METAL(LOID)S DISTRIBUTION IN NORTHERN ATACAMA REGION HYDROLOGICAL BASINS

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Introduction

The Atacama desert corresponds to the driest desert on Earth and is located in the Atacama Region, northern Chile (). The El Salado River is the only water system that drains into the Pacific Ocean in northern Atacama Region, and is one of the most susceptible water systems in this area. Indeed, two highly sensitive ecosystems are present close to this river, the *Nevado Tres Cruces* in the Andes, and the *Pan de Azúcar*, on the coast (Earle et al., 2003; Thompson et al., 2003;).

Northern Atacama Region has been historically affected by mining activities because of the richness of ores in the Andes mountains. In fact, during the early 1900s this area was affected by the Potrerillos mining operations, and afterwards, by the El Salvador mining operations, a porphyry copper deposit (Gustafson and Hunt, 1975). Between 1938 and 1975 mine wastes from the El Salvador operations were dumped into El Salado River, and therefore into the Chañaral Bay () without any treatment (Paskoff and Petiot, 1990).

In this work a preliminary survey of the concentration of 8 metal(loid)s in waters of El Salado River are presented and compared to international water recommendation values and regulations.

Study area

Geology and ore deposits

The current geology in this area is controlled by the Central Volcanic Zone (CVZ) in which <60 Ma Nazca plate lithosphere is subducting bellow Southamerican plate at 7-9 $cm \cdot year^{-1}$, in this zone continental crust is ≥ 70 km thick and basement ages range from Late Pre-Cambrian to Paleozoic (Stern, 2004). Cenozoic volcanism in the Atacama Region has been related to: (1) Early Miocene to Pleistocene andesite–dacite stratovolcanoes of the main arc; (2) Early Miocene to Pliocene silicic ignimbrite deposits and lava domes that occur in the main arc and back-arc regions; and (3) small, Pliocene to Pleistocene basaltic centres in the back arc (Schnurr et al., 2007). Ore deposits in the Atacama Region have been classified in longitudinal metallogenic belts, that from west to east, correspond to: iron oxides copper-gold (IOCG) deposits, Cu-Mo porphyries and Au-epithermal and porphyry deposits.

Numerous Mesozoic IOCG ore deposits are hosted in the coastal cordillera of northern Chile conforming the Upper Jurassic-Lower Cretaceous metallogenic sub-province in the Central Andes (Sillitoe, 2003). The deposits include both, the magnetite-dominated, sulphide-poor deposits of the Chilean Iron Belt (Espinoza, 1990) and productive Cu-Au centres (e.g., Candelaria-Punta del Cobre and Mantoverde districts; Benavides et al., 2007). Continuing to the east, the most important deposit corresponds to El Salvador porphyry Cu-Mo, which formed during the Eocene (42-41 Ma) in the Indio Muerto district (26°15' S; Cornejo et al., 1997). This deposit forms part of the major Cu-Mo porphyries in Chile (Eocene-Oligocene metallogenic belt;). The Maricunga metallogenic belt is located in the Andes between 26-28°S, where mineralization encompasses both, porphyry-type Au and Au-Cu, and epithermal Au and Ag-Au high sulphidation, acid sulphate type deposits (Sillitoe et al., 1991).

Climate and hydrological systems

The climate in this area of the Atacama desert is characterized, from west to east, by: the coastal desert, the normal desert, and the steppe-like and dry climate in the Andes (Inzunza, 2006). In addition, this area of the Andes chain is classified as the Dry Andes (Lliboutry, 1999).

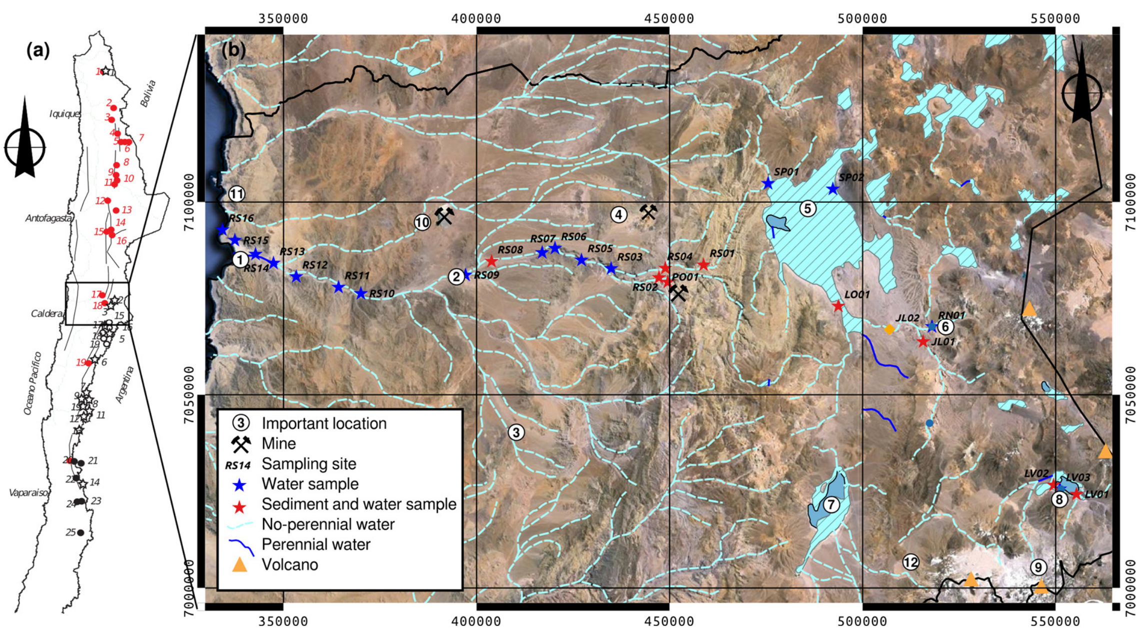
The Atacama Region features numerous salt-flats, the most important being the Pedernales, Maricunga and Laguna Verde. The El Salado river is the main water source in northern Atacama Region.

The Pedernales basin and salt-flat are the largest of the Third Region (). This basin is located at 3,370 m a.s.l. and is a mixture of sedimentary terrains originating from volcanic and intrusive rocks. The salt-flat is a crust of gypsum ($CaSO_4$) and halite (NaCl) with a few lagoons on the border. The basin, salt-flat and lakes surface areas are 3,620, 335 and 0.6 km^2, respectively. Precipitation in Pedernales is scarce, approximate 100 mm year^{-1} in the salt-flat and 150 mm year^{-1} in the eastern border. The potential evaporation is 1,200 mm year^{-1} and the average temperature is 4°C in the salt-flat (Risacher et al., 2003, 1999). In the 1930s a tunnel was drilled that drains salty water from Pedernales to El Salado River (Risacher et al., 1999), so the Pedernales basin has not been endorheic since 1930.

The El Salado river originates in the western Andes, 200 m separate this river of the Pedernales basin. El Salado river used to drain into the Pacific Ocean at Chañaral, yet in the mid 1970s it was channelled to drain 10 km north of Chañaral, at Caleta Palito (Ramirez et al., 2005;). In the eastern area, this river experiences similar climatic conditions to those of the Pedernales basin. In the coast, average precipitation, temperature and humidity are 20 mm year^{-1}, 16°C and 76%, respectively (Inzunza, 2006).

Laguna Verde is located in the Andean range near the Argentina border at 4,350 m a.s.l. The Nevado Ojos del Salado volcano (6,893 m s.n.m.) closes the basin to the south (). The basin and lake surface areas are 1,075 and 15 km² respectively. Precipitation, potential evaporation and temperature are 170 mm year^{-1}, 1,000 mm year^{-1}, and 1℃, respectively. Laguna Verde is a salty lagoon feed by rivers and watersheds, most of them located to the south and west of the basin (Risacher et al., 2003, 1999).

The hot-springs in this area correspond to Juncalito at 4,180 m a.s.l. with temperatures in the range of 30-40℃ (Hauser, 1997), Río Negro at 4,150 m a.s.l. with an average temperature of 35℃ (Hauser, 1997), and Laguna Verde, at 4,350 m



a.s.l., with an average temperature of 40.5℃ (Risacher et al., 2003;).

Figure 1. (a) Figure 1. (a) Upper Eocene-lower Paleocene (red) and Upper Miocene-lower Pliocene (black) metallogenic belts of northern Chile. In the study area: 17. El Salvador (42 Ma); 18. Potrerillos (36 Ma). Upper Miocene-Lower Pliocene: 2. Esperanza (22-21 Ma); 3. La Coipa (23-22 Ma). Modified from (Maksaev, 2001); (b) Sampling sites and important locations: 1 Chañaral Bay; 2 Diego de Almagro; 3 Inca de Oro; 4 El Salvador; 5 Pedernales salt-flat; 6 Río Negro hot-springs; 7 Maricunga salt-flat; 8 Laguna Verde salt-flat and hot-spring; 10 Pampa Austral: 11 Pan de Azúcar National Park; 12 Nevado Tres Cruces National Park.

Sampling sites and methodology

Samples were took in a nearly SE-NW trend in the Altiplano area, where water sources are highly variable. In the El Salado River samples were took in an E-W transect ().

A total of 25 water, and respective filters, samples, 10 sediment samples and 1 precipitation sample (Pedernales salt-flat) were took (). Water samples were kept acidified in acid cleansed, 200 mL propylene vials and at 4°C until analysis, filters were sealed in the field, and sediments were kept in 125 mL sterile sampling bags.

Water samples were analysed for As by AAS in the Chemistry Department of Universidad de Antofagasta. Arsenic, Cd, Cu, Li, Pb, Sb, U and Zn were studied by ICP-MS in the Géosciences Environnement Toulouse (GET) Laboratory. The analytical methods employed were quality checked by analysis of certified international reference water (SLRS-5;). For As, Cu, Pb and Sb accuracy was within 10% of the certified values and the analytical error (rsd) generally better than 10% for concentrations 10 times higher than the detection limits; Cd, U and Zn were over estimated and Li has no stardard ().

Filters were observed by scanning electronic microscopy (SEM) and sediments mineralogy was preliminary characterized by QEMSCAN. These studies were performed in the Electronic Microscopy and in the Research and Mineralogical Service Centre (Centro de Investigación y Servicios Mineralógicos; CISEM) Laboratories, respectively, in the Geology Department of Universidad Católica del Norte.

Table 1. Standards, all values in μg·L^{-1}. Lithium values have no standard, As, Cu, Pb and Sb are precise and exact (less that 10% error), Cd, U and Zn are precise, yet are over estimated.

Standard	As	Cd	Cu	Li	Pb	Sb	U	Zn
SLRS-5-1	0.458	0.0080	15.27	0.563	0.086	0.34	0.111	1.27
SLRS-5-2	0.445	0.0101	15.74	1.921	0.081	0.33	0.108	1.25
SLRS-5-3	0.466	0.0095	16.08	1.379	0.086	0.34	0.110	1.21
SLRS-5 cert	**0.413**	**0.0060**	**17.40**	**-**	**0.081**	**0.30**	**0.093**	**0.85**
SLRS-5 error	**0.039**	**0.0014**	**1.30**	**-**	**0.006**	**-**	**0.006**	**0.095**

Results and discussions

Dissolved fraction

Arsenic. Concentrations of As to the west of Diego de Almagro (RS09;) are under international recommendations (10 μg L^{-1}; United States Environmental Protection Agency-US EPA, 2009; World Health Organization-WHO, 2011). Whereas, east of this locality most samples show concentrations over 1,000 μg L^{-1}. The highest concentration of this metalloid is found in the eastern part of the Salar de Pedernales basin, in which As value is over 10,000 μg L^{-1} (and).

Cadmium. When comparing Cd concentration to WHO recommendations (3 μg L^{-1}; WHO, 2011), eastern Pedernales salt-flat and close to the Potrerillos mining town, Cd concentrations are higher than WHO requirements. Considering US EPA normative, Cd is over the regulation only in the eastern border of the Salar de Pedernales basin (and).

Copper. Despite El Salvador and Potrerillos are characterized by the Cu exploitation and ore treatment, Cu concentration in the studied sites are under US EPA regulations (1,3 mg L^{-1}). The highest concentrations of Cu were determined in Potrerillos and Diego de Almagro (and).

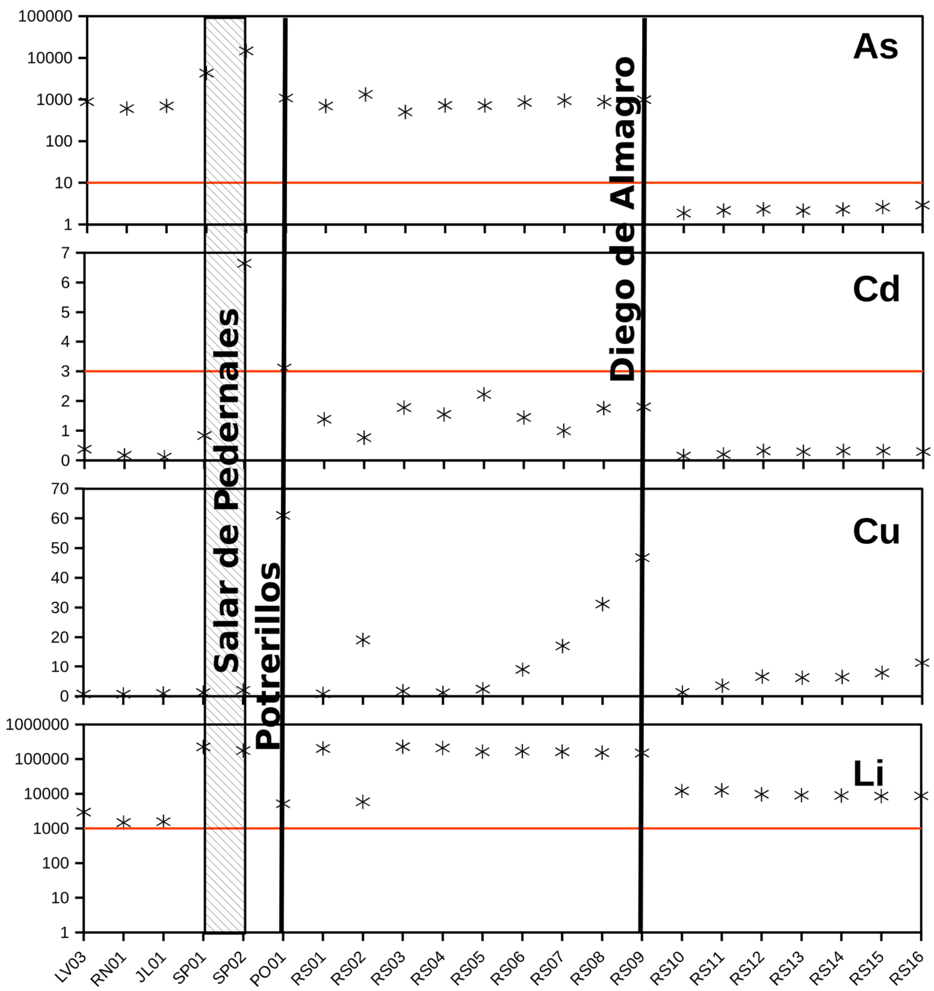


Figure 2. E-W transect of dissolved As, Cd, Cu and Li concentration. In red international water regulation. US EPA (2009) for As and Cu; WHO (2011) for Cd; Aral and Vecchio-Sadus (2008) proposal for Li.

Lithium. For this element it has been recommended a daily intake of 14.3 µg kg^{-1} (Aral and Vecchio-Sadus, 2008), therefore the diary limit for a 60 kg person is in the order of 850 µg. Water of all the studied basins present Li concentrations over 1000 µg L^{-1}, which means that 1 L of northern Atacama Region water contains the maximum dissolved Li concentration that a 60 kg person might ingest by day (and).

Lead. The US EPA regulations indicate that Pb is a highly toxic element in all forms and that this element should not be present in water (US EPA, 2009). In the studied basins, Pb is present in the Pedernales salt-flat and in El Salado River, from Diego de Almagro to the east (and).

Antimony. The US EPA regulations require concentrations under 6 µg L^{-1} for Sb in drinkable water (US EPA, 2009). The study area is characterized by lower concentrations of this element, with the exception of the Potrerillos site (and).

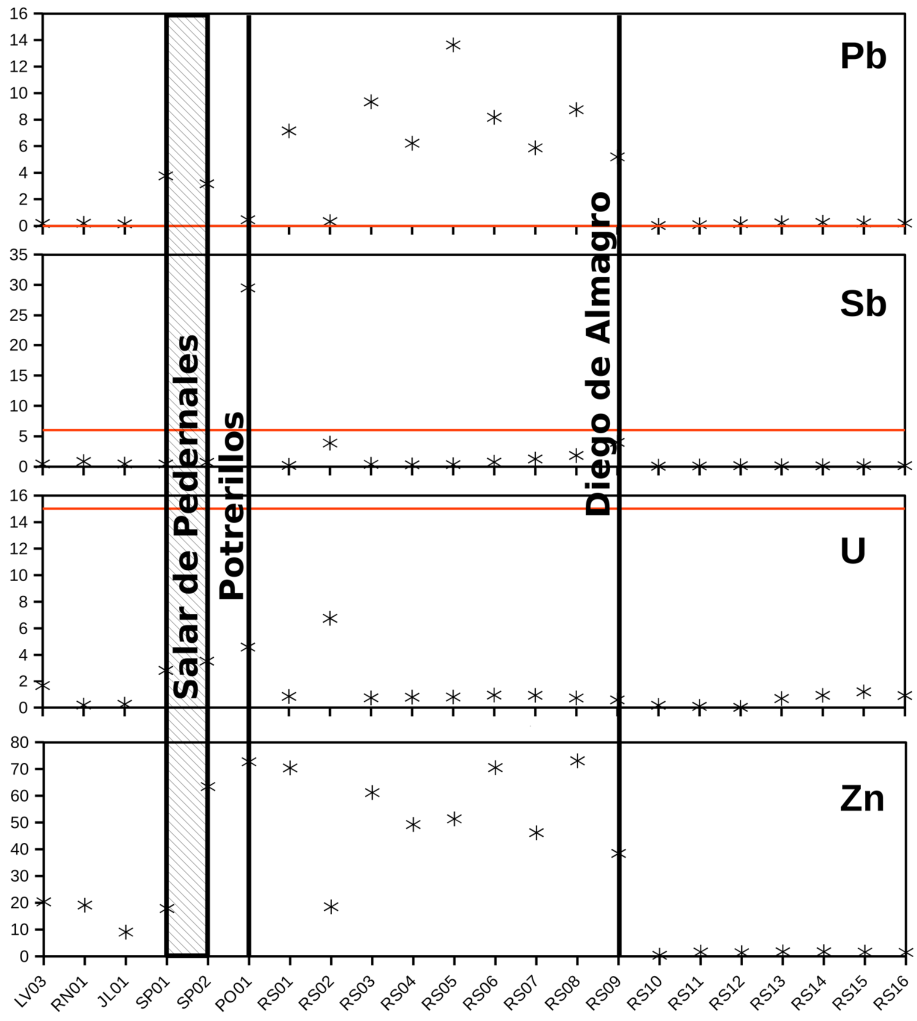


Figure 3. E-W transect of dissolved Pb, Sb, U and Zn concentration. In red international water regulation. US EPA (2009) for Pb, Sb and Zn; Merkel and Hasche-Berger (2006) suggestion fou U.

Uranium. In relation to dissolved metallic U, the regulations and recommendations (without considering the radioactive form) are variable and range from 15 to 30 µg L^{-1} (Merkel and Hasche-Berger, 2006; US EPA, 2009). Therefore this element is below the current international standards for drinkable water in all the studied basins ().

Zinc. The highest concentrations of Zn are associated with the eastern area of Pedernales salt-flat, Potrerillos and El Salado river until Diego de Almagro (from east to west; and).The US EPA recommends dissolved Zn concentration below 5 mg L^{-1}. All samples showed concentrations lower than this standard (US EPA, 2009).

Despite water of Pedernales basin is used in mining, it represents one of the few water resources of northern Atacama Region, this water is mixed with El Salado river through an anthropic channel. In the future is highly probable that this water will be used for human consumption and as shown in this study As and Li are extremely concentrated in the water and therefore the use of this resource might be difficult without the propper treatment.

Table 2. Elements concentration in filtered (0.44 µm diameter) water samples, all values in µg·L^{-1}.

Site	As	Cd	Cu	Li	Pb	Sb	U	Zn
LV03	889.4	0.378	0.73	2957	0.177	0.431	1.660	20.34
RN01	606.6	0.171	0.63	1471	0.194	0.836	0.186	19.12
JL01	699.4	0.109	0.91	1559	0.148	0.431	0.249	9.04
SP01	**4305.6**	0.835	1.19	**224768**	3.764	0.418	2.833	17.85
SP02	**14637.2**	**6.641**	1.98	**175287**	3.166	0.704	3.527	**63.44**
PO01	1085.9	**3.107**	**60.97**	5127	0.454	**29.518**	**4.588**	**72.69**
RS01	697.5	1.385	0.76	202544	7.153	0.196	0.839	**70.42**
RS02	1322.2	0.767	19.08	5845	0.316	3.868	**6.759**	18.50
RS03	502.8	1.776	1.66	228289	9.346	0.379	0.729	61.19
RS04	723.2	1.545	1.14	209033	6.222	0.286	0.780	49.26
RS05	715.6	2.221	2.35	163273	**13.632**	0.323	0.795	51.37
RS06	851.2	1.442	9.00	168323	8.176	0.733	0.936	70.52
RS07	941.3	0.996	17.05	162769	5.877	1.244	0.918	46.20
RS08	873.3	1.754	31.16	152961	8.755	1.831	0.722	73.07
RS09	**993.9**	**1.798**	**46.74**	**149221**	**5.191**	**3.986**	**0.572**	**38.47**
RS10	1.9	0.147	1.24	12039	0.026	0.073	0.167	0.40

RS11	2.2	0.202	3.48	12533	0.079	0.105	0.086	1.59
RS12	2.3	0.321	6.58	9685	0.160	0.151	0.010	1.33
RS13	2.2	0.291	6.23	9104	0.229	0.129	0.677	1.69
RS14	2.3	0.320	6.42	8893	0.258	0.134	0.918	1.71
RS15	2.6	0.316	7.85	8586	0.220	0.153	1.185	1.56
RS16	2.9	0.297	11.35	8680	0.203	0.165	0.903	1.43

Colloidal and solid fraction

The analyses of 0.44 µm diameter filters obtained from water samples filtration showed that halite and gypsum were the main retained minerals (and or molecules) in the Pedernales salt-flat and El Salado River basins (). In the Laguna Verde and Río Negro hot-springs and Juncalito river, filters also retained diatoms (Achnanthidium;).

Preliminary analyses of sediments mineralogy showed that these samples are composed mainly by feldespar group, quartz, k-feldespar, clay group, mica group, calcite, anhydrite. Sulphides and oxides represent less than 1% in the studied samples.

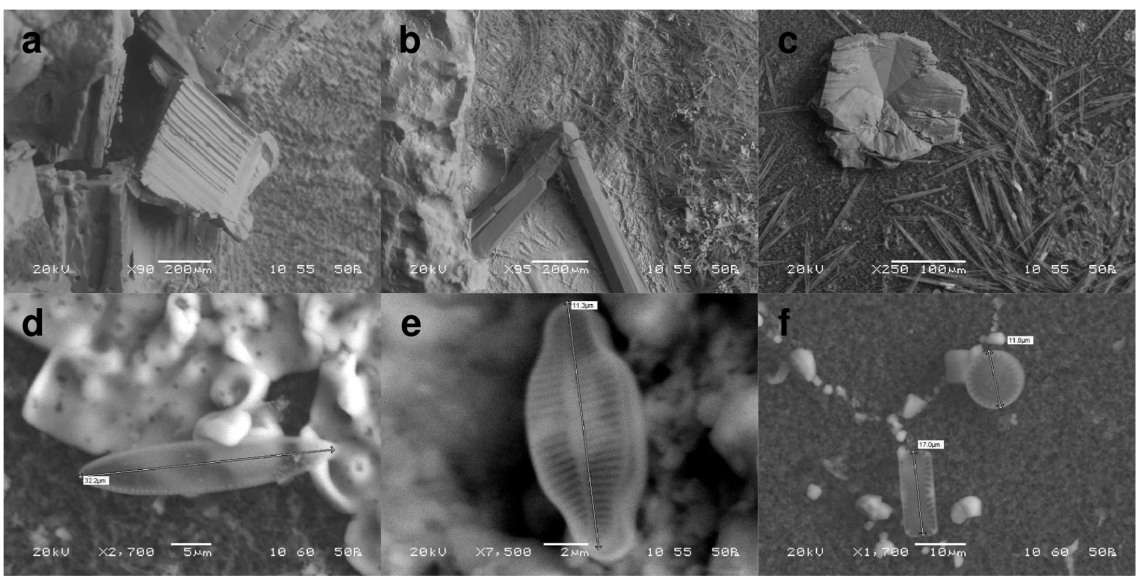


Figure 4. SEM images of studied filters. (a) halite (RS08), (b) gypsum (RS11) and (c) halite (left) + gypsum (right) (RS14) from El Salado River samples, (d) diatoms of Laguna Verde hot-spring (LV02); (e) diatom of Río Negro hot-spring; (f) diatoms of Juncalito River (JL01).

Mineralogies associated with metal(loid)s were not properly determined, yet in three sites As-bearing minerals were observed. In Pedernales salt-flat, the eastern border precipitations presented As mixed with silicates (SP02). In the Potrerillos (PO01) site it was identified an As bearing Fe oxide. In the El Salado river the eastern sediment sample (RS02) exhibited As sulphides.

Conclusions

This preliminary research shows that water of the studied sites is highly concentrated in As and Li. The highest concentrations of As are found to the east of Diego de Almagro and mainly in the Pedernales salt-flat; whereas Li in all the basins shows concentrations considered toxic for drinkable water usage.

Potrerillos mining operations are probably related to high Sb and Cd values, Cd is also found in eastern Pedernales salt-flat.

Following the current regulations, dissolved U concentrations are not considered to threatened this environment. Amazingly and in spite the presence of Cu mining and refining, Cu and Zn values in all the basins are well below international water normative.

Mineralogy in colloidal form corresponds to halite and gypsum, and metal(loid)s bearing mineralogy was hard to asses, yet As bearing Fe-oxides, sulphides and silicates were determined.

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