forest, preserve semi-arid high Andean ecosystems, conserve wild flora and fauna, protect the headwaters of the basin and promote scientific research. Sajama Mountain in the SNP is an important source of surface and groundwater in the area but one of the greatest changes is the deglaciation due to global climate change. Sajama geothermal field is located to the west of the mountain and has more than 80 hot springs that reach temperatures of up to 85 ℃. Thermal water discharges into Sajama River and is believed to be a natural source for As contamination of the river. During the fieldwork, water samples for physicochemical analysis, total As and As redox speciation were collected to better understand the origin and mobility of As in the river (Fig. 3).

Plankton in Los Pozuelos Lagoon (Argentina)

Plankton plays an important role in the aquatic environments of the Altiplano-Puna since it is a vital element for water birds' diets. The Altiplano-Puna region constitutes one important refuge of aquatic habitat within a desert matrix in Central Andes and harbors protected migratory bird species such as High Andean Flamingos (*Phoenicopterus jamesi, Phoenicopterus andinus, Phoenicopterus chilensis*) and

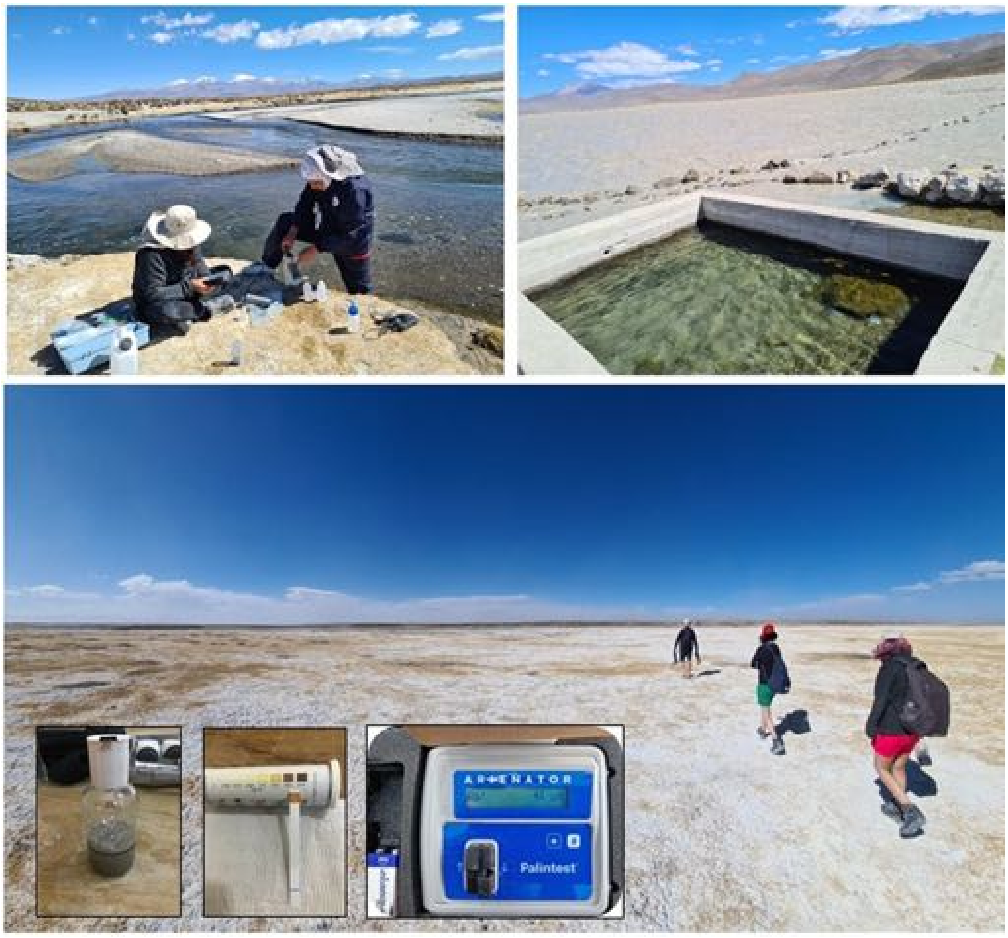

Figure 2. Sampling water and fluvial sediments in Lauca River basin.

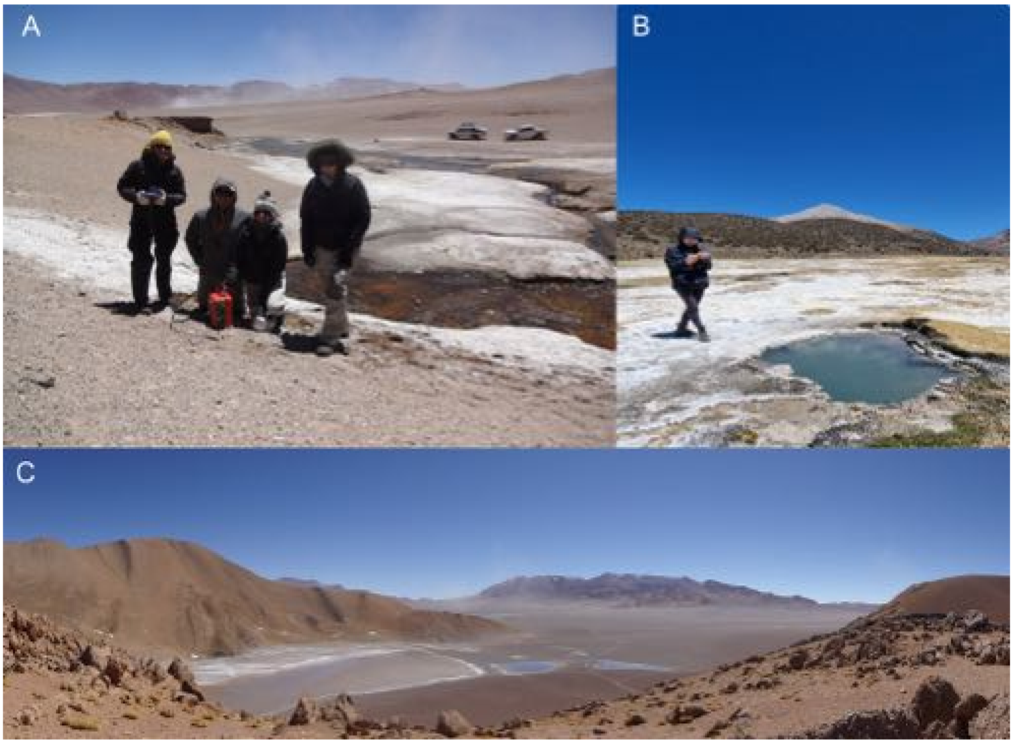

Figure 3. (A) Sampling thermal waters and measuring CO_2 in Cerro Galán volcanic caldera. (B) Sampling thermal waters in Sajama National Park. (C) Panoramic view of Cerro Galán volcanic caldera.

Figure 4. (A) Flamingos in Los Pozuelos Lagoon. (B) and (C) Student Carla Andrea Martinez and Park rangers sampling plankton in Los Pozuelos Lagoon. (D) Crustaceous sampled in Los Pozuelos Lagoon.

other aquatic birds.

A meeting with members of the *High Andean Flamingos Conservation Group*, the *Argentinian National Parks Administration*, the Argentinian *INALI-CONICET institute*, and researchers from Bolivia was achieved to initiate a study on the effect of water chemistry and As on plankton and water birds. In this framework, the first samples of plankton for As and metal determinations were taken in Los Pozuelos lagoon (Fig. 4). This lagoon is situated in Los Pozuelos basin in the Argentinian Puna, which constitutes a UNESCO Biosphere Reserve. The lagoon has been declared a National Natural Monument by the Argentinian government (National Parks Administration), Ramsar Site (Ramsar Sites Information Service), and a site of importance for migratory shore birds (Western Hemisphere Shorebird Reserve Network).

Vegetation in Los Pozuelos basin (Argentina), Sajama National Park (Bolivia, and Lauca River basin (Bolivia and Chile)

The main objective is to identify the adaptation of vegetation to natural high As concentrations and the development of bioremediation techniques in soils affected by As and metals pollution from acid mine drainage. This study is performed in collaboration with researchers from INTA (Instituto Nacional de Tecnología Agropecuaria, Estación Experimental Salta, Argentina); Herbario Nacional de Bolivia (Universidad Mayor de San Andrés, La Paz – Bolivia), and Soil Science and Agricultural Chemistry laboratory at University of Vigo Spain.

Vegetal species present along the Altiplano-Puna region were selected for this study. The most representative species selected in Los Pozuelos basin Argentina were *Parastrephia lucida (Meyen) Cabrera; Parastrephia quadrangularis (Meyen) Cabrera; Distichlis humilis Phil.; Festuca dolichophylla J. Presl.;* and *Ruppia filifolia (Phil.).* In Bolivia, selected plant species were *Parastrephia lepidophylla*, *Baccharis tola* and *Azorella compacta*, all of them collected within the Sajama National Park. In Lauca River basin, Chile, *Festuca orthophylla* and *Parastrephia quadrangularis* were sampled (Fig. 5).

Human health Uru Chipaya Nation (Bolivia)

Blood, urine, and stool samples were taken in Ayparavi, Wistruyani, and Aransaya communities, this work was made in collaboration with the project Microtoxbol: "*Health and environment interactions in people exposed to arsenic*" (Fig. 6). Elevated levels of arsenic in the drinking water in Chipaya were found indicating high risk exposure to As.

Conferences and Courses

Between 2020 and 2022 members of the project actively participated attending and organizing conferences, sessions, and pre-conferences courses.

- ***Virtual Goldschmidt 2020***: Students and leaders of the project

Figure 5. Sampling soil and vegetation at Sajama National Park, Los Pozuelos basin, and Lauca River basin.

Figure 6. Blood sampling by Dr. Noemi Tirado at Uru Chipaya Nation, Bolivia.

gave talks in session 13g Theme 13 (Inostroza et al., 2020; Murray et al., 2020; Sepúlveda et al., 2020).

• ***Geological Society of America Congress: GSA 2020 Connects Online*:** Session T173: Arsenic, Fluoride, Manganese, and Radiogenic Contaminants in Groundwater Systems—Scientific Knowledge, Public Health Concerns, and Removal Technology II. Dr. Joseline Tapia coordinated a session and presented a talk "*Distribution and potential mobilization of As, Cu, and Zn in the Camarones River Basin, Surire Salt Flat, and Caritaya Dam, Northern Chile*".

• ***8th International Congress & Exhibition on Arsenic in the Environment, The Netherlands, 2021*:** Drs. Noemi Tirado and Joseline Tapia participated as speakers with the talks: "*Genetic adaptation and toxicity due to arsenic exposure in women from the Poopó Lake communities*" and "*Geochemical baseline of arsenic in surface water and sediments of Chile: Regional distribution and its relationship to geology and climate*" Dr. Jesica Murray was chairing the session "*Arsenic mobility and fate in soils, sediments and mining wastes*".

• ***Carcinogenesis and environmental teratogenesis Congress (Latin American Association of Mutagenesis), 2021*:** Dr. Noemí Tirado was organizer and speaker in the congress. She also coordinated the round table on drinking water the challenge continues. Her talk was entitled: "*Elimination metabolism and toxicity of arsenic in exposed women from the communities of Lake Poopó – Bolivia*".

• ***Goldschmidt 2022 (Hawaii)*:** Organization of session "*Geochemistry of arsenic in the environment: Source, fate and remediation (Theme 13, session g)*" (Fig. 7). The session was organized in collaboration with Dr. Ilaria Fuoco and Dr. Carmine Apollaro from Università della Calabria, Italy. At the event, Noemí Tirado presided on site over the presentation of 6 posters, as well as the 24 oral presentations where there was a Key Note lecture presented by Professor Prosun Bhattacharya (KTH, Sweden) with the theme: "*Integrating digitalization of the decadal understanding on the hydrogeochemistry of geogenic arsenic and societal aspects for Sustainable Arsenic Mitigation in Bangladesh*".

• ***XVIII Argentinian Geological Congress, Puerto Madrin, Argentina 2022*:** Organization of Session on Sustainability in Mining and a Short Course on Acid mine drainage. The session and the short course were organized by the leaders Dr. Jesica Murray and Dr. Kirk Nordstrom in collaboration with Dr. Karina Lecomte (CICTERRA-CONICET-UNC, Argentina).

• ***29th IAGS 2022, Viña del Mar, Chile*:** Dr. Jesine Tapia was the vice-president of the congress. PhD Student Pablo Paquis gave a talk entitled: "*High-altitude Chilean hot springs: Hydrogeochemstry characterization and biological relationships in Lirima, a window to early Earth*".

Workshop Bolivia 2022

A two-day workshop was held on August-22-23 at Major Universidad de San Andres, La Paz, Bolivia, organized jointly by the Genetics

Figure 7. Participation at Goldschmidt 2022 in Hawaii. Organized Session 13g: Geochemistry of arsenic in environment: source, fate and remediation.

Institute and the Department of chemistry. The first day was devoted to As geochemistry, toxicity, and remediation. Three IGCP-707 leaders gave presentations, one by Dr. Nordstrom on *The geology and water chemistry behind elevated arsenic on the Earth's surface*, one by Dr. Ormachea on *The presence of natural arsenic in Bolivia*, and one by Dr. Tirado on *Elimination metabolism and harmful genotoxicity by arsenic exposure to drinking water among populations of the Bolivian Altiplano.* The second day was devoted to fluoride geochemistry, toxicity and remediation. Dr. Nordstrom gave a keynote on *Fluoride in groundwater: Sources and mechanisms.*

A field trip was also included in the workshop. Participants collected water and mineral samples in the Bolivian Altiplano where waters with contrasting origin and chemistry and As concentrations occur.

Salar de Uyuni: Is the world's largest salt flat of 10,582 km^2 and at an elevation of 3,656 m a.s.l. Lacustrine mud that is interbedded with salt and saturated with brine underlies the surface of Salar de Uyuni. Several natural brine springs emerge from the surface of the crust. Students collected brine water samples for chemical analysis and took field measurements of pH, temperature, and conductivity (Fig. 8). In this emblematic site of Bolivia students and professors also had time to have fun pictures (Fig. 8).

Sol de Mañana: Is a geothermal site in Potosi Department of south-western Bolivia; it extends over 10 square kilometers, between 4800 and 500 m above sea level. The area is characterized by intense volcanic activity and sulphur springs field is full of mud lakes and steam pools with boiling mud. Students collected mud samples and took field measurements of pH, temperature and conductivity (Fig. 9A).

Milluni Mine: The Milluni Valley is located at more than 4000 m above sea level in the Eastern Andes only 20 km north of La Paz city administrative capital of Bolivia. A very large volume of sulfide-rich mine waste has been deposited in this area by different mining operations of Milluni mine, draining a variety of potentially harmful elements including As into the main reservoir used to supply drinking water to the inhabitants of La Paz. Students collected water and mineral samples from acid mine drainage and sediment deposits in the area and took field measurements of pH, temperature, and conductivity (Fig. 9 B and C).

Figure 8. Sampling brines at Uyuni salt flat.

Figure 9. (A) Sampling thermal waters in Sol de Mañana site. (B) and (C) Lessons on acid mine drainage at Milluni Mine with Dr. Kirk Nordstrom.

Results

Scientific Achievements

Several scientific papers were published during this project in which the leaders participated as first authors or collaborators. The IGCP-707 project had an important role because it enhanced the scientific collaborations among the participants. These publications filled scientific gaps on the topic, bringing important knowledge needed for a comprehensive understanding of the origin, distribution, and biogeochemistry of As in the Altiplano-Puna plateau (Escalera et al., 2020; Murray et al., 2021; Plaza-Cazón et al., 2021; Quino-Lima et al., 2020 a, b; Tapia et al., 2021; 2022 a, b, c; Murray et al., 2023). These publications cover a wide range of subjects including geology, geochemistry, environmental sciences, hydrogeology, remediation methods, and human health. Three important works published previously: De Loma et al., (2019); Murray et al., (2019) and most importantly Tapia et al., (2019) settled the scientific bases for the IGCP-707 project.

IGCP-707 leaders participated as guest editors in a Special Issue on Journal of South America Earth Sciences: *The Unique Altiplano-Puna Plateau: Environmental Perspectives* (Tapia et al., 2022b). This Special Issue was dedicated to Earth Science research in the Altiplano-Puna Plateau with emphasis on the environment. The main objective was to present new and comprehensive analyses with interpretations for the extreme, yet pristine Altiplano-Puna region which has been scarcely characterized from an environmental perspective. The research papers published on this edition cover a wide range of topics related to hydrogeochemical, climatic, and anthropogenic processes on the origin and mobility of economically important elements and contaminants, as well as environmental issues and bioindicators of ecological conditions in surface waters. This issue is highly relevant because it inspires future studies in the region with an emphasis on the environment and human health.

Thanks to the IGCP label, additional funding from local and international research agencies was obtained: "*Estimation of the geothermal potential of the Cerro Galán caldera through the study of diffuse CO_2 emissions and fluid geochemistry (Southern Puna- Central Andes-Argentina)*" (granted by MINCyT-Argentina; PICT Project Nr. 2019-03171); "*Remediation of impacted soils in mining areas with bio-adsorbents*" (granted by the Galicia government from Spain; Project Nr. 815A 2021/1); "*Hydrogeochemistry and redox controls on the ori-*

gin and mobility of arsenic and natural hydrogen" (Granted by CONICET Argentina, PIBAA Project 2022-2023). In these projects the IGCP-707 leaders are the Principal Investigators or main collaborators.

Students' Participation

Undergraduate students, masters, and PhD students, and Postdoc fellows belonging to different universities from Argentina, Bolivia, and Chile actively participated on this project. National University of Salta from Argentina (Edgar Emanuel Leguizamón and Carla Andrea Martinez); San Andrés Major University from Bolivia (Lizangela Huallpara, Marizol Flores, Ktlyn Aguirre de la Quintana, Nicole Jimeno Ruiz, Nicol Rodriguez Taboada and Josue Mamaní); Universidad Católica del Norte and Universidad Santo Tomás from Chile (Manuel Inostroza Pizarro, Bianca Sepúlveda). Educational training was performed for students from different disciplines such as geology, chemistry, biology, and medicine showing the interdisciplinary spirit of this project. Students and fellows were actively participating on the webinar activities, attending the courses, workshops, and being part of the field work.

Society and Stakeholders

Regarding the benefits to society, this project is focused on the assessment of water/soils/vegetation/sediments quality and the identification of affected population by As exposure. Arsenic analyses in drinking water were made in different communities of Bolivia and Chile along the Lauca river basin.

Regarding human health, As was detected in the communities of Nacion Uru Chipaya (Aypari, Wistruyani, Aransaya and Manansaya) showing concentrations of As in consumption water which are above limits for human consumption. Population living in the Uru Chipaya communities were exposed to arsenic through drinking water for centuries and preliminary data from biological samples of blood and urine taken from the inhabitants indicate exposure to As.

In terms of remediation strategies, hydrogeochemistry data was exchanged with INTA-Argentina (National Institute of Industry Technology) to support As remedation via the implementation of sustainable As-free water facilities in the rural areas of Los Pozuelos basin. Previous studies in the basin already detected areas requiring implementation of remediation technology (Murray et al., 2019). This scientific knowledge was used to promote such technology which is currently under development.

Project leaders collaborated with stakeholders such as NGO and government institutions. A collaboration with the Argentinian NGO *Fundación Humedales* was developed to identify the effect of acid mine drainage on the concentration of metals (including As) in rivers and the lagoon in Pozuelos Basin. This study identified the negative result of acid mine drainage on rivers and fluvial plains and the potential pollution of aquifers by As mobilization in groundwater.

We met with local authorities and provided reports of the investigations. These activities are of high relevance because they contribute to local knowledge of environmental and epidemiological issues and constitutes the first steps for implementation of mitigation plans and generation of local capacity-building.

Conclusions

The work conducted on the IGCP-707 project provided new scientific insights into the cycle of As in the Altiplano-Puna region of South America and its effect on human health and biodiversity. Our interdisciplinary research and international collaboration had a substantial influence in the region and reinforced the visibility of the As issue at local and international level. This project permitted the creation of a solid research network between the Southern and Northern Hemispheres, fostering the interdisciplinary participation of young researchers, students, and women. An extension of the project was obtained to continue our work during 2023.

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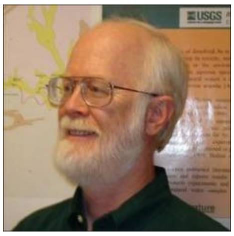
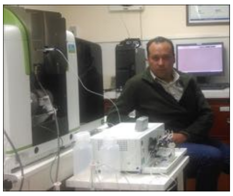


D. Kirk Nordstrom is a senior scientist of more than 40 years experience with the United States Geological Survey (USGS). Dr. D. Kirk Nordstrom is recognized internationally for his research on acid mine drainage, radioactive waste disposal, geothermal chemistry, geomicrobiology, arsenic geochemistry, thermodynamics, and geochemical modeling.



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