Occurrence, Geochemistry and Speciation of Elevated Arsenic Concentrations in a Fractured Bedrock Aquifer System

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Abstract

The presence of elevated arsenic concentrations (≥10 µg L^{-1}) in groundwaters has been widely reported in areas of south east Asia with recent studies showing its detection in fractured bedrock aquifers mainly in regions of north-eastern United States. Data within Europe remains limited; therefore, the objective of this work was to understand the geochemical mobilisation mechanism of arsenic in this geologic setting. Physiochemical (pH, Eh, d-O_2), trace metals, major ion and arsenic speciation samples were collected and analysed using a variety of field and laboratory-based techniques and evaluated using statistical analysis including multivariate analysis. Elevated dissolved arsenic concentrations (up to 73.95 µg L^{-1}) were observed in oxic-alkali groundwaters with the co-occurrence of other oxyanions (e.g. Mo, Se, Sb and U), low dissolved concentrations of Fe and Mn and low Na/Ca ratios indicating that arsenic was mobilised through alkali desorption of Fe oxyhydroxides. Arsenic speciation using a solid-phase extraction methodology (n=20) showed that the dominant species of arsenic present in groundwater was arsenate, with pH being a major controlling factor. The expected source of arsenic is sulfide minerals within fractures of the bedrock aquifer with transportation of arsenic and other oxyanion-forming elements facilitated by secondary Fe mineral phases. However, the presence of methylarsenical compounds detected in the groundwaters illustrates that microbially mediated mobilisation processes were also (co)-occurring. This study demonstrates how field speciation of arsenic can be utilised to overcome analytical limitations of conventional laboratory speciation and to facilitate in the interpretation of the environmental mobility of arsenic within groundwaters.

Introduction

The presence of geogenic arsenic in groundwater remains a major health concern affecting approximately 226 million people (Garelick et al. 2009; Smedley and Kinniburgh 2013; Murcott 2012). In many regions, groundwater is an important source of drinking water and can also be a critical exposure pathway for arsenic (Smedley and Kinniburgh 2002).

The International Agency for Research on Cancer (IARC) classifies arsenic as a Group I carcinogen (IARC, 2012). Short-term exposure (i.e., acute) to high arsenic concentrations (i.e., in Bangladesh) can lead to the development of arsenicosis (van Halem et al. 2009; Naujokas et al. 2013). In contrast, it has been demonstrated that long term exposure (i.e., chronic) of arsenic concentrations <100 µg L^{-1} can also lead to similar adverse health effects (Moon et al. 2012; Bräuner et al. 2014; Stea et al. 2014; Tsuji et al. 2014 and 2019). This is an important consideration as many people rely on private wells for drinking water with a large proportion of rural communities globally reporting arsenic concentrations in the range of 10-100 µg L^{-1} due to the dispersed occurrence of arsenic in the environment and frequent reliance on private wells (Ryan et al. 2013; Bondu et al. 2017; Zheng et al. 2017).

The pentavalent form of arsenic, arsenate (As^{V}) and the trivalent form, arsenite (As^{III}), are the most detected forms in groundwater (Sanexa et al. 2004; Stolz et al. 2006). Arsenate forms the oxyanions $H_2AsO_4^-$ and $HAsO_4^-$ in oxidising environments in natural waters, while arsenite forms the oxyanions $H_3AsO_3^0$ and $H_2AsO_3^-$ in reducing environments with the degree of protonation depending on pH (Stolz et al. 2006; Garelick et al. 2009; Sharma and Sohn 2009). Organic arsenic species may be present in groundwater because of biological activity, but their relative concentrations may be negligible (Cullen and Reimer 1989; Smedley and Kinniburgh 2002). These methylated organic forms of arsenic include the pentavalent dimethylarsinic acid (DMA^{V}) and methylarsonic acid (MA^{V}) which are stable mammalian metabolites (Hughes 2002; Villaescusa and Bollinger 2008).

The mobility, toxicity, adsorption, and biogeochemical cycling of arsenic depends on the oxidation state, or speciation of arsenic (Villaescusa and Bollinger 2008; Garelick. 2009). While the geology, hydrogeology and geochemistry of the aquifer system remain important controls on the mobility of trace elements within the solid-aqueous environment (Garelick et al. 2009), the redox parameters pH and Eh are the dominant geochemical factors controlling oxyanion forming elements in natural waters (Smedley and Kinniburgh 2002; Sanexa et al. 2004). Two geochemical triggers are responsible for arsenic mobilisation: one to release arsenic from the host rock and another to retain arsenic in the groundwater after the initial release (Smedley and

Kinniburgh 2013). Other trace elements present in the host rock or minerals may also be mobilised by the same mechanism as arsenic and thus may also be elevated, e.g. U and Mo.

In Asia, groundwaters with elevated arsenic are generally associated with unconsolidated Quaternary alluvial sediments, with geochemical and hydrogeological conditions favouring the mobilisation of arsenic (Ravenscroft et al. 2005; The World Bank 2005; Ryan et al. 2011; Blake and Peters 2015). Recent research has demonstrated that fractured bedrock aquifers give rise to elevated concentrations of arsenic and other trace elements in groundwater, and which has been observed in many regions of the world including North America, Africa, and certain regions of Asia (Ayotte et al. 2003; Smedley et al. 2007; Drummer et al. 2015; Ryan et al. 2011 and 2015; Andy et al. 2017). While there are a few case studies in Europe reporting arsenic in fractured bedrock aquifers (Reyes et al. 2015; Morrison et al. 2016), knowledge regarding specific mobilisation processes is lacking.

In Ireland, these hard rock aquifers, or poorly productive aquifers (PPA) underlie 60% of the island and provide an important water source for domestic, commercial, and industrial settings (Robins and Misstear 2000). Although not being considered as a source for large public water supplies, they are important for small public group supply schemes and domestic sources, and thus are important in terms of delivering water (and any associated pollutants) via shallow groundwater pathways. Recently, the presence of elevated arsenic (for the purposes of this study elevated arsenic means ≥10 μg L^{-1}) has been observed in clusters around Ireland (McGrory et al. 2017).

Total arsenic concentrations fail to provide detailed information regarding the metabolism, toxicity, ecotoxicity and potential mobility in the environment (Michalke 2003). To overcome this, speciation analysis can be undertaken using a hyphenated system (of high-performance liquid chromatography – inductively coupled plasma – mass spectrometry (HPLC-ICP-MS)). However, species redistribution can occur during storage and transport of the samples, influenced by storage time, redox-sensitive parameters, iron concentration, bottle adsorption effects and microbial activity which can impact on laboratory-based speciation analysis (Leybourne et al. 2014; Ullrich et al. 2016; Kumar and Riyazuddin 2010). An alternative, on-site field speciation of arsenic using solid-phase extraction (SPE) cartridges offers advantages over traditional preservation methods with species alternation processes being minimised (O'Reilly et al. 2010; Watts et al. 2010; Christodoulidou et al. 2012; Sugaŕ et al. 2012; Ullrich et al. 2016; Bondu et al. 2017).

The aims of this study were to i) understand the regional geochemistry of arsenic in groundwater of a fractured bedrock aquifer ii) understand the mobility of arsenic through speciation studies, and iii) elucidate the geochemical triggers which are responsible for the mobilisation of arsenic within the study site.

Study site

The study site is located north of Dundalk town along the border of the Republic of Ireland and Northern Ireland adjacent to the A1/N1 dual carriageway (Fig. 1a). Most residential homes in the area consist of one-off dwellings with a private well as their primary source of drinking water and with an on-site domestic wastewater treatment system (DWWTS). The surrounding area is primarily agricultural (pastures) with forestry to the north (McGrory 2020).

The study area is predominately made up of rocks of the Palaeozoic Southern Uplands-Down-Longford terrane (SUDLT), the Paleogene Slieve Gullion complex with younger intrusives and volcanic rocks to the north, west and east of the study area, and Carboniferous sediments are found to the south. The SUDLT, which extends across Scotland and Northern Ireland and is dominated by Lower Palaeozoic marine sedimentary rocks (lithic arsenites and sandstones) which have undergone low-grade metamorphism (Steed and Morris 1986; Anderson 2004; Lusty et al. 2012; McKinley et al. 2017). The Sothern Uplands-Longford-Down Terrance bedrock is dominated by well-bedded Ordovician and Silurian turbidite sequences consisting of greywacke sandstone, siltstone and mudstone (Anderson 2004; Lusty et al. 2012). Further geological and hydrogeological information is presented in the supplementary information (SI, note 1).

Materials & Methods

Sampling

An extensive water sampling campaign (locations identified from the reconnaissance hydrogeological survey in 2014 which is detailed in note 2 SI, Fig. S1 and Tables S1-S3 with these data not included in the present study as they do not contain dissolved arsenic concentrations) was conducted in June 2015 (n=43) (Fig. 1a). Subsequently, a smaller subset of these monitoring locations (n=20) was sampled in July 2016 (Fig. 1b) to understand arsenic speciation in the groundwater (both laboratory and field-based methodologies) in both boreholes (BH) and dug wells (DW). Samples were collected using appropriate methods such as "clean hands dirty hands" techniques using depth specific low-flow sampling (i.e. 8-10 mbgl) (Puls et al. 1992; Creasey and Flegal 1999; Fitzgerald 1999; Appelo and Postma 2005). To achieve low-flow conditions, a 42 mm stainless steel bladder pump was used with a PCU ProPlus control unit (100 PSI) (In-Situ, UK).

Unstable parameters were monitored using the Sheffield low-flow cell (Waterra In-Situ®, Shirley, UK) which allows parameters such as pH and Eh to be measured without atmospheric exposure, which are parameters key to understanding aqueous arsenic speciation (refer to Fig. S2 of SI). Probes included temperature (Orion™ 972005MD), Eh (Orion™ 9678BNWP), dissolved oxygen (d-O_2, Orion™ 083010MD), pH (Orion™ 9107WMMD) and conductivity (Orion™ 01310MD) monitored using Orion™ 3 and 5 Star meters (Thermo Scientific). Probes were calibrated at each field station using appropriate standards. Relative values for redox potential measured in mV using ZoBell's solution were corrected for temperature and adjusted to a potential relative to the standard hydrogen electrode (SHE) (Nordstrom 1977; Weight 2008). Groundwater unstable parameters were recorded every five minutes while drawdown/static water level (SWL) was monitored using a dipmeter (OTT Hydrometry KL010 100 m) with drawdown being minimised.

Triplicate groundwater samples were collected once the unstable parameters stabilised and were filtered using 20 cm^3 BD Discardit™ II PP/PE syringes (VWR, Dublin, Ireland) and Millex®-LCR 25 mm 0.45 µm hydrophilic polytetrafluoroethylene (PTFE) filter (Merck Millipore Ltd., Cork, Ireland) and acidified to pH < 2 using 16 mol L^{-1} HNO_3 (either using *Optima* HNO_3 (Fisher Scientific, Dublin) or Romil UpA HNO_3 (Lennox, Dublin)) in 60 cm^3 bottles. Additionally, one 250 cm^3 bottle was used to collect an anion sample. Samples for hydrogen carbonate (HCO_3^-) analysis were collected in three 125 cm^3 bottles. Anion samples were not filtered as it was previously demonstrated that there are no significant differences between filtered and unfiltered samples (Daughney et al., 2007). Bottles used for trace metals were washed as per note 3 (SI).

Total dissolved salts (TDS) were estimated from the direct EC measurement of groundwater. This conversion formula is provided in Equation 1 (Hubert & Wolkersdofer 2015).

$$TDS = EC \cdot f \quad \text{(Equation 1)}$$

Where f is the conversion factor with 0.69 used here (based on median conductivity of 300 – 400 µS cm^{-1}) (McNeil and Cox 2000; Hem 1985).

Field determinations

Alkalinity was titrated in the field with aliquots of known volume (either 25 cm^3 diluted with distilled water or 100 mL depending on expected concentration) using a digital titrator (Hach, Model 16900) using either 0.16 N or 1.6 N H_2SO_4 cartridge using bromocresol green–methyl red indicator on the day of collection (Hach-Lange, Dublin, Ireland).

Field speciation of arsenic

Using this technique samples are speciated in the field with subsequent species determined as 'total' concentrations via instrumental analysis in the laboratory with the solid-phase extraction (SPE) methods of O'Reilly et al. (2010) and Watts et al. (2010) being adopted.

For this method, the Varian 500 mg Junior Bond Elut® strong anion exchange (SAX) and 500 mg Junior Bond Elut® strong cation exchange (SCX) cartridges were used (Apex Scientific, Maynooth, Ireland). After the cartridges were conditioned, both were connected in series with a 0.45 µm filter. The sample (25 cm^3) was passed through the assembly with an Agilent 20 cm^3

disposable syringe (Apex Scientific, Maynooth, Ireland). The effluent was retained (i.e. arsenite) and both cartridges were separated and 1 M HNO_3 (Romil, SpA) was passed through the SCX cartridge to collect DMA^V. For the SAX cartridge, 5 cm^3 of HOAc (Fluka Analytical, Trace*SELECT*®, Sigma-Aldrich, Ireland) was used to collect MA^V while iAs^V was collected using 1 M HNO_3.

Confirmatory speciation of arsenic

Confirmatory analysis by HPLC-ICP-MS was completed to validate the SPE field speciation procedure (Reilly et al., 2010). For the July 2016 sampling, arsenic speciation samples were collected following filtration (0.45 µm) with the addition of 500 µL of 0.25 M ethylenediaminetetraacetic acid in order to preserve methylarsenicals (EDTA dipotassium dihydrate, Fluka Analytical, Sigma-Aldrich, Ireland) and stored in the dark at 4°C (McCleskey et al. 2004; Ujević et al. 2010).

Analytical measurement

Trace element determination

Trace element determination was performed with an ICP-MS (Elan DRCe, Perkin Elmer, Waltham, USA) (Table S4). Due to the presence of chloride in groundwaters, arsenic (^{75}As) was measured in dynamic reaction cell (DRC) mode as AsO (m/z 91) with oxygen as the reaction gas in order to correct for the interference at m/z 75 from $^{40}Ar^{35}Cl^+$ (May and Wiedmeyer 1998). Additionally, due to polyatomic interferences, ^{52}Cr, ^{56}Fe, ^{66}Zn and ^{80}Se were analysed in DRC mode using methane as the reaction gas (May and Wiedmeyer 1998).

In each analytical batch samples were analysed with certified reference materials (CRMs), blanks (both field and lab) in addition to calibration checks (every 10-14 samples). Full information on linear-working range and LODs of each analyte are documented in Table S5. Triplicate samples taken at each monitoring location were averaged.

Arsenic speciation analysis

A Perkin Elmer Series 200 HPLC system (Perkin Elmer, Waltham, USA) was hyphenated to an ICP-MS which was used for arsenic speciation. Separation was achieved using the Hamilton® PRP-X100 (4.1 x 250 mm, 5 µm) with NH_4NO_3 as the eluting phase (Xie et al. 2002; Ammann 2010).

Separation was achieved using a gradient elution method (Table S6) which composed of solvent A (4 mM NH_4NO_3) and solvent B (60 mM NH_4NO_3) (99.999% Trace Metal Basis, Sigma-Aldrich, Dublin) both adjusted to pH 8.7 (InoLab pH7110) with NH_4 (Ammonia Solution SpA, Romil, Ireland) (Martínez-Bravo et al. 2001; Watts et al. 2007 and 2008). Arsenate (As^V) and arsenite (As^{III}) calibration standards were prepared from 1000 mg L^{-1} standards (Apex Scientific, Maynooth, Ireland), while organicarsenicals standards were prepared from powders of dimethylarsinic acid ($(CH_3)_2As(O)OH$) and disodium methyl arsenate hexahydrate ($CH_3AsNa_2O_3 \cdot 6H_2O$) (Supelco, Sigma-Aldrich, Ireland) with a calibration range of 12.5 – 100 µg L^{-1}.

Anion Analysis

Analysis of anions was accomplished using a Hach DR 3900™ spectrophotometer (Colarado, USA) and included sulfate (SulfaVer4, 2-70 mg L^{-1} SO_4^{2-}), fluoride (ACCUVAC, 0.02-2.00 mg L^{-1} F^-), and chloride (LCK311 1-70 mg L^{-1} and 70-1000 mg L^{-1} Cl^-).

Quality Control

Overall, CRM (1643e, 1643f, BCR-609 (low-level), BCR-610 (high-level), *Enviro*MAT Ground Water-Low (ES-L-2) and *Enviro*MAT Ground Water-High (ES-H-2)) values fell into the acceptable recovery range of 70-125% for ppb data (AOAC, 2002) and an example of CRM recovery for 1643f can be seen in Table S7. The result of this CRM is comparable with published data (Dial et al. 2015; Andy et al. 2017).

Field duplicate samples were generally within ± 10% relative standard deviation (RSD) for all samples. Both field and laboratory blanks showed that metal concentrations were <LOD.

Charge balances were generally within 10.5%; however, BH-27 (15.3%), DW-7 (15.5%), and BH-46 (12.1%) were higher with the absence of NO_3 not being measured accounting for this discrepancy based on previous work (McGrory et al. 2020).

Data and spatial analysis

Due to the presence of data below the limit of quantification (LOQ) (i.e., censored data) nonparametric survival analysis procedures were employed to analyse the data (Helsel 2012). This was achieved using the non-detects and data analysis (NADA) macros (version 4.4) with the statistical analysis software Minitab® 17 (available from www.practicalstats.com).

Summary statistics

Summary statistics were computed for different groundwater types (i.e., DW and BH). Due to the presence of censored data (i.e., data reported as < LOQ), these summary statistics were calculated using “robust” regression on order statistics (ROS) using %*Cros* macro (Helsel 2012). Where censoring is above 80%, then the maximum value and censoring rate are presented.

Correlation and regression

The nonparametric correlation coefficient Kendall’s tau (τ) and test of significance was used to determine the strength of the monotonic relationship between two variables, x and y using the %*Ckend* macro (Helsel and Hirsch 2002; Helsel 2012). Where censoring was ≥ 80% for a variable then it was removed from the analysis. The degrees of relationship (either positive or negative) are denoted as $|\tau| = 0$ (no relationship), $|\tau| < 0.3$ (weak relationship), $0.3 \leq |\tau| \leq 0.5$ (moderate relationship), and $|\tau| \geq 0.5$ (strong relationship) (Khamis 2008).

To access the difference between filtered and unfiltered concentrations of trace elements Kendall’s tau was computed with the non-parametric regression line associated with Kendall’s tau, the Akrita-Theil-Sen (ATS) line using the %*ATS* macro (Helsel 2012). All tests were computed at the 0.05 significance level.

Multivariate statistical analysis (MSA)

To account for censored data, censored multivariate techniques were employed based on ordinal methods using the %*ordranks* macro (Helsel 2012). Subsequent ranks were used as input for principal component analysis (PCA) and the extraction methods of Varimax rotation and Kaiser normalisation were applied to interpret geochemical data using IBM® SPSS® StatisticsV25. Both Kaiser’s measure of sampling adequacy (KMO) and Bartlett’s test of sphericity were performed to access the sampling adequacy for their suitability for PCA which showed data was suitable for PCA (Bartlett 1950; Kaiser and Rice 1974). Principal components (PCs) with an eigenvalue greater than one were retained (Kaiser 1960). Hierarchical cluster analyses (HCA) were performed on ranked data in Q mode (variables) using Euclidean distance measures with Ward’s methods (Nnane 2011; Wangkahad et al. 2017). HCA was also performed on ranked data in R mode (sampling sites) to access spatial clustering of parameters using ArcGIS 10.6.1 (projection, TM-65; datum, D-TM65).

Aqueous Geochemical modelling

Eh-pH diagrams were constructed for the system As-O-H using the ‘Act2’ program with the Lawrence Livermore National Laboratories (LLNL) thermodynamics database ‘thermo.tdat’ in Geochemist’s Workbench® (Release12.0, Student Edition) (Bethke and Yeakel 2018). Temperature was set at 25°C, pressure at 1 bar and arsenic activity set at 10^{-6} M (Lu and Zhu 2011).

Saturation indexes (SI) for minerals were calculated using PHREEQCI V3.4 (Appelo and Postma 2005) using the WATEQ4F database (Ball and Nordstrom 1991).

Results And Discussion

Groundwater geochemistry

Physiochemical parameters

Statistical summaries of data measured in 2015 are shown in Table 1 (2016 data presented in Tables S8-S9). Eh values are representative of more oxidising conditions in shallow dug wells (range - 2015, 452.85-534.8 mV; 2016, -52-476 mV) when compared to boreholes (range - 2015, 191.6-538.3 mV; 2016, -121.5-460.3 mV). However, some mildly reducing conditions were observed in 2016 in DW-17 and BH-40 with an Eh of -52.1 mV and -121.5 mV with the corresponding pH of 6.7 and 8.0 respectively. Groundwaters from boreholes were acidic to alkaline with pH ranging from 6.3 to 8.6 with dug wells being acidic ranging from 6.1 to 6.9. In comparison, pH values in 2016 increased where groundwater in boreholes was slightly acidic to alkaline with pH ranging from 6.9 to 8.3 with dug wells being acidic to near-neutral ranging from 6.5 to 7.1. The more acidic nature of surface wells may reflect more surface weathering of acidic soil. In addition, previous work in this area has also identified surface wells were contaminated with elevated nitrate arising from inorganic fertilizers (McGrory et al. 2020). Generally, groundwaters were described as alkaline oxidising (or oxic-alkali) for boreholes and acidic oxidising (or oxic-acidic) groundwaters for the shallower dug wells (Fig. S3) and while some boreholes were described as acidic-oxidising, all of these are categorised as low-arsenic wells. Previous studies in Quebec have also demonstrated shallow wells displaying more oxidising conditions compared to bedrock wells (Bondu et al. 2017). The Eh-pH conditions overlap with results obtained for both shallow and deep groundwaters in western Ireland (Gilligan et al. 2016). These oxidising conditions are consistent with the concentrations of d-O_2 measured in 2016 (4.17±6.88 mg L^{-1} for BHs and 5.23±3.06 mg L^{-1} for DWs). Only three sites have low d-O_2 measurements (BH-20, 0.22 mg L^{-1}; BH-47 0.12 mg L^{-1}; and BH-25, 0.485 mg L^{-1}), representative of a suboxic redox state (McMahon and Chapelle 2008). As other wells had d-$O_2 \geq 0.5$ mg L^{-1}, Mn $\leq$ 50 µg L^{-1}, and Fe $\leq$ 100 µg L^{-1}, the redox couple present in these groundwaters is likely O_2 reduction (Thomas 2007; McMahon and Chapelle 2008). However, for other wells where Mn $\geq$ 50 µg L^{-1} and/or Fe $\geq$ 100 µg L^{-1} with d-$O_2 \geq 0.5$ mg L^{-1} this in characteristic for a mixed redox state (Thomas 2007; McMahon and Chapelle 2008). The large variation of d-O_2 for BHs may reflet a combination of different redox states.

Conductivity was higher in shallow surface dug wells compared to deeper boreholes with two wells (DW-11 and BH-23) having high conductivities (>1000 µS cm^{-1}) in 2015 and were marginally lower in 2016.

Generally, SWLs were <9 m with boreholes in the 60-120m category were sometimes greater than 10m. The deepest SWL was recorded in BH-39 in both years (2015, 32.76 m; 2016, 30.15 m). The shallowest BH was BH-18 with a SWL of 0.04m in 2015. A linear regression showed that GWLs in both years (n = 19) are positively correlated (n = 19, $\tau = 0.54$, $p = 0.001$) with GWLs from 2016 being approximately 2.9% higher when compared to 2015.

Major-ion geochemistry and hydrogeochemical facies

According to the Piper diagram (Fig. 2a-b), hydrochemical facies of groundwater is dominated by Ca-Mg-HCO_3 indicating mainly recharged groundwater and the predominant water-type of shallow and deep groundwater was Ca-HCO_3. This reflects the calcareous nature of the Clontail Formation and Dinantian Limestones which most boreholes are drilled in.

Most sites are classified as recharging waters (Ca-HCO_3^-) (Fig. S4a-b) using Chadha's diagram (Chadha, 1999). For 2015 some groundwaters are governed by ion-exchange (Na-HCO_3^-) or reverse ion-exchange waters (Ca-Mg-Cl). In 2016 one well (DW-11) falls into the seawater (Na-Cl) category. Inadequate wastewater treatment may be responsible for the elevated concentrations of both Na and Cl in this surface well (DW-11). In addition, the Gibbs diagram (Gibbs 1970) showed most samples in this locality lie within rock weathering dominance (Fig. S5a-d). A small number of samples lie in evaporation dominance and these wells are associated with high Cl^- and Na^- concentrations (i.e. DW-11), i.e. localised contamination. Thus, the main processes contributing to groundwater geochemistry in this area is rock weathering, i.e. interaction of groundwater with aquifer material. Aquifer rock weathering facilitates in the geochemical process that soluble salts and minerals can become incorporated into groundwater (Talib et al. 2019). In addition, the longer residence times associated with rock-water interactions also aids in this mineral dissolution (Selvakumar et al. 2017; Talib et al. 2019).

All anions and cations were below the regulated concentrations except for F and K where maximum concentration was 2.46 mg L^{-1} (BH-58) and 18.08 mg L^{-1} (BH-06) respectively. Fluoride does not show many correlations with major anions, but a weak negative correlation exists with K (τ=-0.24) (unless otherwise stated all correlations coefficients are for 2015 data with those denoted by * are not significant at the 5% significance level). Several ions are correlated with depth including weak relationships for SO_4^{2-} (τ=0.19*), F^- (τ=0.25), Mg (τ=0.25), Na (τ=0.23), and Si (τ=0.22). Different levels of strength of the monotonic relationship are seen for several ions: strong (SO_4^{2-} and Sr (τ=0.50), HCO_3^- and Mg (τ=0.54), HCO_3^- and Ca (τ=0.54), HCO_3^- and Sr (τ=0.57), SO_4^{2-} and Mg (τ=0.56), Si and Na (τ=0.51), and Sr and Mg (τ=0.65)), moderate (Cl and Na (τ=0.30), Ca and Cl (τ=0.44), Ca and Na (τ=0.30), Ca and K (τ=0.39), Ca and Si (τ=0.30), Mg and Ca (τ=0.30), and Si and K (τ=0.30)), and weak (Cl and Mg (τ=0.25), Cl and Sr (τ=0.24), SO_4^{2-} and Si (τ=0.23), SO_4^{2-} and Ca (τ=0.25), SO_4^{2-} and Na (τ=0.27), SO_4^{2-} and K (τ=0.28), Ca and Sr (τ=0.27), Mg and Si (τ=0.17*), and HCO_3^- and K (τ=0.21)). Sr shows a weak positive correlation with pH (τ=0.23) while K shows a weak negative correlation with depth (τ=-0.14*). Conductivity shows a strong correlation with Ca (τ=0.68), HCO_3^- (τ=0.63), moderate correlation with SO_4^{2-}(τ=0.45), Cl (τ=0.48), Mg (τ=0.46), Na (τ=0.37), Sr (τ=0.40) and K (τ=0.31), and weak for Si (τ=0.26). The strong correlation with Ca and HCO_3^- (τ=0.54) also indicates that these ions are the major ones resulting from rock or soil weathering. Given the correlation of HCO_3^- with Ca and Mg this is indicative of the dissolution of carbonate minerals, i.e. calcite and dolomite (Talib et al. 2019). The molar ratio for calcite and dolomite dissolution is 1:2 and 1:4, respectively (Appelo and Postma 2005). While the molar ratio deviates from the 1:1 line so dissolution of these minerals does not fully account for these cations in groundwater, however some of the data points have a ratio of 1:2 and 1:4. The molar ratio of Na/Cl of nearly 1:1 for these samples is indicative of halite dissolution (Talib et al. 2019). However, ion exchange processes may also be occurring (i.e. Na/Cl<1) while contribution of extra Na may result from silicate weathering given that some samples lie above the equiline of 1:1 (i.e. Na/Cl>1) (Juen et al. 2015). Indeed, given the correlation of Si with cations (Na, Ca, Mg, and K) this further illustrates silicate weathering in the groundwater (Montcoudiol et al. 2014; Bondu et al. 2017). This is supported by the fact that groundwaters are undersaturated with respects to silicate minerals such as anorthite, but the extent of this is not fully known given that PHREEQC calculations indicate that calcite is both under and oversaturated in samples (discussed further in Thermodynamic calculations).

Trace elements

In these groundwaters, most trace elements show a linear relationship of filtered (dissolved) to unfiltered (total) concentrations, indicating that most trace elements exist in dissolved form and are negligible with regards to particulate form (Table S10). However, some occur in greater proportions in particulate form, e.g. Al, Fe, Mn, Ti, and Pb. For the rest of the discussion, unless otherwise stated, interpretations will be made with reference to dissolved aqueous concentrations. In terms of exceedances (besides arsenic) the greatest occurred for Fe, Mn and U. While these exceedances are evident for Fe and Mn in both shallow and deep groundwater, exceedances for U and As only occurred in bedrock boreholes.

Detected trace elements were found at low concentrations in groundwater (with corresponding lower concentrations measured in dug wells) with Al, As, and Ba occurring at higher concentrations. As seen elsewhere, the concentrations of Sb, Cu, Mo, Cd, Se and Be rarely exceed regulatory limits (DeSimone et al. 2009). When Fe and Mn are reported as occurring at higher concentrations, this is generally a result of an outlier. For example, one sampling location in 2015 (BH-66) recorded Mn and Fe concentrations at 611 and 39257 µg L^{-1}, respectively. This anomalously high value in comparison to the lower values in the surrounding area arises from the reductive dissolution of Fe and Mn oxyhydroxides (reducing conditions noted while sampling) as the well is not currently in active use. Indeed, concentrations of these trace elements are usually low with higher concentrations found in private wells elsewhere (DeSimone et al. 2009; Homoncik et al. 2010; McGrory et al. 2018).

Both Mn and Fe can be derived from the weathering of multiple common bedrock minerals which includes silicates, oxides, carbonates and sulfides (Bondu et al. 2017). Both Fe and Mn have high particulate concentrations when compared to other trace elements. These particulate forms of Fe and Mn may have sorbed oxyanions and other trace elements with the sample acidification step promoting their dissolution into dissolved Fe and Mn (Plant et al. 2003). Particulate concentrations for most trace elements are negligible and reflects the natural filtration of the groundwater through the aquifer (Plant et al. 2003).

Several parameters show a positively weak to strong correlation with depth data including pH (τ=0.51), HCO_3^- (τ=0.21), temperature (τ=0.34), F (τ=0.25) and several oxyanions (As (τ=0.52), Mo (τ=0.51), Sb (τ=0.31) and U (τ=0.40)). While Fe and Mn show a strong positive correlation (τ=0.63), both show weak to moderate negative correlations with Eh, pH and depth. Several oxyanions (Mo, Se, Sb, U, and HCO_3^-) also display negative weak to moderate correlations with Fe and Mn. Positive correlation of Fe and Mn have been observed for metasedimentary geologic units (Ayotte et al. 1999), crystalline bedrock (Johnson et al. 2017) and mixed bedrock (Homoncik et al. 2010). Given the strong positive relationship between Fe and Mn they are expected to originate from a common source. Similar trends with Eh, pH and depth are observed with B, Cu, Co, and to a lesser extent with Al, V, Cr, and Ni. Different levels of strength of the monotonic relationship are evident for several transition series trace elements: moderate (Cr and V (τ=0.37), Cu and Zn (τ=0.31), Mn and V (τ=-0.40*), and weak (Cr and Ti (τ=0.22), Co and Mn (τ=0.18), V and Ti (τ=0.24), Ti and Co (τ=0.19), V and Co (τ=0.14), Co and Ni (τ=0.29), Co and Cu (τ=0.16), Ni and Cu (τ=0.21), Pb and Zn (τ=0.19)). While not a transition series trace element, B shows a strong positive correlation with Ni (τ=0.50), Ca (τ=0.56), moderate positive correlation with Na (τ=0.31) and K (τ=0.39) and weak positive correlation with V (τ=0.28), Co (τ=0.24), Cu (τ=0.24), and Si (τ=0.26).

Arsenic geochemistry

Arsenic was the most frequently detected parameter above the regulatory limit (10 µg L^{-1}) with 45.7% and 70.5% of samples having concentrations above the limit in 2015 and 2016 for boreholes with a maximum value recorded in 2016 (73.95 µg L^{-1}). Previous work has identified that arsenic concentrations in this area to the north west of the study site approach 139 µg L^{-1} (McGrory et al., 2017). Arsenic was detected at lower concentrations in dug wells with the maximum concentration reported at 3.7 µg L^{-1} in 2015, comparable to observations noted in a bedrock aquifer in Quebec, Canada where arsenic concentrations in shallow wells did not exceed 4.1 µg L^{-1} (Bondu et al. 2017). Negligible arsenic concentrations were reported in dug wells as no anthropogenic contamination was noted in the area (McGrory et al. 2020). Anthropogenic arsenic contamination (or surface contamination) would show higher arsenic concentrations in dug wells.

Elevated arsenic (≥10 µg L^{-1}) was usually associated with an Eh of >390 mV (lower Eh in 2016 ~>120 mV) and near-neutral to alkaline pH, depth > 70 m and low concentrations of Fe (<2 µg L^{-1}) and Mn (<1.5 µg L^{-1}). One borehole (BH-61) had a low arsenic concentration in 2015 (8.1 µg L^{-1}), but a moderate one in 2016 (15.4 µg L^{-1}) with Fe and Mn measured at 30.5 µg L^{-1} and 0.64 µg L^{-1} in 2015 and 2016, respectively. However total concentrations of Fe measured markedly higher at 1588.6 µg L^{-1} with Mn at 8.5 µg L^{-1} showing that low arsenic concentrations can occur with elevated Fe and/or Mn concentrations. Low arsenic wells usually had a lower pH of 6.4-7.4 with a variable Eh. While considered low arsenic wells, both BH-46 and BH-70 had a pH of 7.9 and 8.3 with arsenic concentrations of 6.04 µg L^{-1} and 8.12 µg L^{-1} respectively (2016). This illustrates that even at low concentrations arsenic may still be mobilised through desorption processes. It has been demonstrated that high arsenic concentrations are associated with concentrations of iron > 100 ppb are often also associated with reducing conditions (Erickson et al. 2019). Given the low Fe concentrations, this also agrees with the oxic-alkali nature of the groundwater in the present study. Furthermore, the level of arsenic contamination is generally lower in oxic aquifers compared to anoxic aquifers (Masuda 2018).

In comparison, elevated arsenic concentrations were mainly distributed between 70-120 m depth (Fig. 3a). A small proportion of boreholes with elevated arsenic concentrations occurs at a depth > 120m. For low arsenic concentration boreholes (i.e. ≤10 µg L^{-1}) these occurred within several depth categories. Elevated arsenic is observed at pH ~ >7.5 (up to 8.57 (Fig. 3b)) and > 390 mV (Fig. S6a). However, another group of elevated arsenic wells occurs between 200-310 mV. This may be indicative of mixed redox state groundwater thereby suggesting a mixing of groundwater (refer to Section 4.1.1). Elevated arsenic at an alkaline pH in addition to lack of relationship with Eh has been shown to occur in oxidising aquifers (Rango et al. 2013). Elevated arsenic concentrations show U concentrations below 6 µg L^{-1}, however, elevated U can be seen in low arsenic wells (Fig. S6b). Elevated arsenic concentrations were observed with low Fe and Mn while elevated Fe and Mn were seen with low arsenic concentrations (Fig. S6c-d). This is seen with a moderate negative correlation with Fe and Mn.

Concentrations of total and dissolved arsenic from both study years were highly correlated (2015, $\tau = 0.93$, $p = 0.0$; 2016, $\tau = 0.96$, $p = 0.0$). A linear regression showed that the unfiltered arsenic concentrations are approximately 12.4% and 2.2% higher than the filtered samples in 2015 and 2016, respectively, indicating that the particulate form of arsenic was negligible in these groundwaters with similar results been observed in private bedrock boreholes (Peters et al. 1999; Ayotte et al. 2003; Kim et al. 2003). A linear regression demonstrated that concentrations of arsenic concentrations sampled in both years ($n = 19$) are positively correlated ($n = 19$, $\tau = 0.87$, $p \approx 0.000$) with samples obtained in 2016 being approximately 8.1% higher. Similar results have been observed for arsenic in private bedrock boreholes in New Hampshire (Ayotte et al. 2003). The absolute value of intra-well differences ranged from 0.06-8.1 μg L^{-1}, with a median difference of 1.44 μg L^{-1}.

Based on results from the correlation matrix, several parameters are associated with arsenic in groundwaters including strong (depth (τ=0.52), Mo(τ=0.51)), moderate (pH (τ=0.45), temperature (τ=0.37), HCO_3^- (τ=0.37), SO_4^{2-} (τ=0.31), Sb (τ=0.44), U (τ=0.32), Sr (τ=0.47), and Mg (τ=0.36)), and weak (conductivity (τ=0.22), Se (τ=0.20), and Ba (τ=0.23)). The previous correlations with several oxyanions (e.g. Se, Mo and Sb) were reported in previous studies (McGrory et al. 2020) with the degree of the monotonic relationship being stronger in this study. As previously mentioned, both Fe and Mn show a negative relationship with arsenic (τ=-0.40 and τ=-0.36 respectively), this is also obvious for Cu which displays a weak negative relationship (τ=-0.27). The strong correlation of arsenic and depth is also evident from low arsenic concentrations in shallow dug wells, but higher concentrations in deeper boreholes, which has been observed elsewhere in Canada (Peters et al. 1999; Bondu et al. 2017).

The small spatial variations in arsenic concentrations reported in the literature can be observed in this study, especially at the dwelling containing BH-61 and BH-60. At this dwelling, BH-61 was drilled in 1995 which had an arsenic concentration of 15.4 μg L^{-1} (2016). BH-60 was drilled deeper in 2007 to avoid high arsenic concentrations but had an arsenic concentration of 73.95 μg L^{-1} in 2016 (well only sampled in 2016 detailed survey). During sampling, the homeowner indicated that the well driller encountered quartz veins at depth**.** These wells are 27.5 m apart which illustrated that arsenic concentrations vary over small spatial scales (Ravenscroft et al. 2009; Smedley and Kinniburgh 2013). In these fractured aquifers, this large spatial variability is mainly governed by groundwater flow through influencing the dilution process and hydrochemistry with previous studies illustrating a similar process (Peters 2008; Smedley et al. 2007; Bondu et al. 2016). Groundwater samples had low Ca/Na ratios with boreholes with elevated arsenic concentrations having lower ratios (Fig. S7a-b). More geochemically evolved groundwater (older) is expected to contain elevated dissolved arsenic from increased reaction time between minerals and water, i.e. low Ca/Na ratios. In comparison, less geochemically evolved groundwater (younger groundwater) contains low dissolved arsenic, i.e. higher Ca/Na ratios (Ryan et al. 2013; Bondu et al. 2016). As the geochemical signature of groundwater evolves along the flow path arsenic concentrations increase with depth (Fig. 3a) (Smedley et al. 2007; Bondu et al. 2016). Ca/Na ratios calculated in this present study are mixed which suggests a mixing of younger and older groundwaters along the flow path presumably at fracture points which is supported given that a significant portion of groundwater is recharge water (Fig S4a-b).

Arsenic speciation

Good recovery from the SPE technique was achieve (Table 2) with confirmatory analysis by HPLC-ICP-MS showing similar results (data not shown) with previous studies (O'Reilly et al. 2010; Watts et al. 2010). The dominant species is arsenate (As^V) which ranged from 0.09-64.3 μg L^{-1}.

Based on the Eh-pH diagrams of 2015 and 2016 data, pentavalent arsenic is in the species form of $HAsO_4^-$ and $H_2AsO_4^-$ (Fig. S8a-b). Both BH-40 and DW-17 appear to be in the form of $As(OH)_3$ and are composed of a small proportion of As^{III}. Eh-pH diagrams from 2015 (Fig. Sxa) show these are present as $HAsO_4^-$ and $H_2AsO_4^-$. These data illustrate that using Eh-pH diagrams solely to infer arsenic speciation must be done with caution, however, it may be useful for informative applications. Both MA^V and DMA^V were detected in groundwaters reaching a maximum concentration of 0.12 μg L^{-1} and 2.25 μg L^{-1}, respectively. The presence of these methylated arsenic species is typical of microbial-medicated methylation reactions (Smedley and Kinniburgh 2013). Despite occurring in many regions of the world, these microbial methylation reactions were considered insignificant with the arsenic cycle being assumed to be limited to redox transformations between arsenite and arsenate (Oremland and Stolz

2003; Maguffin et al. 2015). Elsewhere low concentrations of methylarsenicals have been reported in natural waters resulting from microbial processes (O'Reilly et al. 2010; Christodoulidou et al. 2012; Maguffin et al. 2015; Bondu et al. 2017). In addition, strong correlations are evident with dissolved arsenic and As^{V} (τ=0.93), dissolved arsenic and DMA^{V} (τ=0.89), and moderate correlations with As^{III} and MA^{v} (τ=0.49), As^{V} and DMA^{V} (τ=0.91), and DMA^{V} and MA^{v} (τ=0.38) (correlation coefficients from 2016 used for arsenic species data). These correlations illustrate that there is a biomethyation pathway of inorganic arsenic occurring in these natural waters (Maguffin et al. 2015). The presence of these methylated arsenicals warrants further work as recently the toxicity of these methylated species has been found to be greater than previously considered (Wang et al. 2014; Mestrot et al. 2013) and in order to understand aquifer arsenic cycling.

In this study, the dominant aqueous control is pH rather than Eh (which is usually reported in the literature) which is evident from the correlation of As^{III}/As^{V} with pH (τ=0.34) and lack of correlation with Eh (τ=0.07).

Geochemical controls on groundwater geochemistry

Thermodynamic calculations

Thermodynamic modelling (Table S11) reveals that several Fe, Mn, Cu and Al oxides were supersaturated in groundwater including cupric ferrite, cuprous ferrite, diaspore, $Fe(OH)_2.7Cl.3$, $Fe(OH)_3$ (a), goethite, hematite, maghemite, magnetite, pyrophyllite, K-mica, and adularia. Several minerals were undersaturated, i.e. they could dissolve into solution, and included alunite ($KAl_3(SO_4)_2(OH)_6$), anorthite ($CaAl_2Si_2O_8$), arsenolite (As_2O_3), fluorite (CaF_2) (data not shown) and specific arsenic bearing minerals including scorodite, As_2O_5(cr), and claudetite (As_2O_3)**.** These undersaturated arsenic minerals indicate that mobilised arsenic should remain dissolved (Sappa et al. 2014). Given the high adsorption capacity of Fe and Mn oxyhydroxides and clay minerals (K-mica and kaolinite) these phases can control the reactivity and thus the concentrations of arsenic and other oxyanion forming elements in this groundwater system (Smedley and Kinniburgh 2002; Rango et al. 2013). Several arsenic-bearing phases are undersaturated in the groundwater and have limited influence on the mobilisation of arsenic. Given that concentrations of trace elements are low in groundwaters (i.e. Fe, Mn, Al and Cu) it is more plausible that these mineral phases are controlling arsenic concentrations in the groundwater through desorption processes (Palumbo-Roe et al. 2007). Indeed, the principal pathway of controlling groundwater arsenic is through adsorption-desorption with Fe and Mn oxyhydroxides (Rango et al. 2013). Certain iron minerals (siderite and scorodite) were unsaturated and may explain the low concentrations of iron in groundwater. The poor correlation between Fe and As may result from precipitation of Fe oxyhydroxides. As mainly iron minerals were supersaturated, they can precipitate out and desorb arsenic. During sampling, iron precipitates were noted in many sampling bottles and this would further explain the poor correlation of arsenic with iron and manganese (Sracek et al. 2004).

Multivariate analysis

Results from the PCA analysis explained 90.9% of the variance in 10 principal components (PCs) with 25.1% and 20.2% of the variance in both PC1 and PC2 respectively (Table S12) (interpretations made using 2016 data). Overall PC1 describes general water-rock interactions as strong and moderate positive PC loadings for cations and anions are present (Fig. S9). PC2 is characterised by strong positive PC loadings for As, DMA, As^{V}, Sb, moderate positive PC loadings for depth, pH, MA, Se, Mo, Pb, U and moderate negative PC loadings for Al, Mn, Fe. The inverse loadings for Al, Mn and Fe for PC2 indicate that with increasing concentrations of arsenic (and other oxyanions) in addition to increased well depth and pH values, a decrease in concentration of transition series trace elements is occurring and confirms earlier results. This factor illustrates that the concentrations of oxyanions (As, Se, Mo, Sb, and U) in groundwater are potentially controlled by deeper recharging groundwater at alkaline pH which promotes desorption of oxyanions from oxides of Al, Fe and Mn. While the SI indicated that Cu minerals may also have a role in desorption, the loading of Cu in this PC was weak. Other oxyanions (U, Mo, Se and F) are present as positive loadings with pH and depth and negative loadings of both Fe and Mn in PC4. This may be indicative of another source of oxyanions into groundwater with no association with arsenic.

Similar results were observed with Q-mode HCA showing 5 clusters in each sampling year (Table S13). In the first cluster depth, pH and arsenic are present with other oxyanions (Se, Mo, Sb and U). Redox parameters were associated with Fe, Cu and Mn in addition to transition metals and cations. In both years cluster 4 is associated with HCO_3^-, SO_4^{2-}, Ba, Mg and Sr which may influence groundwater geochemistry.

Additionally, HCA using R-mode analysis showed different spatial clusters for both 2015 (5 clusters) and 2016 (3 clusters) (Fig. 4a-b). For 2015 data there were 6, 11, 10, 5 and 11 sites for Cluster1-Cluster5 while there were 5, 8 and 7 sites for Cluster1-3 for 2016 data respectively. For 2015 both Cluster 1 and Cluster 5 have strong positive loadings for depth, temperature, pH and several oxyanions which are mainly spatially clustered near each other. It is worth noting the main difference in these two clusters is that Cluster 5 has positive loadings for Ca, SO_4^{2-} and HCO_3^- indicating that these elevated concentrations of arsenic are associated with Ca-HCO_3^- waters. Given the dominance of Ca-HCO_3^- groundwaters, the other spatial cluster is not associated with Ca or HCO_3^- indicating potential mixing of groundwater from fracture points in the borehole. Similar observations are seen with Cluster 2 in 2016. In addition, SO_4^{2-} is associated with Cluster 5. Cluster 3 of 2016 and Cluster 2 and 3 of 2015 showed associations mainly to the north of study area and had positive loadings mainly for Al, Mn, Fe, and Cu. This cluster is considered a low-arsenic cluster and interestingly in 2016 d-O_2 was associated with this cluster. These clusters associated with Fe and Mn groundwaters show the greatest spatial diversity.

Geochemical controls on arsenic mobilisation

Elevated arsenic concentrations reported in this groundwater system in north east Ireland result from a geogenic origin. While anthropogenic activity is not expected to be a major contributor of elevated arsenic in groundwater, previous work in this area has identified that some wells receive excess nutrient contamination (particularly NO_3^-) and microbiological contamination from inadequate wastewater treatment facilities (McGrory et al. 2020). In comparison, boreholes with elevated arsenic contained little to no microbiological contamination.

The mobilisation of arsenic in these groundwaters results through desorption at high pH under oxidising conditions (i.e. alkali desorption). In this present work, arsenic is being desorbed from Al hydroxides (e.g. diaspore), Fe oxides (e.g. hematite) and Fe hydroxides (e.g. goethite) as shown elsewhere (Sappa et al. 2014). A general trend was also observed in the same location in 2005 on a smaller subset of wells (McGrory et al. 2020). Al, Mn and Fe mineral phases are potential arsenic adsorbents in these groundwaters given that the major forms of these trace elements, particularly Fe, are particulate based. Under such oxidising conditions the solubility of both Fe and Mn are low (Smedley et al. 2005) and this is observed from the low concentrations of these trace elements in this study. The strong correlation of arsenic and pH under oxidising conditions is characteristic of this geochemical process. Under alkaline conditions, mineral surfaces are negatively charged which limits adsorption of arsenic oxyanions as the pH increases above 7 to 8.5 specific to the mineralogy of the aquifer (Ravenscroft et al. 2009; Bondu et al. 2016). As a result, elevated arsenic concentrations are often found above the threshold pH value of 7 – 8.5 in bedrock aquifers (e.g. Ayotte et al. 2003; Boyle et al. 1998; Rango et al. 2013; Ryan et al. 2013). Indeed, positive correlations of pH and arsenic are consistent with the weaker sorption of As^V to iron oxide surfaces at higher pH values (Smedley et al. 2002; Bhattacharya et al. 2006). This increase in pH promotes the desorption of other oxyanions including U, Se, Sb, Mo, B and V (Bhattacharya et al. 2006; Smedley et al. 2002 and 2005). The correlation of arsenic with other oxyanions has been observed through alkali desorption processes in other oxidising aquifers (Smedley et al. 2002; Bhattacharya et al. 2006; Scanlan et al. 2009; Rango et al. 2013; Sappa et al. 2014). These adsorbed anions will interact with adsorption sites on the oxides in a competitive way to influence the extent of binding of each other (Smedley and Kinniburgh 2013). For example, HCO_3^- can compete with As^V (Appelo et al. 2002) which may be occurring given strong correlation and association through multivariate analysis. In addition, PO_4^{3-} can also compete with As^V, but was not analysed in this study (Hongshao and Stanforth 2001). The presence of phosphate from either fertiliser or wastewater sources may alter the concentration of arsenic in groundwaters in this study. HCO_3^- is the dominant anion in this high-arsenic groundwater, but concentrations are not as high as the often-reported exceedance of > 500 mg L^{-1} for this mobilisation process (Smedley and Kinniburgh 2013). While the association of HCO_3^- and arsenic suggests there may be competition for adsorption sites, however, this may be an indicator of other geochemical processes which increased pH

such as the dissolution of carbonates (Bhattacharya et al. 2006). Furthermore, the dominant arsenic species in these groundwaters is arsenate. The groundwater composition of reducing aquifers reported in areas of south east Asia are generally typified by high concentrations of Fe, Mn, HCO_3^-, P, DOC, and NH_4 in conjunction with low concentrations of NO_3^- and SO_4^{2-} (Ravenscroft et al. 2009; Smedley and Kinniburgh 2013) and do not reflect the geochemical composition of groundwaters in this study.

The source of arsenic

While alkali desorption explains the mobilisation of arsenic in groundwater in this area, it does not fully account for the source of arsenic. The correlation with arsenic and oxyanions, F and Sr are indicative of a volcanic source (Smedley et al. 2002; Bhattacharya et al. 2006; Sappa et al. 2014). Volcanic rocks such as tuffs have been present in numerous sites in relation to the generation of high arsenic waters (Masuda 2018). The weathering by-products of volcanic rock can include secondary silica, Fe/Mn oxides, Al hydroxides and clay minerals (Sappa et al. 2014). These secondary mineral phases play a critical role, and ultimately are a sink for arsenic and other oxyanions until their mobilisation through adsorption-desorption processes described above and elsewhere (Rango et al. 2013; Sappa et al. 2014).

An alternative source for the arsenic for AO waters can occur with sulfide mineralisation in veins and coating fracture surfaces (Ravenscroft et al. 2009). During sampling, it was remarked by the homeowner that quartz veins were noted during drilling of the well (BH-60, 73.95 µg L^{-1}) which may explain the elevated concentration of arsenic in this well given that a well in the same location (27 m apart) (BH-61, 15.46 µg L^{-1}) has moderate arsenic concentrations. This prior weathering from sulfide oxidation can transfer arsenic from sulfides to secondary phases. In this study location, previous work using two bedrock drill cores has shown that disseminated arsenic-bearing minerals with associated Co and Ni being identified within the basaltic dykes (Russel et al. 2018 and 2021). However, no correlations for arsenic, nickel and cobalt were observed. In addition, none were apparent for sulfate, with low levels detected in this location. Generally, mobilisation from sulfide sources (including mineralised areas) would yield high concentrations of sulfate (typically hundreds of mg L^{-1} or higher), acidity, high concentrations of Fe/Mn and variable arsenic speciation (Ravenscroft et al. 2009; Smedley and Kinniburgh 2013). These acid-waters would also give rise to increased concentrations of other trace elements including Ni, Pb, Zn, Cu and Cd with no correlations observed with arsenic. In this present study, the hydrochemistry of sulfide oxidation does not agree with the data in that low concentrations of sulfate, iron and manganese were measured. Whilst both reductive dissolution and sulfide oxidation are oxic in nature, they differ in their pH, with alkaline and acidic waters reported, respectively.

However, it may be possible that in this study both sulfide oxidation and alkali desorption could operate simultaneously within the same geological terrain. This geochemical feature occurs elsewhere where the geology is often granitic, as with the geological setting of this study, i.e. granitoid intrusions into metasedimentary bedrock. For example, this was observed in areas of Finland, British Columbia and New England (Boyle et al. 1998; Ayotte et al. 2003; Loukola-Ruskeeniemi and Lahermo 2004; Ravenscroft et al. 2009). Given the presence of carbonate minerals, the acidity arising from sulfide oxidation can also be neutralised. However, in this study, only a moderate correlation is observed with SO_4^{2-}. In addition, given the presence of methylarsenicals in groundwater, some of the reactions giving rise to elevated arsenic are microbially-mediated, but the extent is not fully known.

Most elevated arsenic concentrations occurred in wells intersected in the calcareous metasedimentary Clontail formation (Fig 1a-b) (calcareous red-mica greywacke) with comparable calcareous metasedimentary aquifers giving rise to elevated arsenic in areas of New England (Peters et al. 1999; Ayotte et al. 2003). Elsewhere in Ireland, similar rock types are intersected with groundwater wells that contain elevated arsenic in isolated hotspots (with concentrations up to 242 µg L^{-1}) (Morrison et al. 2016; McGrory et al. 2017). The prevalence of elevated arsenic in several fractured metasedimentary bedrock aquifers (including calcareous metasedimentary bedrock) as sources of elevated arsenic in groundwater have also been identified in the US (Ayotte et al. 2003 and 2006; Smedley et al. 2007; Ryan et al. 2013 and 2015; O'Shea et al. 2015; Andy et al. 2017; Bondu et al. 2017 and 2018). Oftentimes these fractured aquifers consist of metavolcanics and metasedimentary geology which are intruded granitoids which can be overlain by younger deposits (Bondu et al. 2016 and 2018).

It has been noted that arsenic can be particularly high in certain greywacke-shale sequences in orogenic belts (Plant et al. 1998; Pan et al. 2012). Concentrations of arsenic in greywackes are reported to be about 8 mg kg^{-1} (Wedepohl 1991). In Ireland, Silurian metasedimentary lithology has been found to contain a median arsenic concentration of 24.7 mg kg^{-1} in southwest Dublin (Glennon et al. 2014). Greywackes can also contain high concentrations of manganese (Homoncik et al. 2010).

Conclusions

This study has investigated elevated arsenic occurring in a subset of private water supply boreholes tapping into groundwater flow systems within a fractured metasedimentary bedrock aquifer. The geochemistry of these natural waters show that arsenic was the most detected oxyanion forming element, however both Sb and U were found above regulated limits to a lesser extent. Arsenic was not detected above regulatory limits in surface dug wells but was in deeper borehole wells illustrating that surface processes such as anthropogenic contamination are not contributing to arsenic in the aquifer. Elevated arsenic groundwaters are described as oxic-alkali, low Ca/Na ratios, low Fe and Mn, and co-occurrence of several oxyanions (Mo, Se, Sb and U). Mobilisation of arsenic is through the process of alkali desorption from Fe oxyhydroxides, however microbial processes may be contributing to the arsenic biomethylation pathway in aquifers. The source of arsenic may be sulfide minerals within fractures in the bedrock aquifer, with transportation of arsenic and other oxyanion forming elements facilitated mainly by secondary Fe mineral phases. The dominant speciation of arsenic in groundwater is arsenate, with pH controlling the speciation. The application of SPE based methodology was used to overcome many of the limitations of implementing laboratory-based speciation of arsenic.

Declarations

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Conflicts of interest/Competing interests The authors declare that there are no conflicts of interest

Availability of data and material Data generated as part of this study is available upon request from the corresponding author

Consent for Publication All authors provide consent for publication

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Tables

Table 1. Statistical summary of hydrochemistry data in bedrock boreholes (BH, n=35) and dug wells (DW, n = 8) sampled in 2015

Variable	Groundwater Type	Mean	SD	Min	Q1	Median	Q3	Max	Cen (%)	Limit	% > Limit
Depth (m)	BH	76.6	35.8	9.10	49.3	79.4	104.0	148.8	0.0	-	NA
	DW	4.3	1.8	2.0	2.8	3.8	6.0	7.0	0.0		NA
SWL (m)	BH	6.4	5.8	0.1	2.7	5.2	8.1	32.7	0.0	-	NA
	DW	2.5	1.5	0.5	1.1	2.6	3.2	5.2	0.0		NA
Temp (°C)	BH	11.3	1.2	9.8	10.3	11.4	11.7	16.3	0.0	-	NA
	DW	10.4	0.9	9.7	9.8	10.0	10.8	12.5	0.0		NA
C ($\mu S\ cm^{-1}$)	BH	388.3	220.4	87.7	239.5	374.0	477.7	1405.0	0.0	2500	0.0
	DW	440	320	134	169	399	619	1044	0.0		0.0
TDS ($mg\ L^{-1}$)	BH	266.8	152.8	60.5	159.9	258.1	329.6	969.4	0.0	-	NA
	DW	303.6	221.1	92.2	116.5	275.4	427.1	720.0	0.0		0.0
pH	BH	7.5	0.5	6.3	7.3	7.65	7.96	8.6	0.0	≥6.5 & ≤9.5	5.7
	DW	6.5	0.3	6.1	6.3	6.55	6.83	6.9	0.0		50.0
Eh (mV)	BH	463.1	66.3	191.6	442.7	480.8	499.9	538.3	0.0	-	NA
	DW	483.2	25.0	452.9	468.0	478.5	496.1	534.8	0.0		NA
Cl^- ($mg\ L^{-1}$)	BH	19.7	8.5	1.4	13.8	18.4	24.7	37.9	0.0	250	0.0
	DW	52.5	27.0	76.5	12.2	15.3	17.1	59.9	0.0		0.0
SO_4^{2-} ($mg\ L^{-1}$)	BH	15.7	12.2	8.0	10.0	13.0	17.0	81.0	0.0	250	0.0
	DW	12.2	3.4	9.0	10.0	11.0	15.0	19.0	0.0		0.0
F^- ($mg\ L^{-1}$)	BH	0.2	0.4	0.1	0.1	0.1	0.2	2.5	0.0	1.5	2.8
	DW	0.1	0.0	0.1	0.1	0.1	0.2	0.2	0.0		0.0
Alk ($mg\ L^{-1}$)	BH	119.9	45.8	33.4	76.6	120.1	159.6	203.3	0.0	-	NA
	DW	101.9	70.5	33.7	38.6	85.6	173.5	216.9	0.0		NA
Be ($\mu g\ L^{-1}$)	BH	-	-	-	-	-	-	0.2	97.2	-	NA
	DW	-	-	-	-	-	-	-	100		NA
B ($\mu g\ L^{-1}$)	BH	10.3	4.3	6.3	7.3	9.0	11.8	23.5	0.0	1000	0.0
	DW	14.0	7.9	6.5	7.2	12.7	17.0	30.7	0.0		0.0
Al ($\mu g\ L^{-1}$)	BH	3.5	8.6	0.3	0.7	1.4	2.9	51.3	0.0	200	0.0
	DW	6.0	6.9	0.7	1.3	2.4	11.9	19.4	0.0		0.0
Ti ($\mu g\ L^{-1}$)	BH	0.8	0.9	0.2	0.5	0.8	1.0	5.9	2.8	-	NA
	DW	0.7	0.3	0.4	0.5	0.6	1.0	1.2	0.0		NA

V (µg L^{-1})	BH	1.7	3.4	0.1	0.2	0.5	1.3	15.8	5.7	-	NA
	DW	0.7	0.4	0.4	0.5	0.6	0.9	1.4	0.0		NA
Cr (µg L^{-1})	BH	0.2	0.6	0.0	0.0	0.0	0.1	3.3	65.7	50	0.0
	DW	0.1	0.1	0.0	0.0	0.1	0.2	0.2	37.5		0.0
Mn (µg L^{-1})	BH	20.6	103.2	0.0	0.2	0.3	1.5	611.0	8.6	50	2.8
	DW	26.4	36.2	0.0	0.4	2.5	60.5	89.5	12.5		37.5
Fe (µg L^{-1})	BH	1132	6634	0	0	1	5	39257	45.7	200	5.7
	DW	53.1	112.5	0.1	0.4	3.5	66.8	321.9	12.5		12.5
Co (µg L^{-1})	BH	0.04	0.1	0.0	0.0	0.0	0.0	0.7	71.4	-	NA
	DW	0.2	0.1	0.0	0.1	0.1	0.3	0.3	37.5		NA
Ni (µg L^{-1})	BH	1.2	0.5	0.4	0.8	1.1	1.6	2.6	2.8	20	0.0
	DW	1.2	0.9	0.5	0.6	1.7	2.2	2.6	0.0		0.0
Cu (µg L^{-1})	BH	0.9	0.8	0.1	0.4	0.5	1.0	3.3	5.7	2000	0.0
	DW	7.0	14.3	0.3	0.6	1.7	4.8	42.0	0.0		0.0
Zn (µg L^{-1})	BH	2.9	3.4	0.3	1.0	2.1	2.9	14.1	0	5000	0.0
	DW	20.5	27.5	0.6	0.9	2.6	48.8	67.7	0.0		0.0
As (µg L^{-1})	**BH**	**11.3**	**12.6**	**0.1**	**1.4**	**7.2**	**19.4**	**51.3**	**8.6**	**10**	**45.7**
	DW	**0.6**	**1.3**	**0.0**	**0.0**	**0.2**	**0.5**	**3.7**	**25.0**		**0.0**
Se (µg L^{-1})	BH	0.5	0.9	0.00	0.0	0.1	0.5	4.0	37.1	10	0.0
	DW	0.1	0.1	0.0	0.1	0.1	0.2	0.2	37.5		0.0
Mo (µg L^{-1})	BH	1.8	2.0	0.1	0.2	1.5	2.4	8.1	17.1	-	NA
	DW	0.4	0.1	0.3	0.3	0.4	0.5	0.5	62.5		NA
Ag (µg L^{-1})	BH	-	-	-	-	-	-	0.1	97.1	-	NA
	DW	-	-	-	-	-	-	0.2	87.5		NA
Cd (µg L^{-1})	BH	-	-	-	-	-	-	0.0	97.1	5	0.0
	DW	-	-	-	-	-	-	0.0	87.5		0.0
Sb (µg L^{-1})	BH	0.4	0.7	0.0	0.0	0.1	0.3	3.0	40.0	5	0.0
	DW	-	-	-	-	-	-	0.3	75.0		0.0
Ba (µg L^{-1})	BH	43.5	67.7	0.1	0.6	5.2	77.5	285	0.0	500	0.0
	DW	11.2	10.4	3.0	6.4	7.6	12.9	35.8	0.0		0.0
W (µg L^{-1})	BH	0.3	1.4	0.0	0.0	0.00	0.0	8.0	77.1	-	NA
	DW	-	-	-	-	-	-	-	100		NA
Pb (µg L^{-1})	BH	0.06	0.1	0.0	0.0	0.0	0.2	0.5	77.1	10	0.0

	DW	-	-	-	-	-	-	0.3	87.5		0.0
U (µg L^{-1})	BH	1.6	2.4	0.0	0.2	0.6	2.4	9.3	20.0	30	0.0
	DW	0.2	0.2	0.0	0.0	0.1	0.2	0.8	25.0		0.0
Mg (mg L^{-1})	BH	11.8	8.7	0.6	5.1	9.6	17.7	34.4	0.0	50	0.0
	DW	9.4	7.1	2.1	3.4	7.6	16.5	20.6	0.0		0.0
Si (mg L^{-1})	BH	6.1	1.9	1.0	4.8	5.7	6.9	11.3	0.0	-	NA
	DW	5.9	1.7	3.9	4.6	5.7	7.0	9.1	0.0		NA
Ca (mg L^{-1})	BH	41.6	19.1	11.8	26.5	39.8	56.7	73.7	0.0	200	0.0
	DW	52.5	33.9	14.1	18.5	55.5	80.9	95.0	0.0		0.0
Na (mg L^{-1})	BH	13.6	5.7	2.9	9.7	13.1	16.3	35.9	0.0	200	0.0
	DW	24.6	31.3	8.8	9.8	11.4	27.4	100.0	0.0		0.0
Sr (mg L^{-1})	BH	0.3	0.3	0.0	0.1	0.2	0.5	1.1	0.0	-	NA
	DW	0.1	0.0	0.0	0.1	0.1	0.2	0.3	0.0		NA
K (mg L^{-1})	BH	1.9	2.9	0.4	1.1	1.4	1.8	18.1	0.0	5	2.8
	DW	2.4	2.2	0.7	1.1	1.5	3.2	7.5	0.0		12.5

Table 2. Summary of dissolved arsenic species in groundwater samples from 2016 using SPE methodology (where n=20)

ID	pH	Eh	Dissolved As (μg L^{-1})	As^{III}		As^{V}		DMA^{V}		MA^{V}		Σ As Species (μg L^{-1})	Recovery (%)
				Conc. (μg L^{-1})	%	Conc. (μg L^{-1})	%	Conc. (μg L^{-1})	%	Conc. (μg L^{-1})	%		
DW-11	6.5	475.6	0.3	0.5	59.2	0.1	11.1	0.2	23.8	0.1	5.9	0.9	275.7
BH-23	7.7	460.3	19.2	0.5	1.7	25.3	94.2	1.0	3.6	0.1	0.5	26.9	140.2
BH-20	7.9	367.1	37.2	0.1	0.2	29.4	96.4	1.0	3.2	0.1	0.2	30.5	81.9
BH-21	7.4	440.9	17.9	0.1	0.6	14.5	95.6	0.5	3.5	0.04	0.3	15.3	84.7
BH-64	7.9	400.0	27.2	0.1	0.3	20.9	95.9	0.8	3.8	0.01	0.1	21.7	80.1
BH-47	7.4	441.6	0.1	0.1	21.6	0.1	34.0	0.1	39.7	0.01	4.6	0.3	232.7
BH-46	7.9	452.0	6.1	0.1	2.5	4.8	92.6	0.2	4.7	0.01	0.2	5.1	85.0
DW-17	6.8	-52.1	0.4	0.1	15.1	0.3	47.7	0.2	35.0	0.01	2.2	0.6	143.4
BH-40	8.0	-121.5	14.6	0.03	0.3	11.8	95.5	0.5	4.1	0.01	0.2	12.4	84.8
BH-29	7.9	224.9	15.0	0.1	0.8	10.9	94.8	0.5	4.3	0.01	0.1	11.5	76.4
BH-26	7.8	184.9	21.4	0.2	1.1	16.6	95.1	0.7	3.7	0.02	0.1	17.4	81.2
BH-68	7.4	262.0	1.3	0.1	4.4	0.9	73.9	0.2	20.7	0.01	1.1	1.2	88.2
BH-74	7.4	340.2	3.3	0.1	2.1	2.1	85.8	0.3	11.6	0.01	0.6	2.5	75.2
DW-25	8.1	300.7	56.1	0.4	0.8	42.4	95.7	1.5	3.5	0.02	0.0	44.3	79.1
DW-28	7.1	316.4	2.1	0.03	1.7	1.7	86.9	0.2	10.8	0.01	0.6	2.0	96.1
BH-70	8.3	302.5	8.1	0.01	0.1	6.6	94.4	0.4	5.4	0.01	0.1	7.0	85.8
BH-61	7.6	254.8	15.5	0.6	6.0	9.0	88.3	0.5	5.3	0.03	0.4	10.2	66.0
BH-60	7.5	242.5	73.9	0.04	0.1	64.3	96.5	2.3	3.4	0.02	0.0	66.6	90.1
BH-67	6.9	261.4	3.8	0.04	1.1	2.9	91.4	0.2	7.1	0.01	0.3	3.3	85.3
BH-39	7.8	296.4	30.4	0.6	2.1	25.2	94.3	0.9	3.5	0.02	0.1	26.7	88.1

Figures

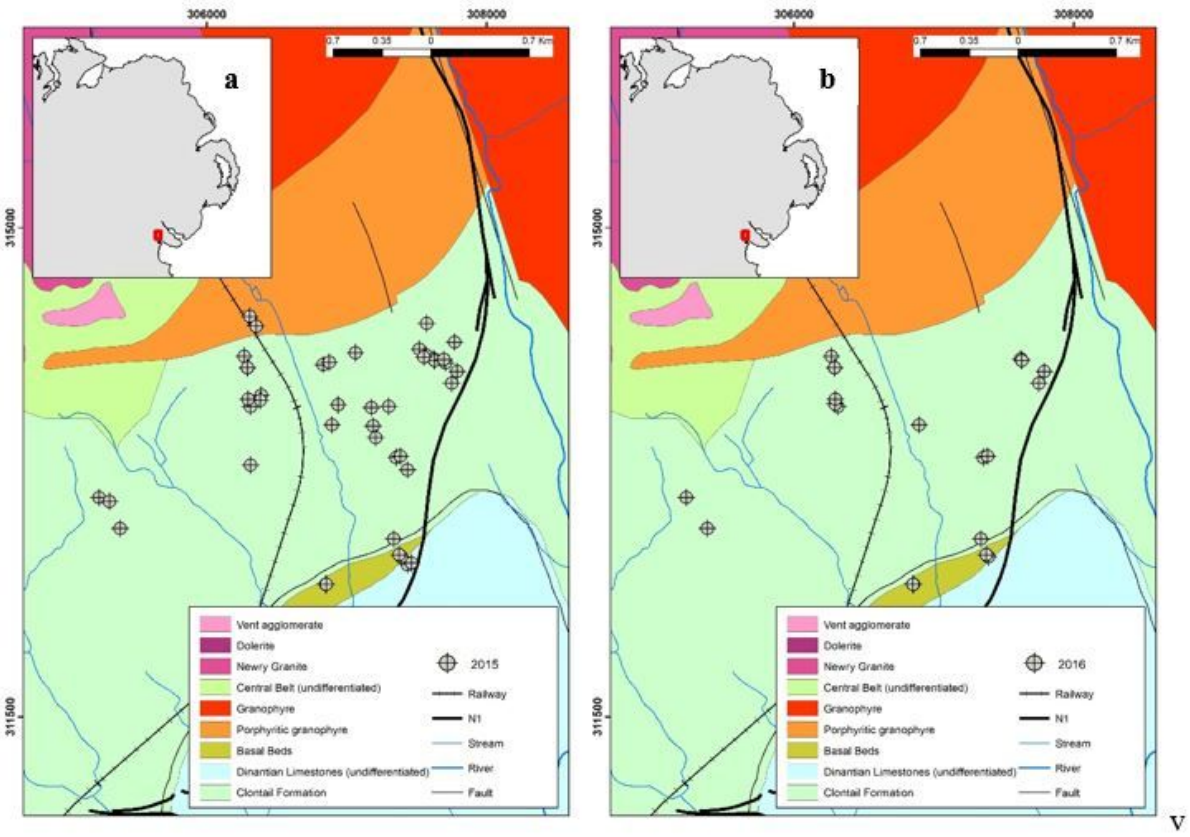

Figure 1

Spatial distribution of groundwater sampling points collected during (a) 2015 (n=43) and (b) 2016 (n=20) overlaid on bedrock geology (1:100K). Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

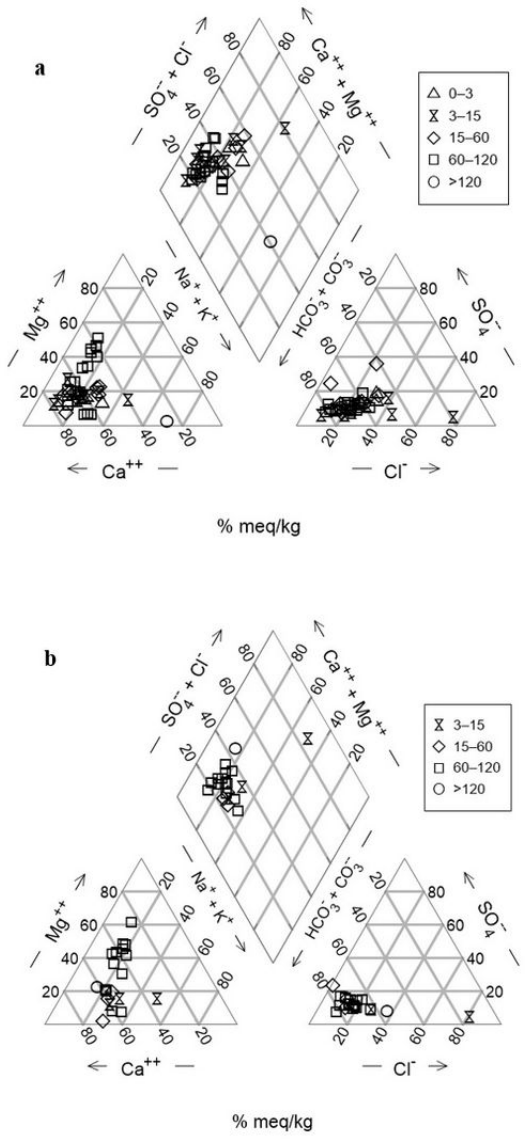

Figure 2

Piper diagram for (a) 2015 and (b) 2016 data. Samples are classified by depth (m).

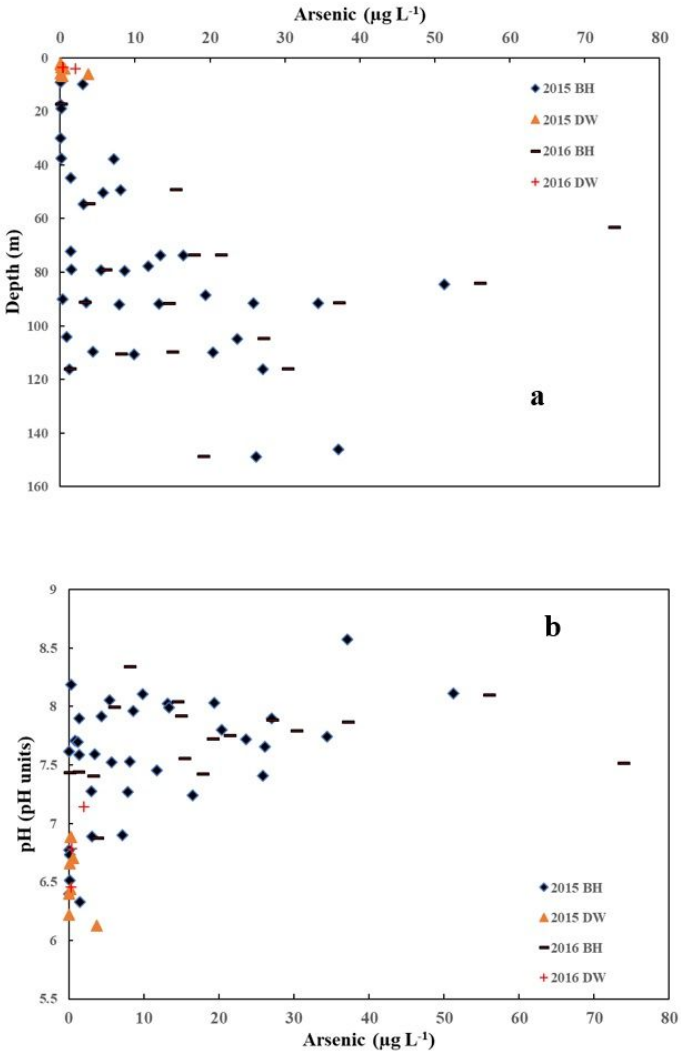

Figure 3

Biplot for arsenic and (a) depth and (b) pH,

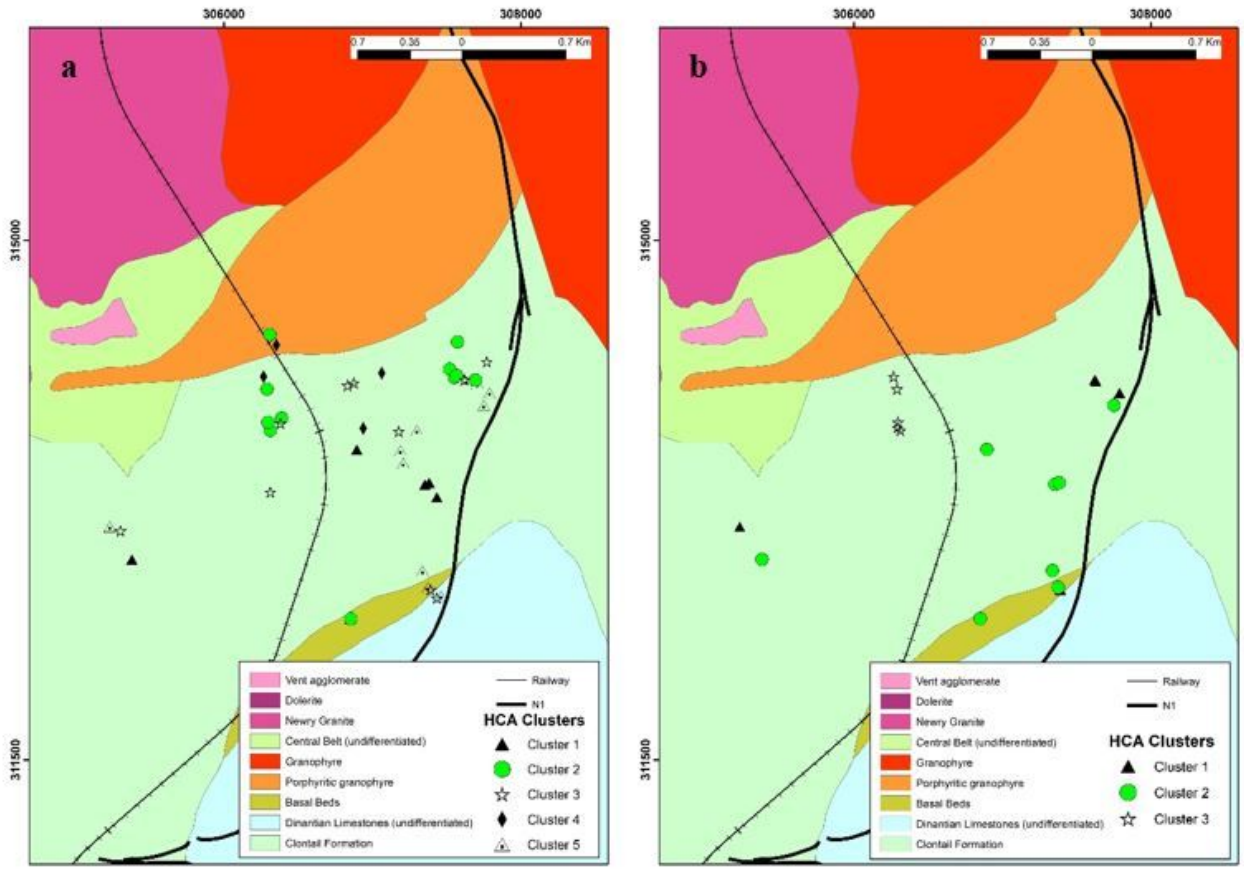

Figure 4

HCA clustering map for monitoring sites in (a) 2015 and (b) 2016 (R-mode) overlaid on bedrock geology (1:100K). Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

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