

# THE MARINE SHORE PORPHYRY COPPER MINE TAILINGS DEPOSIT AT CHAÑARAL, NORTHERN CHILE<sup>1</sup>

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**Abstract.** From 1926 until 1975, the Potrerillos-El Salvador mining district (porphyry copper deposits) sent most of its flotation tailings in suspension through the El Salado River directly to the sea at the Chañaral Bay, Atacama desert, Chile. Over 220 Mt of tailings, containing between 1-2 wt% pyrite, have been dumped into the bay, resulting in a displacement of the shore line over one kilometer further out to the sea. The tailings are estimated to be 10–15 m thick, covering an area of 4.5 km. The hydrology of the tailings system is controlled by a groundwater infiltration of highly saline water (up to 60 g/L Cl and 30 g/L Na) and the tidal cycle. Data suggests that low-saline water (up to 0.9 mg/L Cl and 0.8 mg/L Na), possibly from the municipally water supply or an unknown source, infiltrated into the tailings system. Oxidation resulted in a 70 to 188 cm thick low-pH (0.8 - 4) oxidation zone at the top, which is characterized by jarosite and unidentified orange-brown Fe(III) hydroxides as well as a vermiculite-type mixed-layer mineral as principal secondary mineral assemblage. The oxidation zone is underlain by a neutral primary zone. Mineralogical and hydrogeochemical data indicated, that the bivalent metal cations as Cu, Ni and Zn are liberated in the oxidation zone (up to 2265 mg/L, 18.1 mg/L and 20.3 mg/L, respectively). They are mobile under acidic conditions and are transported towards the tailings surface via capillary processes. These processes led to metal enrichment at the tailings surface (e.g. up to 2.4% Cu) in form of secondary chlorites or sulfates (dominated by eriochalcite [CuCl<sub>2</sub>\*H<sub>2</sub>O] and halite). These secondary minerals are mainly water-soluble and exposed to eolian transport towards the village of Chañaral. Data from sequential extraction show that Cu is present in the beach area (between 1000 and 2000 mg/kg) mainly in the exchangeable (“adsorbed”) fraction. This suggests that when the acid metal-rich solutions from the oxidation zone are in contact with the marine water during the tidal cycle, bivalent cations became adsorbed and their transport in the seawater seems mainly to be associated with particles in suspension. The transport direction seems to be laterally toward the sea during low tide. But also at neutral pH conditions in the lower part of the primary zone (3-7 m depth), Cu and Zn mobility is observed (up to 19 mg/L and 12 mg/L, respectively) associated with the highly saline waters, most probably as chloro complexes. In contrast to the bivalent cations, oxyanions as As and Mo are below detection limit in the pore water of the low-pH oxidation zone due to adsorption to secondary Fe(III) hydroxides, shown by sequential extractions. Below, in the saturated neutral zone, high concentrations of As and Mo were encountered with up to 608 and 10266 µg/L, respectively. The residual concentrations of As in the tailings at the surface, which are exposed to eolian transport, are between 14 and 61 mg/kg mainly associated to the Fe(III) hydroxide fractions.

Two element flow directions (towards the tailings surface via capillarity and towards the sea) and two element groups with different geochemical behavior (cations such as Cu, Zn, Ni and oxyanions such as As and Mo) can be differentiated. It can be postulated, that the sea is mainly affected by As, Mo, Cu, Zn contamination by seepage from tailings and the El Salado River, while the population of Chañaral is mainly exposed to high concentrations of Cu and minor Ni and Zn via eolian transport in form of water-soluble secondary mineral particles.

**Additional Key Words:** Copper, Arsenic, tidal influence, high saline water, eolian transport, bioavailability

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## **Introduction**

A marine shore tailings deposit at Chañaral, located in the Atacama desert of Northern Chile, was studied to understand the influence of the marine environment and in particular of marine and highly saline waters on geochemical processes in tailings deposits. The Bay of Chañaral is located at 26°21' S and 70°42' W.

### **Ore deposit and treatment processes**

Tailings deposited at Chañaral originate from two deposits of the El Salvador-Poterillos district, located around 120 km east of Chañaral in the Atacama desert. From 1926 to 1959 the Poterillos porphyry copper deposit was exploited. Hypogene alteration led to a feldspar-biotite-chlorite-quartz-ankerite-anhydrite mineralization with chalcopyrite, pyrite, bornite, molybdenite, enargite, and sphalerite as sulfide mineral assemblage (Camus, 2003).

Up from 1959 the El Salvador deposit was exploited. The primary mineralization of the 41 m.y. El Salvador mining district is characterized by alkali feldspar-biotite-anhydrite-chalcopyrite-bornite and chalcopyrite-pyrite mineral assemblages. Supergene enrichment formed an ore body of 1.5 km diameter and a thickness of 200 m, with replacement of chalcopyrite and bornite by mostly chalcocite and covellite (Gustafson and Hunt, 1975). Tailings deposited at Chañaral were from the secondary enrichment zone.

The alkaline (pH 10.5) flotation process for Cu and Mo extraction was controlled by lime addition and the resulting tailings were deposited in the Chañaral Bay.

### **Deposition history**

From 1926 until 1974, 150 Mt of tailings were sent into the bay Bahia Chañaral de las Animas covering 4.5 km<sup>2</sup>. This resulted in a displacement of the shoreline of 1 km and the accumulation of a 10-15 m thick layer of tailings on top of the original beach sediments. The deposition point migrated northward during the deposition period. The tailings originated from the Potrerillos mine from 1926 until 1959 and after 1959 from the El Salvador mine. Between 1975 and 1989 130 Mt of tailings were sent to the sea at Caleta Palito, 8 km north of Chañaral, and were exposed to the marine current. The deposition through the natural Rio Salado (the salty river) ceased in 1989 because of a court decision. Today, the tailings are deposited onshore close to the “El Salvador” mine in the “Pampa Austral” tailings impoundment. Only the “clear water” of the decantation pond of the Pampa Austral tailings impoundment mixe with highly mineralized waters outcropping in the riverbed close to the El Salado village. These waters are still discharged to the sea at Caleta Palito.

### **Ecological impact**

Various studies showed the total biological sterility regarding sandy beach macrofauna and impacts to the ecosystem in the northern discharge area (e.g. Castilla and Nealler, 1978; Castilla, 1983) during the discharge period. This effect was explained by the high sedimentation rate and toxicity of the tailings material. Recent research found a clear association between tailings and high Cu concentrations in seawater and pore water (Lee and Correa, 2005). These factors showed negative correlations with diversities and densities of the meiofauna (Lee and Correa, 2005).

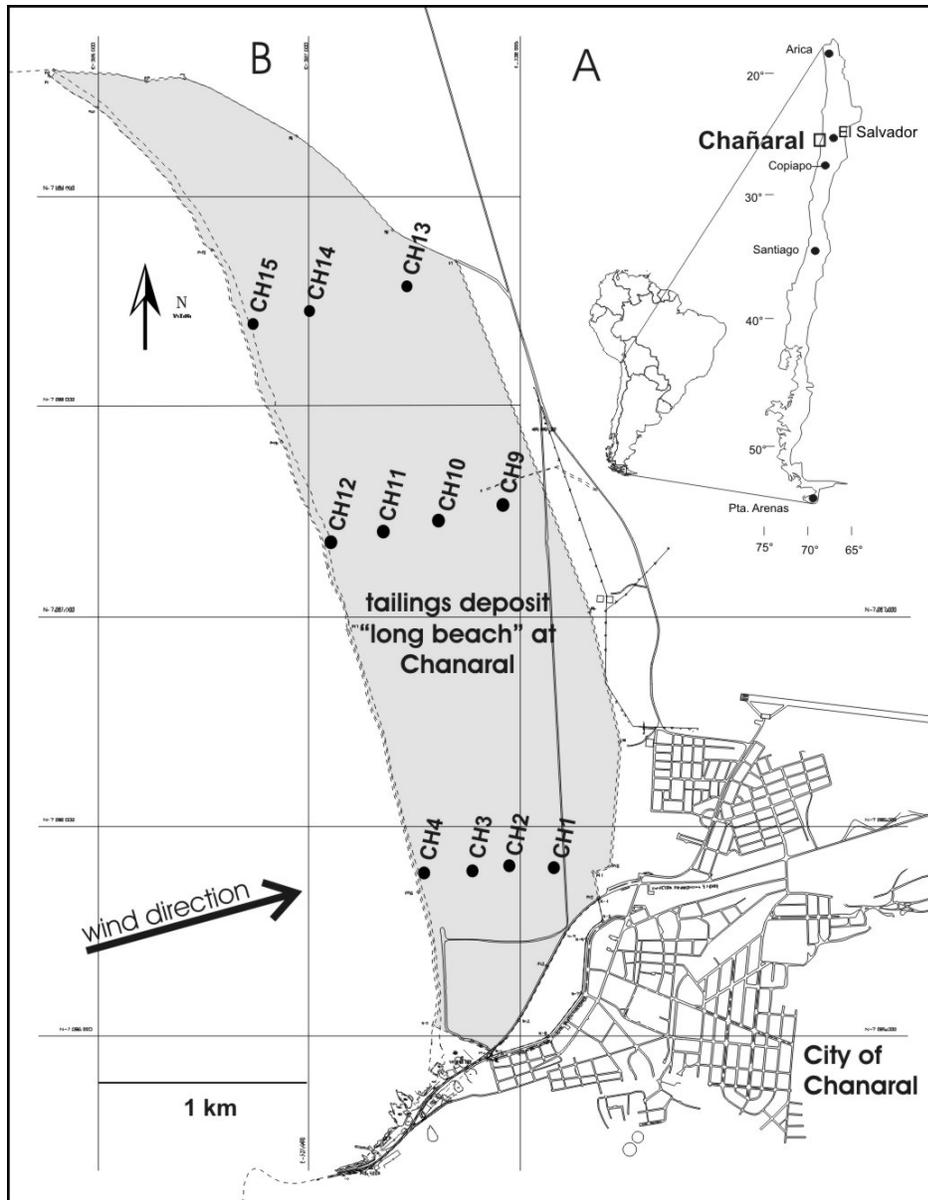


Figure 1: A) Location map of Chañaral. B) Map of the Chañaral tailings impoundment and City of Chañaral.

### Methodology

During a first field campaign in 2003, the tailings deposit was studied by a profile of three piezometer nests (3, 4, 5, 7, 9m depths) (CH1 – CH3; Fig. 1; Dold, 2005). In 2005, two additional piezometer transects were installed (Fig. 1). At the same locations, pore water samples from the unsaturated zone were taken by coring with 3” Al tubes and pore water was extracted by a modified method based on Patterson et al. (1978). At locations CH1-CH3 and CH9-CH12, excavation profiles and percussion drilling equipment were used to obtain solid samples of the oxidation zone and underlying tailings material. In-situ pH was measured (MEND, 1991) using a Sentix SP probe with a WTW® pH-meter and the material was described

including color, grain size and mineralogical characteristics. Pore gas composition ( $O_2$ ,  $CO_2$ ,  $H_2S$ ) was sampled with a transportable Draeger® Multiwarn II. Reference samples (PPA) of uncontaminated beach sediments were taken at Pan de Azucar, 30 km north of Chañaral. Temperature, pH, Eh (calculated to standard hydronium electrode) and electrical conductivity (all equipment WTW®) were measured directly at sampling locations. Samples were filtered in the field through 0.2  $\mu m$  cellulose membrane filters and split into four sub-samples. Samples for cation analysis were acidified with  $HNO_3$  supra pure. Samples for As(III)/As(V) determination were taken in dark bottles and acidified with HCl, following the procedure of McCleskey et al. (2004). A fifth sample was taken with 1  $\mu m$  cellulose filters and acidified for cation analysis. Water samples were analyzed by ion chromatography (IC; Dionex DX-120) for major cations and anions and for trace cations by inductively coupled plasma-mass spectroscopy (ICP-MS; Hewlett-Packard 4500). Solid samples were analyzed mineralogically by X-ray diffraction (XRD; Philips 3020) and geochemically by X-ray fluorescence (XRF; Philips PW 2400). Selected samples (n=15) were analyzed by sequential extractions following the method described by Dold (2003).

## **Results and Discussion**

At the northern discharge sites at Caleta Palito, tailings consisted only of sandy material. During sedimentation finer particles were transported to the open sea due to exposure to the oceanic currents. In contrast, the closeness of the Bay of Chañaral to the oceanic currents allowed the deposition of the tailings in sequences of sandy material alternating with clay and silty layers, as typical for onshore deposition of tailings (Dold & Fontboté, 2001).

In the southern transect, sand accumulated in still growing dunes (actual height ~180 cm) covering the tailings surface in parts. In the northern zone of the deposit, sand accumulated in a shallow modulated and continuous cover. Most likely these two regimes depend upon different wind energies. The onshore winds are blocked by a near mountain wall in the north. The whole central and southern zone of the tailings facility have interbedding of alluvial fans.

### **Mineralogy**

Since deposition ceased in 1975, an oxidation zone of varying thickness had developed. In the southern transect CH1 to CH4, a low-pH oxidation zone (pH 2.6 - 4) of 70 cm depth at CH1, 73 cm at CH2 and 188 cm at CH3, was developed. At CH4, the first 150 cm consisted of loose fine sand of eolian-marine origin and prevented the excavation of the oxidation zone. In the central transect, at CH9 and CH10, the tailings were overlain by more than 2 m of an alluvial blanket. At CH11, a 70 cm oxidation zone was developed with pH 2-3.4 and CH12 showed 140 cm of well oxidized yellowish fine sand with pH 0.8 – 2.4. The mineralization of the oxidation zone was dominated by jarosite, a vermiculite-type mixed layer mineral, gypsum and another ferric mineral of ochre to orange color (still to be determined by differential XRD). The primary mineralization of the Chañaral tailings deposit was characterized by quartz, feldspar (albite-anorthite), muscovite-biotite, kaolinite, magnetite and rutile with pyrite >> chalcopyrite and chalcocite as main sulfur minerals. The tailings contained between 1 and 2 wt% of pyrite.

### **Geochemistry**

The major elements (Al, Si, Ti, Fe, S) showed a homogeneous distribution in the primary zone and the lower part of the oxidation zone. In the two uppermost samples, these elements showed a decrease in concentration, whereas S, Cl and Cu showed an increase in concentration

(up to 4.2, 15, and 2.4 wt%, respectively). This can be explained by capillary potential upwards mass transport of Cu,  $\text{SO}_4^{2-}$  and Cl towards the surface, and the subsequent dilution of the major element concentrations (Al, Si, Ti, Fe) of the tailings material (Dold and Fontboté, 2001). This is confirmed by the predominance of  $(\text{CuCl}_2 \cdot \text{H}_2\text{O})$  and halite (NaCl) at the tailings surface.

The heavy metals as Cu and Zn showed a strong enrichment towards the surface due to high mobility under the acid conditions in the oxidation zone. In contrast, Pb does not show this enrichment, possibly due to anglesite ( $\text{PbSO}_4$ ) formation, which showed a lower solubility than Cu and Zn sulfates.

Arsenic showed a decrease from the primary zone (143 - 243 mg/kg) towards the oxidation zone (30 - 90 mg/kg) in CH1 and CH2. Additionally, a decrease in concentration from CH1 (143 - 243 mg/kg) towards CH4 (26 -52 mg/kg) can be observed. This indicated a leaching of As from the oxidation zone and a washout at the beach area. In Table 1, concentrations of relevant heavy metals and As of Chañaral were compared to the background concentrations of a natural beach in the area (Playa Pan de Azúcar) and some international background concentrations of soils.

Table 1. Concentrations (XRF) of relevant heavy metals and As in the tailings of Chañaral compared to concentrations found at Playa Pan de Azúcar and concentrations in reference soils (\*data from Reimann and Caritat (1998)).

	<b>Cu</b>	<b>Zn</b>	<b>Ni</b>	<b>Pb</b>	<b>Mo</b>	<b>As</b>
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
tailings Chañaral	1000-24100	24-223	5-370	<3-26	19-186	30-281
mean tailings Chañaral	3500	52	102	10	72	111
Playa Pan de Azucar (PPA)	34	26	54	16	15	<3
Background soils *	36	140-300	35	85-100	10	29

### Hydro-geochemistry

Electrical conductivity measurements in the field and major element measurements by ion chromatography showed the presence of three types of water in the tailings deposit. Representatively, data of the southern transect CH1-CH3 is shown in Fig. 2. Highly saline water up to 117 mS/cm; up to 60 g/L Cl and 30 g/L Na with pH ~7) infiltrated the deposit most likely as groundwater of the river channel sediments of the “El Salado” valley and influenced the profiles of CH1 – CH13. In the piezometers of CH09 – CH11, only this highly saline water was encountered, whereas in the piezometers near the shore line (CH04 above 4 m and CH12 above 5 m), marine water (53 mS/cm, pH 7.8) was found. The northern zone (transect CH13 – CH15) is only slightly influenced by the groundwater inflow of highly saline water. CH13 and CH14 represent a mixing zone with conductivities up to 71 mS/cm with a decreasing trend towards the shore line. At CH1 and CH2, less mineralized water (15 mS/cm; up to 0.9 g/L Cl and 0.8 g/L Na with pH 7), infiltrated the tailings at CH1 up to a depth of 300 cm and at CH2 up to 150 cm. Most likely, this water originated from the Chañaral water supply system or an unknown source.

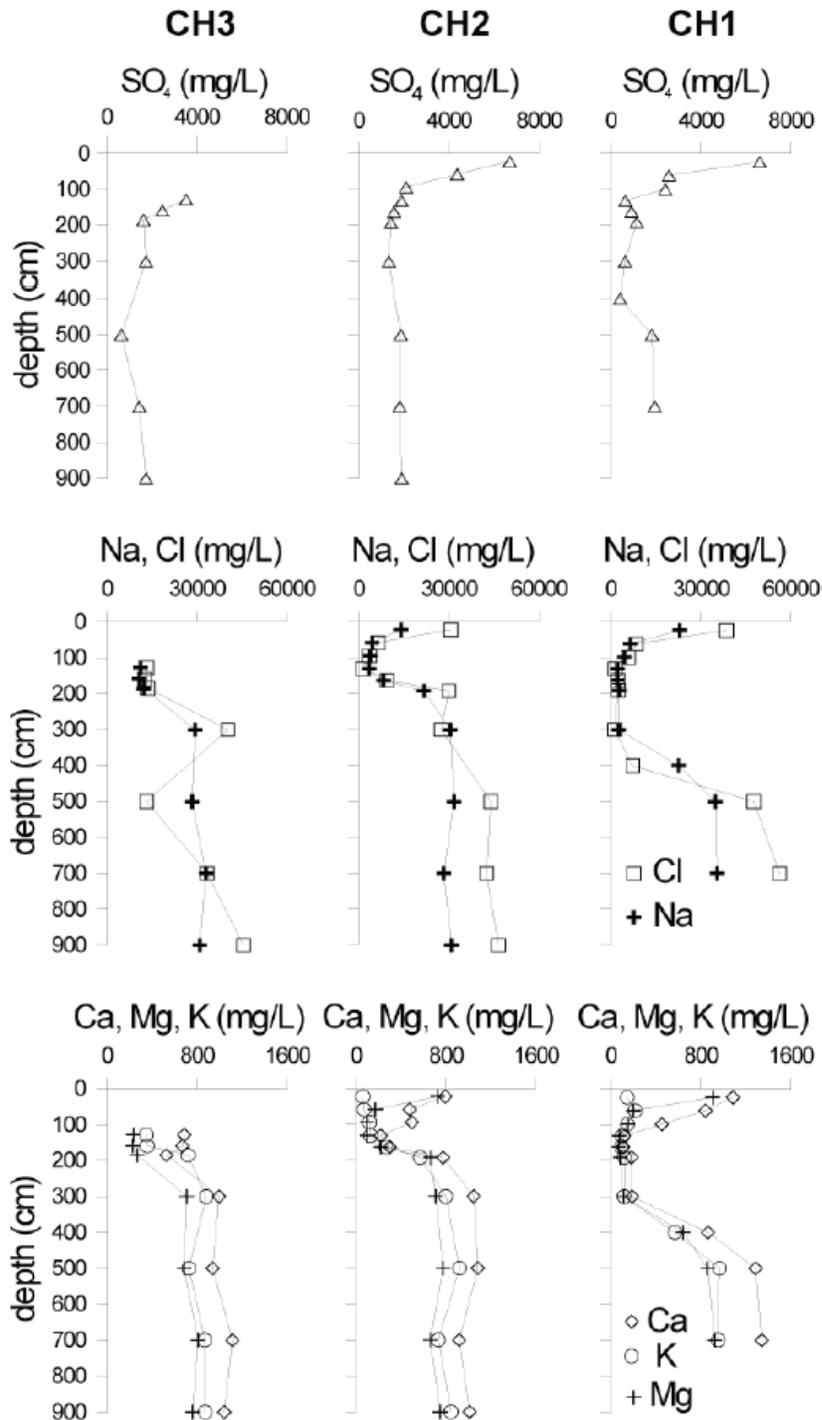


Figure 2: Major cations and anions data for the southern piezometer nest transect CH1, CH2 and CH3.

The redox potential (Eh) showed values up to 600 mV in the oxidation zone and decreased to 200 mV in the reducing environment of the saturated zone (Fig. 3). The alkalinity was about 160 mg/l CaCO<sub>3</sub> in the saturated zone. Towards the oxidation zone, the alkalinity decreased due to the neutralization by the H<sub>2</sub>SO<sub>4</sub> acid produced during the sulfide oxidation.

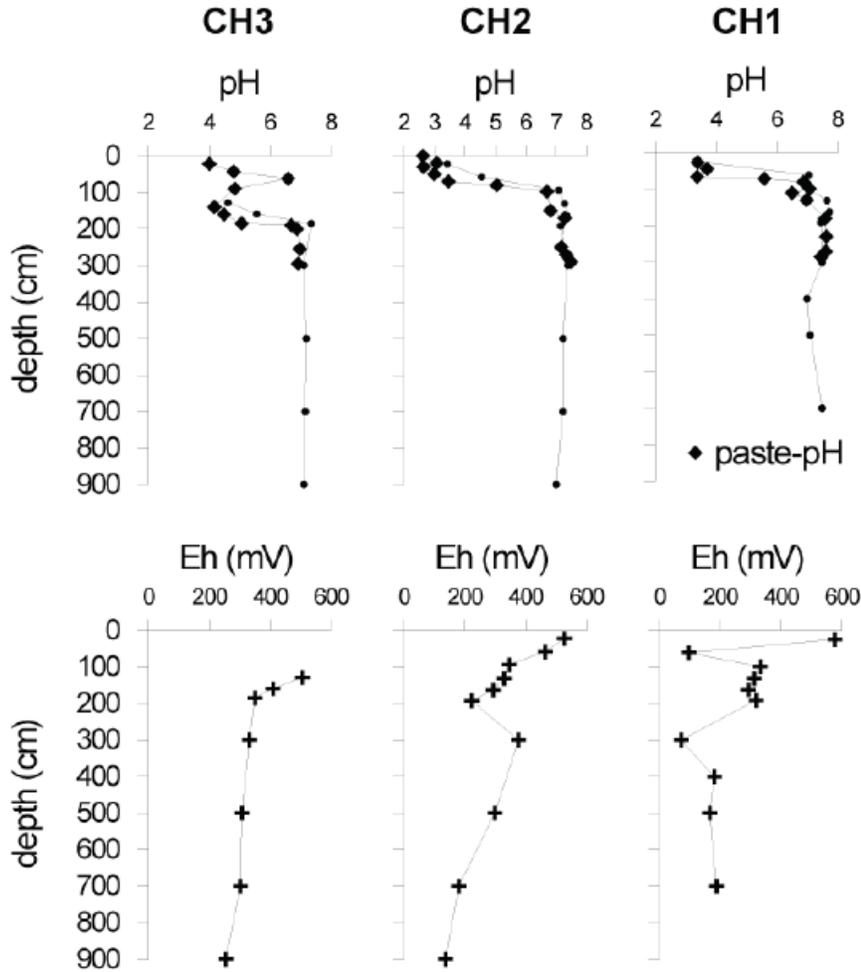


Figure 1: pH and Eh of piezometer nests CH1, CH2 and CH3 of the southern transect.

The concentrations of the bivalent metals dissolved in the pore water of the tailings increased strongly towards the oxidation zone (up to 2265 mg/L Cu, up to 20 mg/L Zn, up to 18 mg/L Ni, up to 183 mg/L Fe, respectively) (Fig. 4). In the neutral saturated zone, the mobility of Cu and Zn should be zero due to absorption. However, a high mobility can be observed (up to 19 g/L Cu and 12 mg/L Zn, respectively). This could be explained by complexation of these metals by Cl and the subsequent increase of their solubility. The elements, which are stable as oxyanions as Mo and As, are below detection limit in the oxidation zone, which can be explained by their adsorption to the secondary  $\text{Fe}^{+3}$  hydroxides at low pH conditions (Dold and Fontboté, 2001). This is supported by the sequential extraction data showing the presence of As below the oxidation front mainly in the exchangeable fraction and still associated to the sulfide fraction. In the saturated zone, these elements showed a plume (up to 608  $\mu\text{g/L}$  As and up to 10266  $\mu\text{g/L}$  Mo, Fig. 4), where higher pH and more reducing condition increased their mobility. In Table 2, concentrations of relevant heavy metals and As in the pore water of the tailings of Chañaral are shown.

Table 2: Concentrations (ICP-MS) of relevant heavy metals and As in solution in the pore water of the tailings Chañaral of the oxidation and the primary zone.

	<b>Cu</b>	<b>Zn</b>	<b>Ni</b>	<b>Pb</b>	<b>Mo</b>	<b>As</b>
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
oxidation zone	2265	20	18	0.046	<DL	<DL
primary zone	19	12	0.28	0.005	10	0.608

### Pore gas

Gas measurements showed values similar to atmospheric composition at most sampling points and all depths except CH11 below 60 cm depth near the water table (1.35 vol% CO<sub>2</sub> and 19.2 vol% O<sub>2</sub>), and at CH12 in 125 cm depth (0.25 vol% CO<sub>2</sub> and 7.8 vol% O<sub>2</sub>). Ongoing research of the microbiology in the impoundment should answer the question, if this can be interpreted as the result of a low microbiological activity or of a rapid tidal forced pore gas exchange.

### Conclusions

The preliminary study of the shore mine tailings disposal at Chañaral, Chile indicated that two flow directions (towards the tailings surface and towards the sea) and two different contaminant groups with different geochemical behavior (cations as Cu, Zn, Ni and oxyanions as As and Mo) can be differentiated. The hydrology of the tailings system is controlled by the tidal cycle and the infiltration of groundwater of the Rio Salado. Conclusions are:

1. The bivalent metal cations as Cu, Ni, and Zn, liberated in the oxidation zone, were mobile under acid conditions and were transported to the tailings surface via capillarity, where super-saturation leads to a precipitation of these metals as secondary chlorides or sulfates (e.g. eriochalcite). These secondary minerals are mainly water-soluble and exposed at the tailings surface to eolian transport towards the village of Chañaral.
2. In contrast, As and Mo do not show any mobilization towards the surface of the tailings, due to strong adsorption to secondary Fe<sup>+3</sup> hydroxides in the low-pH oxidation zone. The residual concentration of As at the tailings surface, which is exposed to eolian transport, was between 14 and 61 mg/kg. The data suggested that an important part of As and Mo was leached out in dissolved form towards the sea.

It can be postulated, that the sea was mainly affected by As, Mo, Cu, Zn contamination via infiltration, while the population of Chañaral was mainly exposed to contamination via eolian transport of Cu, Ni, and Zn in water-soluble form.

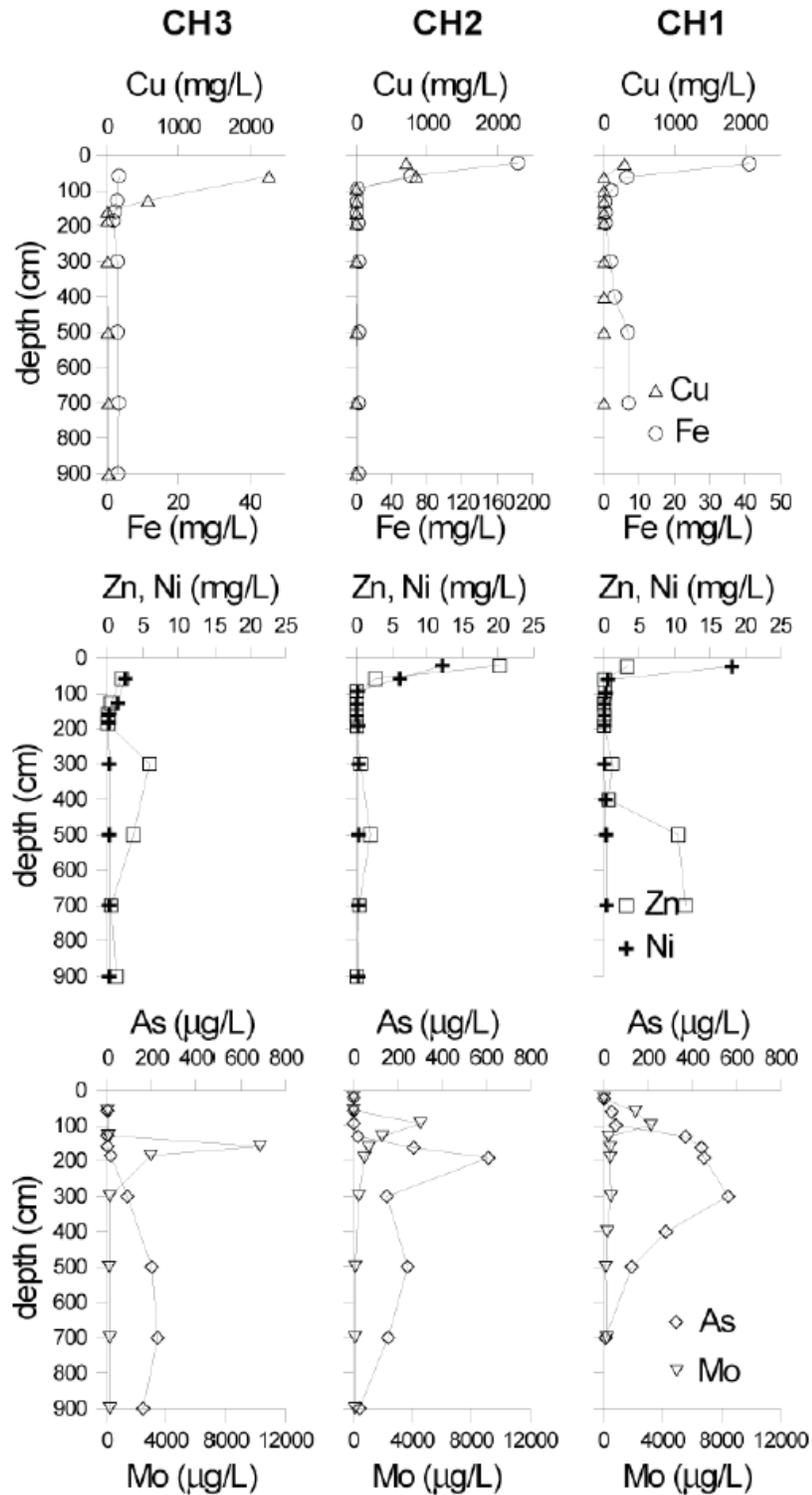


Figure 4: Hydrogeochemical data of heavy metals Cu, Fe, Zn, Ni and oxyanions As and Mo of the southern transect CH1, CH2 and CH3.

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