

Hydrogeochemistry of Arsenic and other Problem Constituents in Groundwaters from La Pampa, Argentina

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Groundwater is a vital resource in the semi-arid Chaco-Pampean Plain of Argentina and is relied upon heavily for potable supply and agriculture. However, significant quality problems occur from high salinity and high concentrations of harmful elements such as As, F, NO₃-N, B, Mo and U. Arsenic constitutes one of the most severe health threats. Symptoms typical of chronic arsenic poisoning, including skin lesions and some internal cancers, have been recorded in some of the areas. Chronic exposure to fluoride in the drinking water has also given rise to dental fluorosis. The extent of the groundwater-quality problems is not well-defined, but is believed to cover an area of around 10⁶ km².

A hydrogeochemical investigation has been carried out in northern La Pampa Province of central Argentina. Shallow aquifers of the area are composed of Quaternary loess deposits which comprise mainly brown silts and fine sands with volcanic material (dacitic and rhyolitic ash, volcanic glass and pumice). The sediments have been diagenetically altered and have abundant calcrete and occasional manganese-oxide nodules and cements.

Groundwaters from wells and boreholes have variable chemical compositions. Concentrations of TDS are high in many (up to 11400 mg l⁻¹). Groundwaters also typically have high alkalinity (up to 1440 mg l⁻¹ as HCO₃) and a large range of concentrations of As (5300 µg l⁻¹), F (0.03–29 mg l⁻¹), B (0.5–13.8 mg l⁻¹), V (0.02–5.4 mg l⁻¹), Mo (2.7–991 µg l⁻¹) and U (6.2–248 µg l⁻¹). Of the groundwaters investigated, 95% exceed 10 µg l⁻¹ (the WHO guideline value for As in drinking water) and 73% exceed 50 µg l⁻¹ (the Argentine national standard). In addition, 83% exceed the WHO guideline value for F (1.5 mg l⁻¹), 99% for B (0.3 mg l⁻¹), 39% for Mo (70 µg l⁻¹) and 100% for U (2 µg l⁻¹). The groundwaters are universally oxidising with high dissolved-oxygen concentrations and redox potentials. Groundwater pHs are neutral to alkaline (7.0–8.7). Arsenic is present in solution predominantly as As(V).

Groundwater As correlates positively with pH, alkalinity (HCO₃) and with F and V. Weaker correlations are also observed between As, B, Mo, U and Be. The mobilisation of these

elements is most likely achieved by desorption from iron, manganese and aluminium oxides in the sediments, particularly under the high-pH and high-alkalinity conditions. Mutual competition between these anions and oxyanions for sorption sites on oxide minerals may also have enhanced their mobilisation. Concentrations of As and other anions and oxyanions appear to be particularly high in groundwaters close to the low-lying depressions which act as localised groundwater-discharge zones. Concentrations up to 7490 µg l⁻¹ were found in porewaters extracted from a cored borehole adjacent to one such depression.

Arsenic concentrations in the aquifer sediments are similar to average values for silty and sandy sediments, although high groundwater concentrations show some spatial relationship with high sediment concentrations. The sediments contain no discrete As minerals. Total As concentrations lie in the range 3–18 mg kg⁻¹, the highest values being found in finer-grained sediments. Oxalate-extractable As concentrations (associated with mixed amorphous oxides, especially iron oxides) vary between 0.5–9.6 mg kg⁻¹ (mean 2 mg kg, roughly half the total As present) and hydroxylamine-extractable concentrations (associated with manganese oxide) vary between 0.02–4.7 mg kg⁻¹ (mean 1.0 mg kg⁻¹). A significant amount of As present in the sediments therefore appears to be associated with poorly structured iron and manganese oxides and is relatively labile. Release into solution can therefore be readily achieved given the appropriate pH and redox conditions. This suggests that the As problem arises as a result of “mobilisation” under favourable conditions, rather than the “source” (i.e. high As in the aquifer) being the root of the problem.

The development of groundwaters with high pH and alkalinity results from silicate and carbonate reactions under closed conditions, facilitated by the arid climatic conditions. These factors, together with young age of the loess sediments and slow groundwater flow conditions has enabled the accumulation of high concentrations of As and other elements in solution without significant opportunity for flushing of the aquifer to enable their removal.