Arsenic Contamination of Fractured Bedrock Aquifers in the Palaeozoic Units of South-East Ireland

Alex Russell, Frank McDermott, Tiernan Henry, Liam Morrison

Background

Long-term exposure to dissolved inorganic arsenic (As) through contaminated drinking water has been linked to numerous health risks including skin ailments and cancers. The World Health Organisation (WHO) has set a global recommended limit of 10 μg/L in drinking water for this reason. In Ireland, up to 200,000 unregulated private water supplies are in active use, but reliable metadata/metalalised data at the μg/L remain scarce. Three areas were identified using existing geochimistry and Tellus datasets for focused work on As contamination of private wells across South-East Ireland (Fig. 1).

Arsenic is odourless, tasteless, and colourless, and so can effectively remain ‘invisible’ in drinking water alongside other naturally-occurring or ‘geogetic’ contaminants such as chromium, and uranium. Identifying potential geogenic contamination is essential to best protect the health and wellbeing of well users.

1. Louth: Silurian Greywackes

An area of elevated As-concentrations in private wells (up to 60 μg/L) was identified along the contact between the Tertiary Slate Gullion Complex and the Silurian Longford-Down Terrane (Fig. 2). The Geological Survey Ireland (GSI) drilled two cores (Feade & Faught) to identify potential sources of arsenic (Fig. 3).

Common to both cores are basaltic core sheets, with whole-rock As-concentrations up to 80 mg/kg present at c. 136 m depth in the Faught core (Fig. 3). The average across this core set is 23 mg/kg which represents an enrichment of arsenic relative to global and regional averages of 2 – 5 mg/kg for basalts and dolerites (Fig. 4).

![SEM-EDX analysis was carried out on samples of As-enriched basalts. As-bearing sulphides (≥20 μm) were identified as the only As-bearing phases within these basalts, (Fig. 5). Correlations are seen with Co and Ni, indicating a calcite-type mineralogy. Oxidation of these sulphides by groundwater percolation through fractures in the basaltic intrusives is the likely mobilisation mechanism for As-contamination in this area.](image)

![2. Dublin: Silurian Greywackes](image)

An As stream sediment anomaly was used to identify a region of elevated levels of arsenic in groundwater (up to c. 50 μg/L) (Fig. 6), after sampling 29 private wells. The bedrock geology is Silurian greywacke and clays units, forming a poorly-productive fractured bedrock aquifer. Detailed sampling was completed on 14 wells, directly from the well or nearest tap, using low-flow & clean-hand/dirty-hand sampling protocols. In-situ measurements of pH, ORP and conductivity were recorded (Fig. 7). A further 4 stream samples were found to be elevated in arsenic (up to 85 μg/L).

![SEM-EDX analysis and mapping has identified weathered As-bearing sulphides (Fig. 8), associated with iron (Fe), giving an arsenopyrite mineralogy (FeAsS). Sulphide oxidation is the likely As-mobilisation mechanism, although iron-oxides may also act as a secondary source/sink. There is evidence of arsenopyrite weathering to form iron oxides (Fig. 8).


A further area identified from anomalous As-concentrations in stream sediments was shown to contain significantly elevated groundwater As, with concentrations up to 60 μg/L. A total of 21 private wells were sampled within a poorly productive fractured bedrock aquifer comprised of Ordovician meta-sediments and Carboniferous dolerites (Fig. 9). Detailed sampling was completed on 9 wells, directly from the well or nearest tap, using low-flow & clean-hand/dirty-hand sampling protocols. In-situ measurements of pH, ORP and conductivity were recorded (Fig. 10).

Arsenic is primarily dissolved, as shown by similar concentrations in filtered/unfiltered samples (0.45 μg/L) (Fig. 10). The samples exhibit a range of correlations between As and physiochemical parameters (Fig. 10a-d). Higher ORP (>350 mV), conductivity (<200 μS/cm), pH (~<7) and alkalinity (<100 mg/L) are all associated with higher As-concentrations. Waters at pH <6.5 are low in arsenic, with possible Fe(OH)₃ adsorption effects in the aquifer systems at this pH range. Sulphate (SO₄) does not trend with arsenic (Fig. 10a), however, samples (InD66 blue) outliers for both sulphate and cobalt (Co) (Fig. 10f). A surface water sample collected flowing from an outcrop of quartz veins in Ordovician meta-sediments in the area yielded 134 μg/L As, (Fig. 11a).

![SEM-EDX analysis has shown that several As-bearing phases exist, associated with both quartz veins and disseminated within the Ordovician meta-sediments, (Fig. 11). These range in composition from arsenopyrite (Fig. 13b) to Co-As bearing phases (Fig. 11c), which may explain possible trends with cobalt within groundwater samples. Oedotropic weathering of these sulphides likely represents the primary sources of arsenic within this area.

Conclusions

1. Regional geochemical mapping of the surface environment including stream waters, soils, and sediments are useful tools in the identification of geogenic As groundwater contamination.
2. Localised sulphide oxidation represents the primary mobilisation process across all three study areas in the Palaeozoic units in SE Ireland, with an association to cobalt in two of the areas.
3. A health risk exists for rural populations where water quality testing for geogenic contaminants has not been carried out, especially given the existence of similar geological environments elsewhere e.g. Dalradian meta-sediments in NW Ireland.