

# Trace Element (As, F, U) Contamination and Hydrogeochemistry in the Vicinity of a Mexican Ore Mine

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## Abstract

Dissolved fluoride (F), arsenic (As) and uranium (U) concentrations in ground and surface waters around the San Antonio el Grande Mine in Chihuahua, Mexico, exceed WHO drinking water limits for F and As, and the German guideline value for U in 72.8%, 64.0% and 58.4% of all samples, and thus threaten the most important drinking water source in the region. To address the question of the origin of elevated concentrations and the underlying mobilisation and transport processes, element distributions of 125 water samples were analysed and evaluated. Lithology is dominated by acidic igneous rocks and limestones with numerous mineralisation zones. Solution processes were identified as the main driver for the increased concentrations depending on pH value, temperature and redox potential.

**Keywords:** Metal ore mining, Mexico, uranium, arsenic, fluoride

## Introduction and study area

Groundwater around the San Antonio el Grande Mine in Chihuahua, Mexico, was found to partly contain elevated concentrations of several trace elements of toxicological concern, amongst them arsenic (As), uranium (U) and fluoride (F). Their origin, distribution and mobilization were unknown which gave rise to the present study.

The study area forms part of the eastern edge of the Sierra Madre Occidental (400 km wide and 1500 km long structure in the north-western part of Mexico), is semi-arid (average annual precipitation from 280–420 mm/year) with a mean annual temperature of 17.3–20.1 °C and ephemeral streams. It is located in the North America tectonostratigraphic terrane characterized by Tithonian to Albian basal conglomerate, limestone, fine grained marine siliciclastic rocks, deposited in the Chihuahua Trough (Sedlock et al. 1993). Massive limestone (Lower Cretaceous), light grey micrite and biomicrite with locally abundant biostromes and chert beds, outcrop in the Santo Domingo mountain (Fig. 1). It is

overlain by a thin-bedded limestone-arenite and a thin to medium-bedded limestone-mudstone with bioclasts and hematite concretions (Upper Cretaceous). Tertiary rocks (Eocene-Oligocene) unconformably overly the Cretaceous sequence; magmatic rocks in the area include mostly felsic plutonic and volcanic rocks of the upper volcanic complex (pyroclastic and polymictic conglomerate, dacite, rhyolitic porphyry, rhyolitic ignimbrite-tuff, rhyolite and basalt) of McDowell and Keiser (1977). Most of these rocks were erupted from overlapping caldera complexes. Tectonic extension during Miocene to Pleistocene created large-scale N-S oriented horst and graben structures occupied with basin fill sediments.

The Santa Eulalia mining district within the study area consists of calc-silicate skarns and massive sulfide orebodies containing Pb-Zn-Ag deposits. The mineralization is associated to felsite intrusions, ore textures indicate mineralization occurred primarily by limestone replacement (Megaw 1990). At the time of field work, the San Antonio mine was

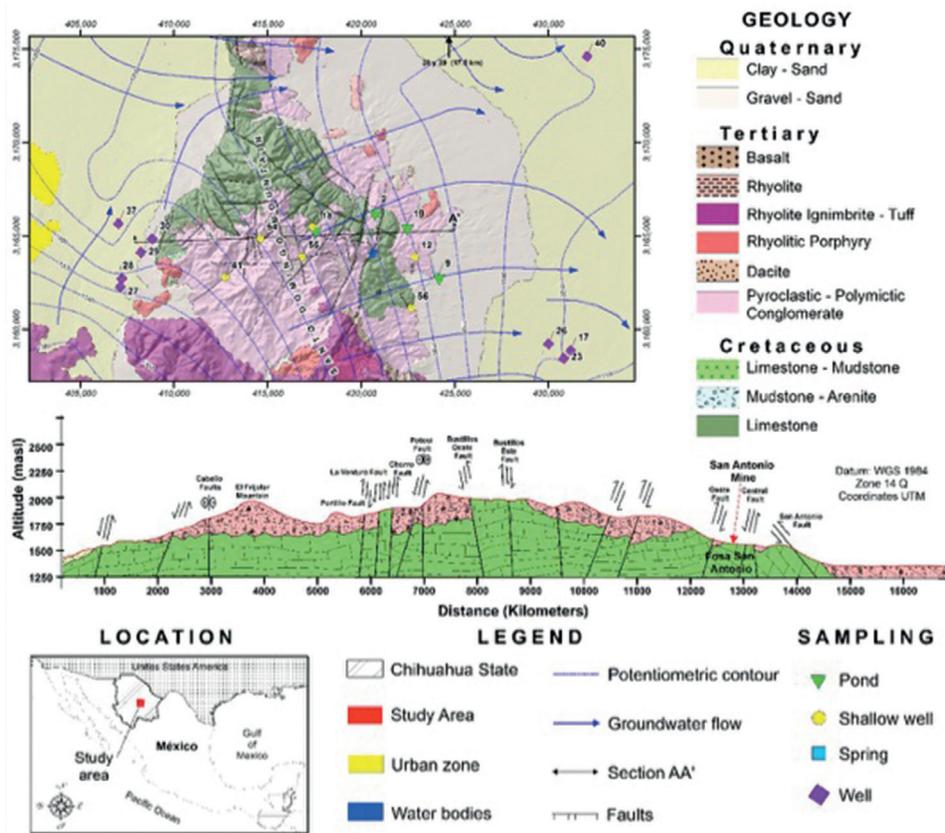


Figure 1 Geological and piezometric map, and geological cross section through the study area.

producing Pb-Zn-Ag concentrate, nowadays the mining operation has been terminated after a big flood event inside the mine.

The granulometric distribution and thickness of the basin fill sediments is determined by the graben geometry, gravel and sand sediments are generally associated with alluvial fan deposits, to clay-sand deposits in the playa region. The identified hydrogeological units in the study area include: i) karstic unit (Cretaceous massive limestone), ii) fractured unit (Tertiary volcanic rocks) and iii) granular unit (basin fill and alluvial sediments). Groundwater flow determined from water level measurements in wells and in the mining operation, indicate a south to north direction in the western flank of the Santo Domingo mountain, a northeast flow direction from side to side of the Santo Domingo Mountain flowing through the karstic unit; and groundwater flow from west to east along the basin fill sediments eastern edge of the mountain (Fig. 1).

### Methods

The data set consists of 125 water samples – 118 groundwater samples and seven surface water samples – all taken between December 2013 and December 2015. Parameters such as pH, temperature, redox potential, electrical conductivity, dissolved oxygen and alkalinity were determined in the field. In addition, 75 elemental analyses of main and trace elements as well as 74 isotope ratio values for oxygen and hydrogen were determined. The geographical and (hydro)geological situation of the study area was characterized and visualised by evaluation of available information. For the concentrations of the three trace elements, isoline maps were created and related to the geology of the study area. Stability fields of dissolved species were visualized by means of Eh-pH diagrams. Using the knowledge gained from all these perspectives, it was then possible to derive and discuss the origin, mobilisation, transport and accumulation processes of relevant trace elements in the study area.

## Results

Median pH of all waters is 7.60, values are generally circumneutral to slightly alkaline (Tab. 1). However, the maximum value of 10.9 indicates that there are also waters with more alkaline pH values. Median temperature is 31.7 °C (Tab. 1). The maximum value of 47.0 °C indicates the presence of thermal water. In total, 20 of the 125 samples have a temperature of more than 35 °C.

The measured F concentration is up to 19.6 mg/L and 2.59 mg/L on average (Tab. 1). The WHO drinking water limit of 1.5 mg/L is exceeded in 72.8% of the samples. The As content of the water reaches up to 1422 µg/L at a mean value of 56.6 µg/L (Tab. 1). The drinking water limit value of 10 µg/L is exceeded in 64% of the samples. U concentration is up to 122 µg/L and 21.5 µg/L on average. The German guideline value of 10 µg/L is exceeded in 58.4% of the samples. (See Table 1)

Figure 2 shows the relation between dissolved U and water temperature. R<sup>2</sup> of 0.16 indicates a weak but statistically significant (p<0.01) linear relationship between the two parameters. All water samples below 29 °C have U concentrations <50 µg/L, while the 12 samples >50 µg/L U plot in the T range of 29 to 37.5 °C. However, the two samples with highest T (>43 °C) show relatively low U values. In total, Fig. 2 also shows that the

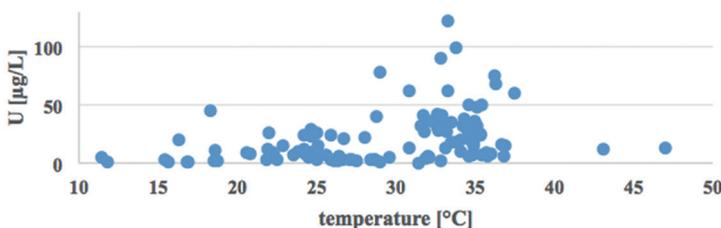
majority of the values clearly exceed the drinking water limit value of 10 µg/L.

The 125 water samples were taken at 67 different sites, 43 of them are located closely to the mine (Fig. 3). The interpolated distribution of F concentration (Fig. 3, left) indicates lowest concentrations in the range from <0.1 to 1.5 mg/L are located in the west of the mountain range and increase continuously towards the east in the northern area. In the area of the San Antonio Mine, a more diffuse picture can be seen, which, however, is also caused by the extremely high density of measuring points in this area compared to the rest of the map. Concentrations of around 6 mg/L are reached here. The highest F contents are found in the southeast in Quaternary alluvial sediments with up to 10 mg/L. However, the maximum concentration is found in only one sampling point with only 4 or 2 mg/L in the two directly adjacent measuring points.

Figure 3 (right) shows the distribution of U concentrations in the study area. Values range from <1 to 42 µg/L with the lowest values in the south and the highest values around the mine. Concentration increases from the southwest to the northeast, reaches its peak at the mine and continues to decrease to the northeast until it increases again to 26 µg/L. The U concentration pattern looks quite different from the similar F

**Table 1** Trace elements hydrochemistry and physico-chemical parameters (n=125).

	pH	T [°C]	F [mg/L]	As [µg/L]	U [µg/L]
mean	7.77	29.3	2.59	56.6	21.5
median	7.60	31.7	2.25	12.1	14.8
maximum	10.9	47.0	19.6	1422	122
minimum	6.68	11.4	<0.1	1.06	0.37
guidelines	6.5-9.5	-	1.50	10.0	10.0
max. factor	1.14	-	13.1	142	12.2
exceedence frequency %	0.8	-	72.8	64.0	58.4



**Figure 2** Correlation of U concentration and temperature, n = 125.

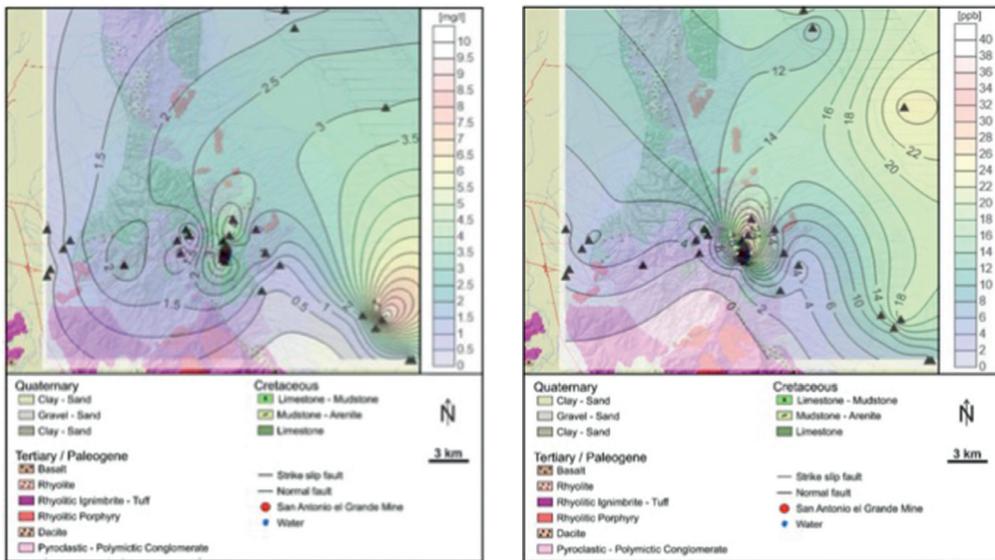


Figure 3 Isolines of F (left) and U (right) concentration in relation to the geological map of the study area.

and As (not shown) distribution patterns, potentially indicating different sources and/or mobilization processes.

Dissolved As and U species are presented in Eh-pH diagrams in Fig. 4. Fluorine species were also investigated, but as expected, only fluoride (F-) was present (diagram not shown). Based on Fig. 4 (left), a clear As species distribution of almost exclusively  $\text{HAsO}_4^{2-}$  can be assumed under the given conditions. Only one sample is in the

field for  $\text{H}_2\text{AsO}_4^-$ . Both species contain pentavalent As. Figure 4 (right) shows the U species distribution. Here, samples are divided into  $\text{UO}_2\text{OH}^+$  and  $(\text{UO}_2)_3(\text{OH})_7^-$ . The proportion of  $\text{UO}_2\text{OH}^+$  outweighs that of  $(\text{UO}_2)_3(\text{OH})_7^-$ . Both species contain hexavalent U, arguing for high U mobility. Though not included in Fig. 4 (right), it can be assumed that Ca-U(VI)- $\text{CO}_3$  complexes play a major role in U speciation (e.g., Riedel and Kübeck, 2018).

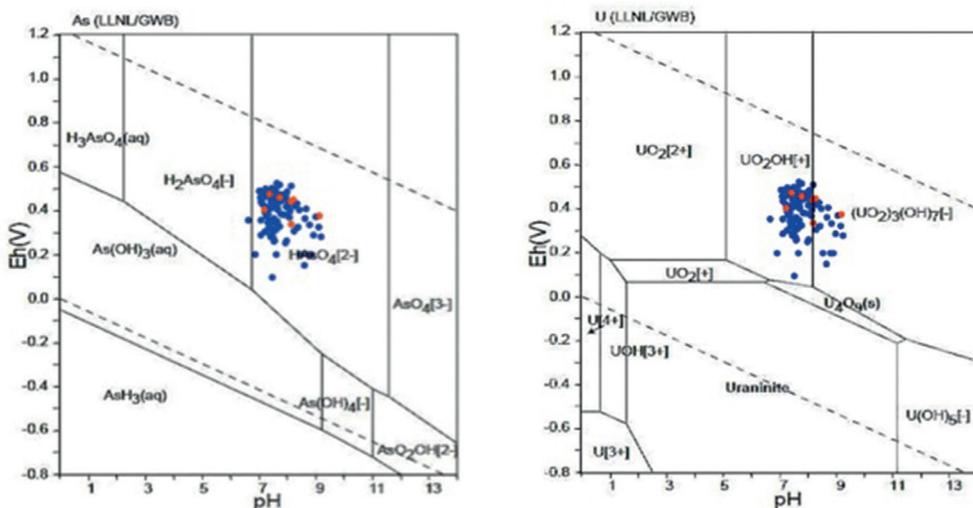


Figure 4 Eh-pH diagrams of As (left) and U (right) (modified after Takeno, 2005; blue dots: groundwater, red dots: surface water).

Figure 5 shows the 74 available data sets for deuterium ( $^3\text{H}$ ) versus oxygen ( $^{18}\text{O}$ ). Groundwater and surface water samples are plotted in addition to the global meteoric waterline and the local meteoric waterline for Chihuahua. The four surface water samples show significantly higher levels of deuterium and oxygen than the groundwater samples, as well as greater scattering. The groundwater values are concentrated in a much narrower area.

## Discussion

The fact that the drinking water limit values for F, As and U are exceeded in 72.8%, 64.0% and 58.4%, respectively, of all studied samples around the mine is alarming (Table 1). The massive exceedances of the guideline value in the case of As can represent an enormous health risk for the human population and ecosystems. Due to the numerous private wells in the study area, there is often no control authority and contaminated water is thus not detected.

The dissolution capacity of the water for most mineral phases increases with rising temperature. The thermal waters therefore have the greatest potential to dissolve the trace elements from their host phases, probably mainly silicates, sulphides and volcanic glass. Increased solution and mobility of U at elevated temperatures is indicated. Elevated F contents can also be caused by a temperature above 30 °C. Only As mobility does not seem to be controlled by water temperature.

The spatial distribution patterns of the trace elements must be regarded a rough estimate. Observation points are inhomogeneously distributed and concentrate to a large extent on a very small area around the San Antonio

Mine. In wide areas in the west and east of the mountain range there are only very few measuring points, which causes the isolines in these areas to be very uncertain. The highest concentrations were often found only once in single measuring points but strongly influence the overall picture of the isolines. On the one hand, for more reliable isoline representations, the spatial distribution of the measuring points should be reconsidered and more homogeneously distributed. It would be helpful to supplement the knowledge gained from this work with recent water samples and measurements of trace element concentrations in previously unconsidered parts of the study area. On the other hand, the diffusely distributed concentration patterns can also indicate fluctuating redox conditions, rapidly changing solution capacities, or small-scale heterogeneities of source rocks. It is noticeable that F and As have very similar distribution patterns, which indicates a common source and simultaneous solution. Uranium, on the other hand, shows a different distribution patterns. Especially in the area of the San Antonio mine, maximum concentrations are measured, whereas in the case of As in the same area, rather low concentrations occur. Arsenic is more mobile under reduced conditions, U under oxidized conditions. The results of the spatial distribution patterns underline this very well. High As and U concentrations are not to be expected simultaneously in the water although they are known to derive from the same source rocks (Banning et al. 2012). Fluoride, on the other hand, is not redox-sensitive and the increased mobility is mostly controlled by the higher pH value. The latter is also valid for As, explaining the similar spatial

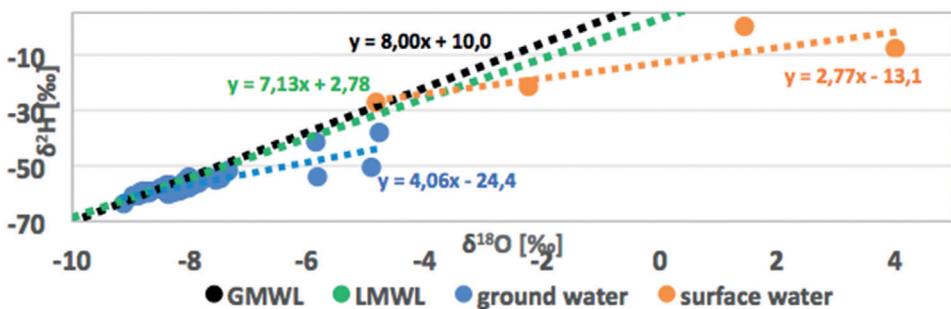


Figure 5 Scatter diagram of isotope values for oxygen and deuterium.

groundwater distribution of both elements.

As seen in the Eh-pH diagrams, As(V) and U(VI) are the dominant redox species. The pentavalent As shows that mostly oxidized conditions prevail (Masscheleyn et al. 1991), where also the hexavalent U is easily soluble. Both trace elements have a high mobility in the study area. From the isotope diagram, clear evaporation tendencies of the surface and ground waters are visible. Due to evaporation, especially in the case of surface waters, the light isotopes pass into the gas phase and heavy isotopes accumulate in the remaining water. From the diagram, it can be concluded that these waters are mainly of meteoric origin, and rather not from a deep source.

The predominantly acidic character of the magmatic rocks in the study area supports the thesis of them being the main source of high trace element concentrations based on the incompatible character of F, As and U and their enrichment in late magmatic lithologies. The carbonates also represent a possible source of U and As (Riedel and Kübeck 2018, Banning et al. 2012). Karst formation and dissolution processes of limestones can cause increased concentrations. In addition to the acidic igneous rocks, the ore enrichments with minerals such as pyrite also represent a source of the trace elements. 50 km northwest of Santa Eulalia in the Sierra Peña Blanca, there is for example the El Nopal Mine, where U ores are mined.

## Conclusions

The increased concentrations of F, As and U in ground and surface waters in the area around the San Antonio el Grande Mine in Chihuahua, Mexico, are of geogenic origin. The incompatible elements accumulated in the course of magma differentiation in the predominantly acidic igneous rocks in the study area. In addition, the frequent mineralization zones and limestones are further potential sources. Mobility of F and As seems to be mainly controlled by pH with alkaline values causing higher concentrations. Especially for the mobility of U, water temperature seems to be a decisive factor. However, dissolved F concentration is also increased by elevated temperatures. Fluorite precipitation, on the other hand, does not seem to be a decisive control mechanism. The San Antonio mine likely increases the

dissolved trace element concentrations in the waters by creating larger contact areas with the acidic igneous rocks and ore minerals, and new pathways.

The ever decreasing groundwater level will lead to further problems in the future. It is likely that more and more deep water will be pumped, which could further increase the content of the dissolved trace elements. In order to ensure the long-term security of the drinking water supply in the study area and to protect the population from the potentially toxic trace element concentrations, urgent measures to reduce the dissolved contents should be implemented. A possible precipitation of fluoride via the mineral fluorite could be considered. Also, controlling pumped groundwater temperature – as it was suggested for other parts of Mexico (Cardona et al. 2018) – might be a promising approach.

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