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NUI Galway
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**Environmental aqueous geochemistry of arsenic in
groundwater: occurrence, speciation and
biogeochemical processes**

by

Ellen R. McGrory BSc (Hons) MRSC

in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

in the subject of

Earth and Ocean Sciences

Earth and Ocean Sciences,
School of Natural Sciences and Ryan Institute,
National University of Ireland Galway,
Ireland

Supervisor

Dr Liam Morrison

January 2020

“Happiness can be found even in the darkest of times if one remembers to turn on the light”

-Albus Dumbledore

“Fascinating”

-Mr. Spock

“Somewhere, something incredible is waiting to be known”

-Carl Sagan

Dedication

This dissertation is dedicated to the memory of Carmel Traynor.

Declaration of Authorship

I, Ellen McGrory, hereby declare that I am the author of this thesis, titled “*Environmental aqueous geochemistry of arsenic in groundwater: occurrence, speciation and biogeochemical processes*”. The work presented in this thesis is my own. Credit has been given when work was carried out as part of a collaboration, and acknowledgements given to work or contributions by others. The work was carried out at the Department of Earth and Ocean Sciences and Ryan Institute, National University of Ireland Galway, and this dissertation has not been submitted elsewhere for any other degree or qualification.

Signed: _____

Date: _____

Table of contents

Table of contents	i
Acknowledgements	vi
List of publications	vii
Abstract	ix
Chapter 1 – Arsenic in groundwater	1
1.0 General overview.....	2
1.1 Chemical nomenclature and terminology.....	3
1.1.1 Arsenic species nomenclature.....	4
1.2 Trace elements in the environment.....	6
1.2.1 Trace element classification.....	7
1.3 Arsenic in groundwater.....	8
1.3.1 Toxicological considerations.....	8
1.3.2 Arsenic in groundwater – the global situation.....	10
1.3.3 Arsenic in groundwater – the Asian perspective.....	11
1.3.3.1 Arsenic in groundwater of the BGM region: case study.....	11
1.3.4 Regulatory framework.....	14
1.3.5 Mineralogy and geological settings.....	16
1.3.5.1 Mineralogy.....	16
1.3.5.2 Geological settings.....	16
1.3.5.3 Arsenic in bedrock aquifers.....	18
1.3.6 Arsenic mobilisation mechanisms.....	18
1.3.6.1 Reductive dissolution.....	20
1.3.6.2 Alkali desorption.....	20
1.3.6.3 Sulphate oxidation.....	22
1.3.6.4 Geothermal.....	22
1.3.7 Aqueous speciation.....	22
1.3.7.1 Aqueous arsenic speciation.....	22
1.3.7.2 Inorganic arsenic speciation.....	23
1.3.7.3 Organic arsenic speciation.....	25
1.3.7.4 Groundwater arsenic ratios.....	26
1.3.7.5 Other organic arsenic species.....	27
1.3.8 Role of microbial communities and microbial biomethylation.....	27
1.4 Commonly encountered trace elements in groundwater.....	28
1.4.1 Iron (Fe) and manganese (Mn).....	29
1.4.2 Uranium (U) and selenium (Se).....	30
1.4.3 Fluorine (F).....	30
1.5 Less commonly encountered trace elements in groundwater... ..	31
1.5.1 Chromium (Cr), copper (Cu) and zinc (Zn).....	31
1.5.2 Molybdenum (Mo).....	32
1.5.3 Mercury (Hg) and lead (Pb).....	32
1.6 Mobilities of trace elements in the environment.....	32
1.7 Dissertation objectives and general structure.....	33
1.7.1 General research aims and objectives.....	33
1.7.2 Dissertation structure.....	34
Chapter 2 – Methodological approach and experimental rationale	35

2.0 Trace element geochemistry.....	36
2.1 Sample bottle decontamination.....	37
2.2 Groundwater sampling.....	38
2.2.1 Traditional purging.....	38
2.2.2 Low-flow purging.....	38
2.2.3 Sampling indicator parameters.....	39
2.2.4 Sampling pumps.....	40
2.3 Speciation.....	42
2.3.1 Laboratory speciation.....	42
2.3.2 Field speciation.....	43
2.4 Analytical instrumentation.....	44
2.4.1 Analysis by ICP-MS.....	44
2.4.1.1 Interferences in ICP-MS applications.....	46
2.4.2 Separation science.....	47
2.4.3 Analytical sensitivity.....	48
2.5 Quality assurance.....	49
2.5.1 Certified reference materials.....	50
2.5.2 Blanks (field and lab).....	51
2.5.3 Duplicate samples.....	52
2.5.4 Chemical analyses accuracy.....	52
2.6 Statistical methods.....	53
2.6.1 General statistics.....	53
2.6.2 Censored data analysis.....	53
2.6.3 GIS and spatial prediction methods.....	57
Chapter 3 - Arsenic contamination of drinking water in Ireland: A spatial analysis of occurrence and potential risk.....	58
3.0 Introduction.....	60
3.1 Materials and methods.....	62
3.1.1 EPA database.....	63
3.1.2 Statistical analysis.....	63
3.1.2.1. Rationale for the reclassification of the 27 ‘groundwater rock units’ into 11 rock types.....	67
3.1.2.2 Handling of non-detect data.....	68
3.1.2.3 Inverse distance weighting (IDW) interpolation.....	69
3.1.2.4 Local indicator of spatial association (LISA).....	71
3.1.2.5 PAA subsoil monitoring points.....	71
3.1.2 HSE and local government.....	71
3.2 Results and discussion.....	72
3.2.1 EPA database.....	72
3.2.1.1 Geological and hydrogeological constraints on aqueous arsenic concentrations.....	74
3.2.1.1.1 Removal of sites for statistical analysis.....	74
3.2.1.1.2 EPA-Total database.....	77
3.2.1.1.3 EPA-NPPA database.....	78
3.2.1.2 Interpolation and hot-spot analysis.....	78
3.2.1.2.1 Local indicator of spatial autocorrelation (LISA) hot-spot analysis.....	79

3.2.1.2.2 Inverse distance weighting (IDW) interpolation.....	81
3.2.1.3 Statistical differences in the removal and retention of subsoil monitoring locations.....	82
3.2.2 Regional studies.....	83
3.2.3 Global comparisons of arsenic concentrations in groundwater.....	86
3.2.4 Rationale for statistical approach in this study.....	87
3.2.5 Limitations, recommendations and future work.....	88
3.3 Conclusions.....	89
3.4 Summary.....	90
Chapter 4 – Arsenic in groundwater in south west Ireland: occurrence, controls and hydrochemistry.....	91
4.0 Introduction.....	93
4.1 Methodology.....	95
4.1.1 Study area.....	95
4.1.1.1 Borehole design and construction.....	96
4.1.2 Data description.....	98
4.1.3 Groundwater sampling and analysis.....	99
4.1.4 Explanatory variables.....	100
4.1.5 Statistical analyses.....	102
4.1.6 Interval mapping.....	103
4.1.7 Hot-spot analysis.....	103
4.2 Results.....	103
4.2.1 Interval mapping.....	103
4.2.2 Hot-spot analysis.....	107
4.2.3 Geological constraints on groundwater parameters	110
4.2.3.1 Arsenic.....	110
4.2.3.2 pH.....	113
4.2.3.3 Electrical conductivity.....	113
4.2.3.4 Iron.....	114
4.2.3.5 Manganese.....	114
4.2.3.6 Major cations.....	114
4.2.4 Correlation of arsenic with other variables.....	114
4.3 Discussion.....	116
4.3.1 Source of arsenic: geogenic or anthropogenic?.....	116
4.3.1.1 Lithology.....	116
4.3.1.2 Aquifer and groundwater vulnerability classification.....	118
4.3.1.3 Land use categories.....	119
4.3.2 Linking arsenic concentrations with historic mining activities.....	120
4.3.3 Relationship of other hydrochemical parameters.....	123
4.3.4 Comparison with other regions.....	123
4.4 Conclusions.....	124
4.5 Summary.....	124
Chapter 5 – Assessment of groundwater processes using censored data analysis incorporating non-detect chemical, physical, and biological data.....	125
5.0 Introduction.....	127
5.1 Materials and methods.....	129

5.1.1	Study site and initial desk study.....	129
5.1.1.1	Geological, hydrogeological and environmental setting.....	130
5.1.1	Groundwater sampling.....	133
5.1.2	Chemical analysis.....	133
5.1.3	Data analysis.....	134
5.1.3.1	Rationale for statistical testing of one monitoring season.....	134
5.1.3.2	Handling of data with multiple DLs.....	134
5.1.3.3	Analysis by depth.....	134
5.1.3.4	Correlation analysis.....	135
5.1.3.5	Multivariate methods.....	135
5.1.3.6	Spatial mapping.....	136
5.1.3.7	Aqueous geochemical modelling.....	136
5.2	Results.....	137
5.2.1	Descriptive statistics.....	137
5.2.2	Saturation indices.....	138
5.2.3	Spatial mapping.....	141
5.2.4	Hierarchical clustering.....	145
5.2.5	Organic geochemistry.....	147
5.3	Discussion.....	147
5.3.1	Trace element and arsenic groundwater geochemistry.....	147
5.3.2	The source of nutrient, microbial and organic contamination.....	150
5.3.3	Multivariate analysis.....	153
5.3.4	Strengths and recommendations.....	154
5.4	Conclusions.....	154
5.5	Summary.....	155
Chapter 6 – Geochemical investigations of elevated geogenic arsenic concentrations and speciation in groundwater of a fractured bedrock aquifer in the Southern Uplands-Down-Longford Terrane in northeast Ireland.....		156
6.0	Introduction.....	158
6.1	Study area.....	160
6.1.1	Geological setting and hydrogeology.....	162
6.2	Materials and methods.....	164
6.2.1	Desk study.....	164
6.2.2	Reconnaissance hydrogeological survey.....	165
6.2.3	Extensive water chemistry.....	165
6.2.3.1	Sample bottle decontamination.....	165
6.2.3.2	Sampling.....	166
6.2.3.3	Field determinations.....	168
6.2.3.4	Field speciation of arsenic.....	168
6.2.3.5	Samples for laboratory speciation of arsenic... ..	169
6.2.4	Instrumental analysis.....	170
6.2.5	Health Implications.....	170
6.2.6	Data and spatial analysis.....	170
6.2.6.1	Summary statistics.....	170
6.2.6.2	Correlation and regression.....	171
6.2.6.3	Multivariate statistical analysis (MSA).....	171

6.2.6.4 Aqueous geochemical modelling.....	172
6.2.6.5 Spatial analysis.....	172
6.3 Results and discussion.....	172
6.3.1 Quality control.....	172
6.3.2 Initial site characterisation.....	173
6.3.3 Physio-chemical parameters.....	178
6.3.4 Major-ion geochemistry and hydrogeochemical facies..	184
6.3.5 Trace elements.....	191
6.3.6 Arsenic geochemistry.....	193
6.3.7 Arsenic speciation.....	198
6.3.8 Multivariate analysis.....	202
6.3.9 Thermodynamic calculations.....	206
6.3.10 Oxyanion behaviour.....	207
6.3.11 Health implications.....	209
6.3.12 Comparison with historic data.....	210
6.3.13 Geochemical controls on arsenic mobilisation.....	212
6.3.14 The source of arsenic.....	213
6.4 Conclusions.....	214
6.5 Summary.....	215
Chapter 7 – Overview, key findings and recommendations for future research.....	216
7.0 General overview.....	217
7.1 Key findings.....	217
7.2 Limitations.....	219
7.3 Recommendations for further work.....	220
Appendix (A1).....	222
Appendix (A2).....	227
Appendix (A3).....	233
References.....	238

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List of publications

Peer Reviewed Publications

McGrory, E.R., Brown, C., Bargary, N., Williams, N.H., Mannix, A., Zhang, C., Henry, T., Daly, E., Nicholas, S., Petrunic, B.M., Lee, M., Morrison, L., 2017. Arsenic contamination of drinking water in Ireland: a spatial analysis of occurrence and potential risk. *Science of the Total Environment* **579**, 1863-1875 (This paper forms the basis of chapter 3).

McGrory, E., Holian, E., Alvarez-Iglesias, A., Bargary, N., McGillicuddy, E.J., Henry, T., Daly, E., Morrison, L., 2018. Arsenic in groundwater in south west Ireland: occurrence, controls, and hydrochemistry. *Frontiers in Environmental Science* doi.org/10.3389/fenvs.2018.00154 (This paper forms the basis of chapter 4).

Further publications obtained during this PhD

Morrison, L., Bennion, M., McGrory, E., Hurley, W., Johnson, M.P., 2017. *Talitrus saltator* as a biomonitor: an assessment of trace element contamination on an urban coastline gradient. *Marine Pollution Bulletin* **120**, 232-238.

Book chapters

Morrison, L., McGrory, E., Brown, C., 2016. National assessment of arsenic within groundwater: a case study with Ireland. In: *Proceedings of the Sixth International Congress on Arsenic in the Environment (As 2016)* (Bhattacharya P., Vahter M., Jarsjö J., Kumpiene J., Ahmad A., Sparrenbom C., Jacks G., Donselaar M.E., Bundschuh J., Naidu R., Eds). CRC Press, Boca Raton, pp. 33-34.

Presentations (Oral)

McGrory, 2012. Arsenic in Irish drinking water: a case study from Counties Louth, Sligo and Kerry. Griffiths Research Jam. Geological Survey of Ireland, Beggars Bush, Dublin (7th December).

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McGrory, E., Brown, C., Bargary, N., Zhang, C., Petrunic, B.M., Henry, T., Daly, E., Lee, M., Williams, N.H., Mannix, A., and Morrison, L., 2015. Exposure to arsenic from groundwater in Ireland: a geostatistical based approach. The 24th Environmental Researchers Colloquium. Sligo Institute of Technology, April 8th-10th, 2015.

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McGrory, E., Morrison, L., 2014. *Geogenic arsenic concentrations in Irish drinking water*. The 24th Environmental Researchers Colloquium. Trinity College Dublin, February 26th-28th, 2014.

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Abstract

The presence of arsenic and other trace elements within groundwater has become a global concern due to the health risks from drinking water associated with elevated concentrations in the last three decades. Whilst ample information is available in areas of south east Asia (e.g. West Bengal) where arsenic is being mobilised via microbial-mediated reductive dissolution, there is comparatively little research in Europe. Recently, research has demonstrated that elevated arsenic is occurring in fractured bedrock aquifers in many regions, e.g. New England. While not being regarded as sources for large public water supplies in Ireland, these fractured bedrock aquifers are important for private groundwater sources and may show elevated concentrations of geogenic contaminants. The objectives of this dissertation were to assess the spatial distribution of arsenic and other trace elements in fractured bedrock aquifers, understand the geochemical processes giving rise to elevated arsenic and determine the speciation of arsenic in groundwater. Firstly, existing datasets at national-level scale in addition to regional-scales were collated. Due to the presence of left censoring (i.e. arsenic values below an analytical detection limit) and changes in detection limits over time, the application of conventional statistical methods would inhibit the generation of meaningful results. In order to handle these issues, several arsenic databases were integrated and modelled using statistical methods appropriate for non-detect data. In addition, geospatial methods were used to assess principal risk components of elevated arsenic related to differing geological, hydrogeological and land-use classifications. Significant differences were noted between different aquifer lithologies, indicating that Rhyolite, Sandstone and Shale (Greywackes), and Impure Limestone presented a greater risk of elevated arsenic in groundwaters. Significant differences also occurred among aquifer types with poorly productive aquifers, locally important fractured bedrock aquifers and regionally important fissured bedrock aquifers presenting the highest potential risk of elevated arsenic. Comparable results were observed in regional settings. In addition to these previous approaches, a study incorporating secondary geochemical data (collected as part of road construction) found elevated arsenic concentrations (i.e. low-to-moderate levels) within groundwater in north east Ireland (in addition to nitrate, iron and manganese), which was the focus of detailed ultra-trace aqueous geochemical sampling and speciation studies. Aqueous arsenic concentrations showed positive associations with well depth with speciation using field methodology indicating arsenate as the dominant arsenic species in oxic-alkali groundwater. The speciation of arsenic was controlled by groundwater pH, with mobilisation of arsenic occurring at elevated pH through alkali desorption processes.

Indeed, 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). Low concentrations of methylated arsenicals were detected in groundwaters which suggested microbial mediated mobilisation of arsenic may also be occurring in small clusters. This research contributes to the understanding of arsenic mobilisation processes and will facilitate in guiding future development, testing and treatment requirements of groundwater resources. In addition, it will provide a focus of the arsenic problem (and other geogenic trace element contaminants) arising from fractured bedrock aquifers in Europe which is important with respects to both public health and drinking water resources.

Chapter 1

Arsenic in groundwater

1.0) General overview

Sources of drinking water can originate from either surface waters (including lakes, rivers and streams) or groundwater (including wells) (Giri et al., 2012). Groundwater is a major source of drinking water of the global population at approximately 50% rising to 75% for Europe, 51% in the United States of America (USA) and 25% for Ireland (Sampat, 2000; Sharma et al., 2005; Daly, 2009; McGarrigle et al., 2010). However, in Ireland this figure rises to ~100% for certain regions (McGarrigle et al., 2010). Groundwater is often preferred as a drinking water source over surface due to the latter being more prone to biological contamination. However, the possibility that groundwater could contain potentially toxic elements was not considered until health conditions arose from its consumption in south east Asia (Mitchell et al., 2011). In the last number of years, it has become evident that the contamination of groundwaters by anthropogenic and/or geogenic contaminants has limited the quality of these potable water sources around the world (Mukherjee et al., 2008).

Elements such as arsenic, antimony, chromium, mercury and lead are present in water supplies and in numerous chemical forms which can adversely affect human health (Gupta et al., 2012). Groundwater passes through different geological formations and soils. This interaction at the water-rock interface can lead to these elements becoming dissolved within the groundwater which can then be transported to boreholes that are used as drinking water sources. Different geological formations will contain varying concentrations of elements that reflect its geochemistry and mineralogically. It is widely considered that the parent bedrock acts as one of main geochemical controls on arsenic mobilisation in groundwater (Ravenscroft et al., 2009).

Water quality has become of increased interest as water represents a dietary exposure for a host of substances that could pose a risk to human health (Cullen, 2008; Bundschuh et al., 2010; Smedley and Kinniburgh, 2013). Water can also be contaminated with microbiological pathogens and pose a health risk. For instance, up to the early 1980s (and before this) surface water was used as a source of drinking water in India which caused widespread sickness (Cullen, 2008). Groundwater was then used as an alternative water source; however it became evident years later that arsenic was present at high concentrations in which Smith et al. (2000) has described as the ‘largest mass poisoning of a population.’

Arsenic, a metalloid, is an element with such a diverse history that is synonymous with poison in Victorian literature (Rosen, 1999; Cullen, 2008). Two incidents have led to increased research into arsenic in the environment: i) the reports of mass contamination of the Gangetic Delta of Bangladesh, and ii) the United States Environmental Protection Agency (USEPA)

reducing the maximum contaminant level (MCL) from 50 $\mu\text{g L}^{-1}$ to 10 $\mu\text{g L}^{-1}$ in drinking water in 2006 (Mudhoo et al., 2011). From the early 1990s when the initial cases of arsenic poisoning (arsenicosis) were discovered in India a global concern over arsenic has been initiated. Arsenic contamination is present in groundwaters affecting drinking water quality in all the continents. This is of concern at the local, national and international levels (Mudhoo et al., 2011). In addition to public health concerns, the presence of arsenic in groundwater at elevated concentrations poses a problem for environmental sustainability (Bundschuh et al., 2010).

Since the developments in Asia there has been an increase into arsenic research in the last 30 years, particularly with instrumental techniques and the role of arsenic toxicity on public health. In recent years, the speciation of metals including arsenic has become a new area within analytical chemistry which can be used to understand the bioavailability and thus potential toxicity of arsenic. In this area, the different chemical forms of an element are determined, which dictates the toxicity (Bose et al., 2011).

1.1) Chemical nomenclature and terminology

In many areas of environmental science, the term 'heavy metals' has been used to describe toxic metals in the different environmental compartments. Historically, it has been used to describe a group of metals and semimetals (metalloids) that are associated with contamination that have potential toxicity (Duffus, 2002). Generally, this term was defined as being restricted to transition metals, i.e. metals of environmental concern having anthropogenic sources (Batley, 2012). However, many of these heavy metals would also be considered essential for certain biological functions (Batley, 2012). The use of the prefix, heavy, is rather ambiguous, however, mainly due to its inconsistency in use. This is evident as heavy metals have been defined by their density, based on toxicity and atomic number (Hodson, 2004). If the definition is based on toxicity then i) the effect of a metal on a living system depends on the concentration, and ii) several of these metals are essential for the metabolism of cells (Appenroth, 2010). Equally, if the definition is based on specific gravity then the lanthanides and actinides must be included in the term heavy metal. These are not considered to be heavy in the traditional use of the term. Equally, the use of prefix heavy, when used in the literature can also describe an inferred or assumed toxicity due to its use, particularly with respects to cadmium (Cd).

It is evident that this terminology is misleading, uninformative and has been used inconsistency and without distinction throughout the literature. Due to these inconsistencies in the literature (and as a poor scientific term), many alternatives exist (Duffus, 2002; Hodson, 2004). Alternative suggestions include 'potentially toxic elements' (PTEs) (Ritchie and

Sposito, 2002; Bacon and Davidson, 2008; McKinley et al., 2013; Zeiner and Cindrić, 2017), ‘potentially toxic metals’ (PTMs) (Adamo and Zampella, 2008), ‘potentially harmful elements’ (PHEs) (Plant et al., 2001), potentially harmful inorganic elements (Plant et al., 2005), ‘HSAB principle’ (Class A, Class B and borderline metals) (Nieboer and Richardson, 1980) and ‘toxic trace elements’ (TTEs) (Vázquez et al., 2015). Other suggestions include replacing the term with metals (or metalloids for B, Si, Ge, As, Sb, Te, Po, At and Se) (Chapman, 2007). It has also been suggested to keep the current term of heavy metals and use alternatives such as toxic, bioavailable or trace (each having constrained meanings) as subclasses of the term (Bately, 2012). Criticisms of any terms with toxic prefix, however, can mean almost any element, provided that enough is accumulated and depends upon the studied organism, can be toxic (Duffus, 2002; Madrid, 2010).

More descriptive alternative terms include ‘trace metals’ (TMs) and ‘trace elements’ (TEs) which have been used with some success. The term, trace, also is a more unbiased term (i.e. compared to potentially toxic) and is inclusive of metalloids (Madrid, 2010). For this work, the term, TEs was adopted.

1.1.1 Arsenic species nomenclature

Similarly, to the use of the term heavy metal, there are several terms that are used in the discipline of environmental geochemistry that are incorrect. In reference to this present work, the naming convention of the different arsenic species in the environment has gained recent interest due to lack of naming uniformity, despite recommendations from the International Union of Pure and Applied Chemistry (IUPAC) (Francesconi and Kuehnelt, 2004). Additionally, due to absent systematic terminology there are several abbreviations used for each arsenic species in the literature (Mestrot et al., 2013). For reasons of clarity and consistency, one type of abbreviation will be used for each species in this work. For the inorganic species, the terms arsenate and arsenite and their abbreviations, arsenate(V) and arsenite(III), can be used. While the inorganic abbreviations of As(V) and As(III) are commonly used in the literature, they are not used here due to the violations of chemical nomenclature regarding oxidation state (Leigh, 1990). The abbreviations As^V and As^{III} are good alternatives.

The organic arsenic species are designated as simple methylated species rather than their respective acids (in natural waters these species are anionic), i.e. methylarsonate rather than methylarsonic acid. These include methylarsonate (CH₃AsO₃, MA^V), dimethylarsinate ((CH₃)₂AsO₂, DMA^V), methylarsonite (CH₃AsO, MA^{III}) and dimethylarsinite ((CH₃)₂AsO,

DMA^{III}). In the literature, MA^V has been referred to as its acidic form using the term monomethylarsonic acid (MMA or MMAA), however this term has no strong basis since in naming convention the ‘mono’ would not be used as a prefix (Francesconi and Kuehnelt, 2004). Figure 1.1a and 1b show the species of arsenic and their respective structures relevant to this current work. Table 1.1 shows the formula, compound and abbreviations of the arsenic species. For this dissertation, reference made to arsenic will mean total arsenic. When referring to individual arsenic species they will be referred as Table 1.1 (species name).

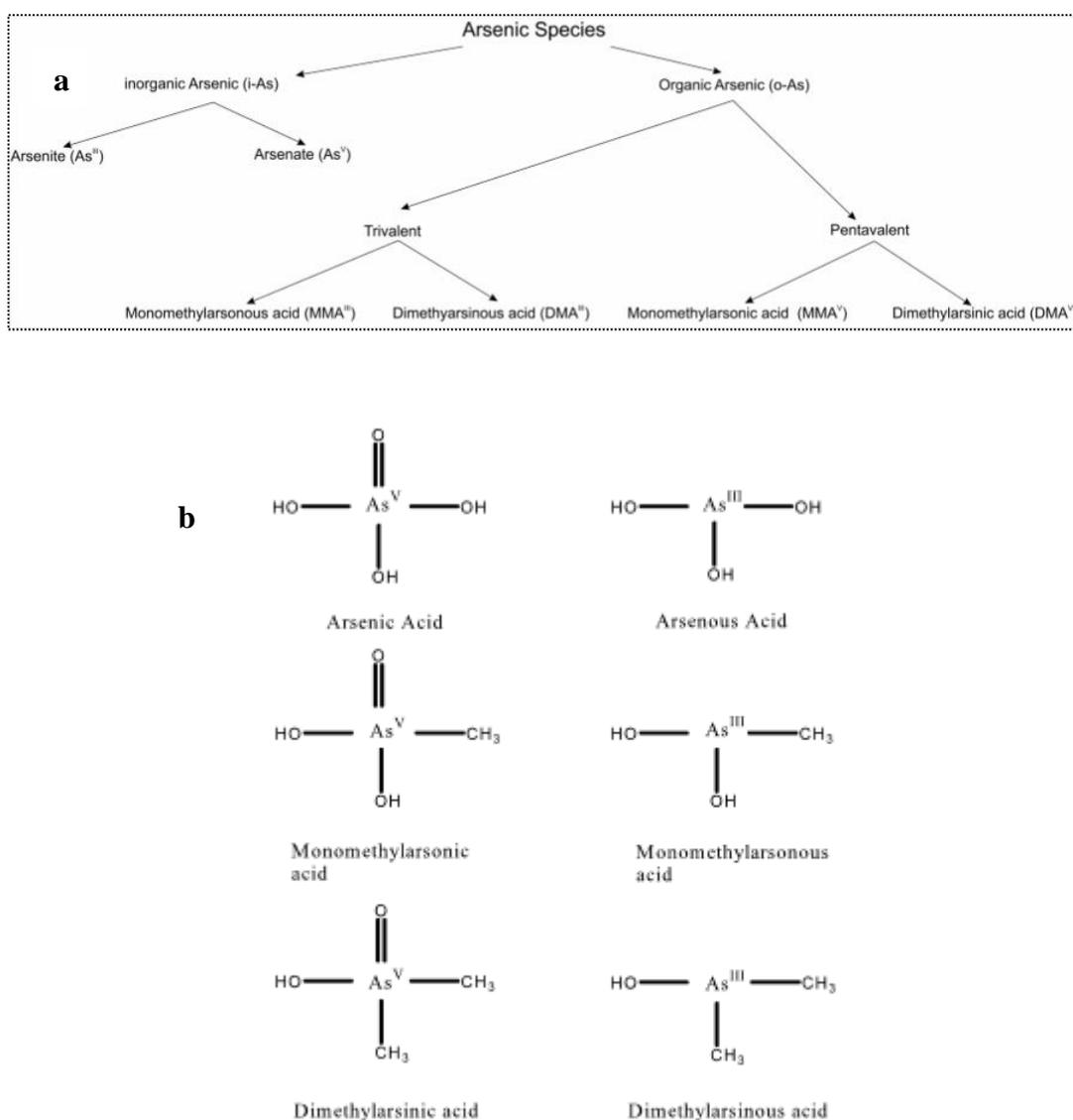


Fig. 1.1. Arsenic species based on (a) designation by oxidation state, and (b) designation by structure (source: authors own).

Table 1.1. Structural information and names of inorganic and organic arsenic species

Arsenic name	Species	Abbreviation	Chemistry	Formula	Valency	Anionic name
Arsenite	As ^{III}		Inorganic	H ₃ AsO ₃	III	Arsenous acid
Arsenate	As ^V		Inorganic	H ₃ AsO ₄	V	Arsenic acid
Methylarsonate	MA ^V		Organic	CH ₃ AsO ₃	V	Methylarsonic acid
Dimethylarsinate	DMA ^V		Organic	(CH ₃) ₂ AsO ₂	V	Dimethylarsonic acid
Methylarsonite	MA ^{III}		Organic	CH ₃ AsO	III	Methylarsonous acid
Dimethylarsinite	DMA ^{III}		Organic	(CH ₃) ₂ AsO	III	Dimethylarsonous acid

1.2) Trace elements in the environment

Metals or metalloids (or metal(oids)) are naturally present in the different environmental compartments (i.e. hydrosphere, lithosphere, biosphere, atmosphere, pedosphere) from either geogenic or anthropogenic sources. Concentrations of trace elements from geogenic sources represent the natural background or concentrations resulting from geological processes except when modified by mining activities. However, anthropogenic sources result from the influence of human activity.

Trace elements can prove to be a public health issue through their individual geochemical pathways in the environment. For example, trace elements in rocks can be leached into water (Fig. 1.2). Geochemical principles govern element distribution, accumulation and depletion of trace elements in environments (Dissanayake and Chandrajith, 2009). This can lead to situations where a population can be exposed to excesses of a trace element. Exposure to these trace element contaminants can occur through a variety of routes including water, food and air. Drinking water sourced from groundwater is another potential exposure pathway that must be considered as globally, groundwater is used as a drinking water source for 50% of the population (Sampat, 2000).

While these trace elements are frequently grouped as “metals” in monitoring programs, they generally must be considered individually as properties and impacts vary in the Periodic Table.

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Fig. 1.2. Geochemical pathways of trace elements entering the human body (source: adapted from Dissanayake and Chandrajith, 2009).

1.2.1) Trace element classification

Generally, the elements can be classes as major, minor and trace elements depending on their relative abundance in the environment. Moreover, elements in the environment can be classed as essential elements or toxic elements depending on their impact on human health. Essential elements include i) elements considered essential for human or animal health (e.g. F, Na, Mg, Si, P, S, Cl, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Mo and I), ii) elements probably essential for health (e.g. Li, Be, Sc, As, Rb, Sr, Nb, Sn, Te, and Ba), and iii) non-essential elements (e.g. B, Al, Ga, Ge, Br, Y, Ag, Cd, In, Sb, W, Au, Hg, Tl, Pb, Bi, Po, and U) (Dissanayake and Chandrajith, 2009). Similarly toxic elements can be classed as i) elements considered to be toxic or undesirable in excessive amounts and for which maximum admissible concentrations (MACs) have been set by the Commission of the European Community (CEC) (e.g. F, Na, Mg, Al, K, Mn, Fe, As, Se, Y, Ag, Cd, Hg and Pb) and ii) elements considered undesirable in excessive amounts but for which no statutory limit exists by the CEC (e.g. Be, B, Si, Cl, Ca V, Cu, Zn and B) (Dissanayake and Chandrajith, 2009). This brief overview provides one of many different types of trace element classification for human health. However, many elements are unregulated, simply because they are not traditional historic pollutants like Hg or Cd, but little is known about their toxicity, e.g. Mo.

1.3) Arsenic in groundwater

Under Victor Goldschmidt's classification of trace elements, arsenic is a semi-volatile chalcophile in the earth's crust, but can also act as a siderophile (Goldschmidt, 1937; White, 2013). Arsenic can be mobilised in the environment through a combination of several processes such as weathering reactions, volcanic emissions, biological activity in addition to anthropogenic activities (Bodwell et al., 2014).

The geology, hydrogeology and geochemistry of the aquifer system are important controls of arsenic speciation and mobility within the solid-aqueous environment (Garelick et al., 2009). In addition, the distribution of arsenic within groundwaters is strongly dependant on geological, biological, and to a lesser degree, anthropogenic processes (Polya and Lawson, 2016). The relative importance of these processes in various contexts depends on i) the nature of the biogeochemical environment and ii) the species in which arsenic occurs and the subsequent biogeochemical reactivity of these species (Polya and Lawson, 2016). While the concentrations of naturally-occurring arsenic found in aquifers is generally low, they are constrained by the strong adsorptive behaviours of As^{III} and As^{V} onto the solid phases of much more abundant trace elements such as iron, manganese and aluminium (Orelmand et al., 2009).

Aqueous arsenic concentrations (and other trace elements of geogenic origin) are controlled by three important factors: the source of arsenic, ii) its solubility and attenuation, and iii) its subsequent transportation and distribution (Smedley and Kinniburgh, 2002). Changes in the hydrochemical behaviour of aquifers and the water-sediment interactions (i.e. dissociation, adsorption, association, desorption and dissolution) including other abiotic and biotic processes, can result in the mobilisation of arsenic into the groundwater (Sar et al., 2014).

Arsenic contamination of groundwater has been reported globally from different climatic, tectonic, geomorphological, lithological and depositional settings (Ravenscroft et al., 2009).

1.3.1) Toxicological considerations

Arsenic has a long toxicological history from its use as a poison (as arsenic trioxide – As_2O_3) in crime fiction popularised by Agatha Christie in the 20th century (Cullen, 2008). Arsenic, a sulfhydryl-reactive metal adversely affects both biochemical and nutritional processes (Dani, 2010). Despite its toxicity arsenic is considered an essential toxin; however, its beneficial qualities are more subtle when compared to the essential toxin selenium (Stolz et al., 2006; Bose et al., 2011). Arsenic can promote angiogenesis and increased respiratory capacity (Stolz et al., 2006). Additionally, in prokaryotes arsenic is involved in a range of metabolic functions

including methylation, assimilation, detoxification, and anaerobic respiration (Stolz et al., 2006). Given the toxicity of arsenic, it has been included in the USEPA list of priority pollutants (Ilgen et al., 2011). Arsenic is carcinogenic, mutagenic and cytotoxic element; classed as a Class I carcinogen by the International Agency for Research on Cancer (IARC, 2012). So far, it has been demonstrated as the only contaminant to cause human cancers following exposure from drinking water (Fawell and Nieuwenhuijsen, 2003).

The acute and chronic toxicological effects of arsenic are well documented (Hughes, 2002; Kapaj et al., 2006; Anetor et al., 2007; Vahidnia et al., 2007; Naujokas et al., 2013; Mitchell, 2014) which include development of cancers (e.g. skin, bladder and lung), in addition to cardiovascular, endocrine and nervous conditions (Fawell and Nieuwenhuijsen, 2003; Akter et al., 2005; Duker et al., 2005). This long-term exposure can lead to the development of arsenicosis, a term used to describe related diseases and conditions caused by arsenic exposure (van Halem et al., 2009). In contrast, recent studies have provided evidence to suggest that long-term low-dose arsenic exposure, i.e. 1 – 100 $\mu\text{g L}^{-1}$ (Spuches et al., 2005) can induce varying chronic health effects (Moon et al., 2012; Bräuner et al., 2014; Stea et al., 2014; Tsuji et al., 2014). In addition, the toxicity of arsenic depends on its chemical form (see section 1.1.1) with arsenite being more toxic than arsenate (Duker et al., 2005; Kapaj et al., 2006).

Once ingested, arsenic is absorbed from the gastrointestinal tract (GI tract) and undergoes a series of detoxification steps where it is finally excreted in the urine (Gong et al., 2002; Duker et al., 2005). As^{V} is reduced to As^{III} and transported to the liver (McClintock et al., 2012). After As^{V} reduction, As^{III} is methylated to MA^{V} via As^{III} methyltransferase (AS3MT) and subsequently reduced to MA^{III} (Hopenhayn 2006; McClintock et al., 2012). Subsequently MA^{III} undergoes oxidative methylation to form DMA^{V} which is then reduced to DMA^{III} (McClintock et al., 2012). For years this was considered the detoxification step. Recently it has been shown that not all inorganic arsenic is methylated, and some methylated species are still toxic (Hopenhayn, 2006; Qin et al., 2006).

Generally trivalent arsenic (both o-As and i-As) is more toxic than pentavalent arsenic and inorganic arsenic more toxic than the organic forms (Duker et al., 2005; Hughes et al., 2007). As^{III} is 60-80 times more toxic than As^{V} because As^{III} has great thermodynamic stability with the thiol group (-SH) of the protein of interest (Villaescusa and Bollinger, 2008). It has been demonstrated that arsenic causes inactivation of 200 enzymes, mostly involved in the cellular energy pathway and DNA synthesis and repair (Akter et al., 2005). However, recently it has been shown that the trivalent mono and dimethylated species (MA^{III} and DMA^{III}) may

be more toxic than their parent inorganic counterparts due to the greater efficiency of DNA breakdown (Qin et al., 2006).

1.3.2) Arsenic in groundwater – the global situation

It is estimated that arsenic is present in natural waters of 105 countries affecting potentially 226 million people worldwide (Murcott, 2012). Although arsenic is abundant in both the solid and aqueous environment, its presence within groundwater has received much attention as groundwater represents a major drinking water resource (Smedley and Kinniburgh, 2002; Ng et al., 2003; Naujokas et al., 2013). Dissolved arsenic concentrations are greater in groundwater compared to surface water, because of the higher solid-to-solution ratio within the groundwater system, longer residence times, and the oxidising conditions present in many surface environments (Akter et al., 2005; Smedley and Kinniburgh, 2005; Brusseau and Tick, 2006). Generally, As^V is more predominant in surface waters (Impellitteri and Scheckel, 2006). However, recently it has been demonstrated that As^{III} was the major arsenic species in surface waters thus potentially indicating a greater influence from reductive processes (O'Reilly et al., 2010).

Arsenic exposure is now a global occurrence with new areas continuing to be discovered (Hopenhayn, 2006). These include Vietnam (Berg et al., 2001; Kim et al., 2011a; Postma et al., 2012), Korea (Kim et al., 2012), Latin America (McClintock et al., 2012), Argentina (O'Reilly et al., 2010; Watts et al., 2010; Farnfield et al., 2012), Cambodia (Kim et al., 2011a), Thailand (Kim et al., 2011a), Asia (Kohnhorst, 2005; Shukla et al., 2010; Kim et al., 2011a; Kim et al., 2012; Ahn and Cho, 2013), Bangladesh (Smith et al., 2000; Smedley and Kinniburgh, 2002; Mudhoo et al., 2011), Hungary (Sugař et al., 2013), Nepal (Thakur et al., 2011), New Zealand (Lord et al., 2012), United States (Welch et al., 2000; Ayotte et al., 2003; Verplanck et al., 2008; Yang et al., 2009; Munk et al., 2011; Sanders et al., 2012; Torrance et al., 2012; O'Shea et al., 2015; Ryan et al., 2011, 2013 and 2015a; Andy et al., 2017), Canada (Wang and Mulligan, 2006; Klassen et al., 2009; McGuigan et al., 2010; Drummer et al., 2015; Bondu et al., 2017a), Africa (Smedley et al., 2007) and Europe (Tisserand et al., 2014; Parviainen et al., 2015; Reyes et al., 2015; Zkeri et al., 2015).

Areas of high-arsenic groundwater provinces have been seen in different hydrogeological and geochemical environments. For example, while arsenic is known to occur in reductive environments in Bangladesh, arsenic has also been seen in arid oxidising environments, most notably in Mexico, Chile, Argentina while mixed oxidising and reducing environments has been identified in south-western USA, i.e. Nevada, California and Arizona

(BGS and DPHE, 2001; Smedley and Kinniburgh, 2005 and 2013). Arsenic associated with geothermal waters has been shown in areas of USA, Japan, New Zealand, Chile and France (BPS and DPHE, 2001). In addition, arsenic has also been seen in areas associated with zones of ore mineralisation due to the high concentrations of arsenic found in sulphide minerals (Smedley and Kinniburgh, 2002). These areas of sulphide mineralisation (exacerbated from mining activities) have been found in areas of USA, England (Cornwall), Brazil, and Greece (Smedley and Kinniburgh, 2002 and 2005).

However, while arsenic has been found to be elevated in many of these regions, generally the concentrations of arsenic in most groundwaters is $<10 \mu\text{g L}^{-1}$ (Edmunds et al., 1989; Welch et al., 2000). Indeed, most concentrations are below the limit of detection (Plant et al., 2003).

1.3.3 Arsenic in groundwater – the Asian perspective

Most of the recent research has been focused on unconsolidated sedimentary aquifers set in alluvial plains and deltas, particularly in Asia (Bondu et al., 2016). In Asia, most of the areas associated with high arsenic are located within the flood and delta plains of the major Himalayan rivers (Mukherjee et al., 2008; Fendorf et al., 2010; Edmunds et al., 2015), e.g. the Ganges-Brahmaputra-Meghna (GBM) plain and delta in Bangladesh and India (Bhattacharya et al., 1997 and 2007), Red River delta in Vietnam (Berg et al., 2001; Winkel et al., 2011), Indus plain in Pakistan (Naseem et al., 2001; Podgorski et al., 2017), lowlands of Sumatra, Indonesia (Winkel et al., 2008b), Yellow River plains of China (Wen et al., 2013; Guo et al., 2014) and the Mekong river delta of Cambodia and Laos (Feldman and Rosenboom, 2001; Benner et al., 2008). These densely populated deltaic environments of south east Asia have several characteristics in common: i) flat topography, ii) rapid Holocene sedimentation fed by large rivers, and iii) abundance of degradable organic material (Winkel et al., 2008a). Other areas with similar combinations of these geological, geochemical, geomorphological and hydrological characteristics may also be at risk for arsenic contamination in groundwater such as the Mississippi River delta in south Louisiana, USA (Yang et al., 2014 and 2016), and the Great Hungarian Plain (BGS and DPHE, 2001; Smedley and Kinniburgh, 2002).

1.3.3.1 Arsenic in groundwater of the BGM region: case study

Prior to the BGM region using shallow boreholes most of the population used surface-water as their drinking water source which was contaminated by water-borne diseases as a result of poor sanitation management (e.g. cholera and dysentery) (Ravenscroft et al., 2005). As a result a

program was initiated to transition from surface water to groundwater (to avoid surface based bacterial contamination) with the installation of millions of hand-pumped tube wells (typically a depth of 20 – 70m) which were drilled in the last few decades since the 1970s (Ravenscroft et al., 2005). Access to groundwater free of bacterial contamination gave rise to a reduction in outbreaks of waterborne pathogenic diseases. However, the presence of arsenic within the shallow groundwaters was not realised until 1983 for West Bengal and 1993 for Bangladesh (Sar et al., 2014). Due to the extent of arsenic contamination in the Bangladesh region and the affected population, this area has been the most examined when compared to any other country or region (Mitchell et al., 2011).

The arsenic present in the reducing environments from the alluvial and deltaic BGM aquifers represent the most serious occurrence identified globally with concentrations ranging from $<0.5 \mu\text{g L}^{-1}$ to around $3200 \mu\text{g L}^{-1}$ (BGS and DPHE, 2001; Mukherjee et al., 2008). These young aquifers are prone to developing and preserving groundwaters with high concentrations of arsenic (Edmunds et al., 2015). In the region of GBM the alluvial sediment was formed through the sedimentation of the rivers Ganges, Brahmaputra and Meghna, which represents the largest fluviodeltaic basin in the world. Here, arsenic contamination mainly occurs in shallower aquifers formed during the Holocene with concentrations of arsenic in the solid phase being consistent and represented for the most part by As^{V} (Sar et al., 2014). Arsenate has been shown to be co-precipitated in or co-adsorbed on various Fe and Mn-rich clastic and authigenic minerals or mineral phases (Sar et al., 2014). However, in contrast aqueous arsenic is dominated by As^{III} with its concentration showing high spatial and depth variations (Sar et al., 2014) with many mechanisms been proposed for the mobilisation of arsenic. The most commonly accepted geochemical process involves the microbial-mediated reductive dissolution of arsenic-bearing Fe^{III} -oxides/oxyhydroxides (Bhattacharya et al., 1997; Harvey et al., 2002 and 2005; Islam et al., 2004; Zheng et al., 2004; Polizzotto et al., 2008; Yang et al., 2014). A conceptual diagram illustrating the key geochemical processes involved in the deployment of arsenic-contaminated groundwater of the BGM plains in Fig. 1.3.

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Fig. 1.3. Conceptual diagram showing the key geochemical processes involved in the development of arsenic-contaminated and its mobility in groundwater in the Bengal Basin (source: adopted from BGS and DPHE, 2001).

1.3.4) Regulatory framework

Both the European Union (EU) and the World Health Organisation (WHO) have set the parametric value of arsenic in groundwaters at $10 \mu\text{g L}^{-1}$ (EC, 2007; WHO, 2011). By comparison, the USEPA has set the maximum contaminant level (MCL) of arsenic in water also at $10 \mu\text{g L}^{-1}$ when it was lowered from the old standard of $50 \mu\text{g L}^{-1}$ in 2001 (Hughes et al., 2007). However, this standard came into force in 2006 (Mudhoo et al., 2011). This MCL of $10 \mu\text{g L}^{-1}$ has been questioned with scientists suggesting a new MCL of $0.5 \mu\text{g L}^{-1}$ in order to lower the risk of cancer from 1 in 500 to 1 in 10,000, the highest risk the USEPA allows in tap water (Hughes et al., 2007; Salaün et al., 2007). Due to the advanced analytical instrumentation required to detect at this level this goal may be unfeasible in many regions of the world which uses older technology and/or limited financial scope. This is evident as there is a struggle to reach the arsenic standard of $10 \mu\text{g L}^{-1}$ with many countries (e.g. India, Vietnam, and Bangladesh) still using the earlier guideline of $50 \mu\text{g L}^{-1}$ (0.05mg L^{-1}) as a national standard or either as an interim target (Berg et al., 2001). This inability to quantify arsenic at these lower limits is mainly due to the lack of adequate analytical facilities (Smedley and Kinniburgh, 2002; Meharg and Raab, 2010). Having the appropriate infrastructure is a critical aspect, but also the economic resources to implement both the WHO and EU standard may not be feasible in the short term. In 33 countries, the WHO provisional guidelines of $10 \mu\text{g L}^{-1}$ (or 0.01mg L^{-1}) has been adopted as a drinking water standard for arsenic (Mudhoo et al., 2011; Murcott, 2012). By comparison 34 countries (mainly the Asian and African regions) use the old standard of $50 \mu\text{g L}^{-1}$ with 36 countries have no stated arsenic standard (Murcott, 2012). The old standard of $50 \mu\text{g L}^{-1}$ is being used as many countries do not have the analytical infrastructure to reach the lower value of $10 \mu\text{g L}^{-1}$.

In Ireland a lower arsenic concentration of $7.5 \mu\text{g L}^{-1}$ is set as the groundwater threshold value (GTV), i.e. 75% of the Irish legal limit for arsenic in drinking water at $10 \mu\text{g L}^{-1}$ (EC, 2010). For the purpose of clarity, any concentration $\geq 7.5 \mu\text{g L}^{-1}$ of arsenic, unless otherwise stated, would indicate the presence of elevated concentrations. The parametric values are based on different legislation sources (i.e., EU, USA (based on Safe Drinking Water Act (SDWA))) of relevant metals and nutrients can be seen in Table 1.2. For arsenic, these limits are based on total concentrations, rather than species specific concentrations. Only Australia ($7 \mu\text{g L}^{-1}$) holds an arsenic water standard that is lower than the WHO, EU and USEPA standard of $10 \mu\text{g L}^{-1}$.

It must be stated that private sources of groundwater are classes as exempt supplies and thus it is the responsibility of the owner to ensure water quality. Similarly, in the United States,

private sources are also unregulated which serves approximately 40 million people (Ryker, 2001 and 2003).

Traditionally total concentrations have been used to evaluate the toxicity of arsenic, regarding the toxicity and potential mobility in the environment (Fodor 2001; Michalke, 2003; Meharg and Raab, 2010). Indeed, all arsenic regulations are based on total arsenic concentrations and not based on individual species. However, this assessment and interpretation, based on total metal concentration data may give rise to misleading conclusions, especially from a health and clinical perspective. For this reason, it is critical to incorporate speciation data of relevant trace elements (i.e. arsenic) in the groundwater system to firstly understand the trace element of interest and secondly to protect human health. Thus, for human risk assessment, appropriate speciation data (i.e. arsenate and arsenite) must be used (Chung et al., 2014).

Table 1.2. Comparison of drinking water quality values of metals in various regions

Analyte	Unit	European Drinking Water Regulations (EC, 2007)	Irish Groundwater Regulations (EC, 2010)	WHO Drinking water guideline values (WHO, 2011)	USEPA Drinking water standards (USEPA, 2009)	Guidelines for Canadian drinking water (FPTCHE, 2008)	New Zealand Drinking Water Standards (NZ, 2008)
B	mg L ⁻¹	1	0.75	2.4		5	1.4
F	mg L ⁻¹	0.8 ^a , 1.5 ^b		1.5	4	1.5	1.5
Na	mg L ⁻¹	200 ^c	150	50		≤200	
Al	µg L ⁻¹	200 ^c	150			100/200	
Cl	mg L ⁻¹	250 ^c	24 – 187.5			≤250	
Cr	µg L ⁻¹	50	37.5	50	100	50	50
Mn	µg L ⁻¹	50 ^c				≤50	400
Fe	µg L ⁻¹	200 ^c				≤300	
Ni	µg L ⁻¹	20	15	70			20
Cu	mg L ⁻¹	2	1.5	2	1.3	≤1	2
Zn	mg L ⁻¹					≤5	
As	µg L⁻¹	10	7.5	10	10	10	10
Se	µg L ⁻¹	10		40	50	10	10
Mo	µg L ⁻¹			70			70
Ag	µg L ⁻¹						100
Cd	µg L ⁻¹	5	3.75	3	5	5	4
Sb	µg L ⁻¹	5		20	6		
Ba	µg L ⁻¹			700	2000		
Hg	µg L ⁻¹	1	0.75	6	2	1	2
Tl	µg L ⁻¹				2		
Pb	µg L ⁻¹	10	18.75	10	15	10	10
U	µg L ⁻¹			30		20	20
NO ₃	mg L ⁻¹	50	37.5	50	10 ^f (44)	45	50
NO ₂	mg L ⁻¹	0.5	0.375	3/0.2 ^e	1 ^f (3)		3/0.2 ^e
SO ₄ ²⁻	mg L ⁻¹	250 ^c	187.5			≤500	

^a fluorinated supplies

^b supplies with naturally occurring fluoride

^c indicator parameters

^d groundwater threshold value (range)

^e short/long term exposure

^f measured as N

1.3.5) Mineralogy and geological settings

1.3.5.1) Mineralogy

Arsenic is present as a component in some 245 different minerals and thus has a great abundance in geological materials (Prohaska and Stingeder, 2005). Of these 60% are arsenates and 20% are sulfides or sulfosalts while the remaining 20% comprise a combination of arsenates, arsenites, oxides, elemental arsenic and oxides (Prohaska and Stingeder, 2005). The greatest concentration of these minerals occurs in mineralised regions including areas the United States, Canada and some European countries found in close association with transition metals in addition to silver, gold, antimony, cadmium, lead, phosphorus and molybdenum (Akter et al., 2005).

The most important arsenic-bearing minerals are mixed sulphides of the $M^{II}AsS$ type, where M^{II} can be Fe, Ni, Co and to a lesser degree other divalent metals (Matschullat, 2000). In the environment arsenic is present as mineral deposits (realgar, arsenic disulfide – As_2S_2 ; orpiment; arsenic trisulfide – As_2S_3 ; arsenopyrite, ferrous arsenic sulfide – $FeAsS$ and cobaltite, cobalt arsenic sulphide, - $CoAsS$), secondary minerals (scorodite) or alteration by-products (olivenite) (Paikaray, 2012). For example, when arsenic is discarded from the ore processing of arsenopyrite as tailings, the resulting weathering and oxidation of associated sulphates results in the acidification of mine waters, i.e. acid mine drainage (AMD) (Villaescusa and Bollinger, 2008).

Arsenopyrite (or artisan pyrite) has received most of the attention as this mineral is believed to be the main source of arsenic contamination of groundwaters in Bangladesh (O'Day, 2006; Chouhan and Flora, 2010). Arsenic which is present in rocks is usually found as sulfide minerals such as arsenopyrite ($FeAsS$). Oxidation of minerals can cause arsenic to become soluble and leach into the environment via water transport (Ali and Jain, 2004). It has been established that both As^{III} and As^V can be sorbed to the surfaces of oxides which are dependent upon pH and Eh (Smedley and Kinniburgh, 2002). At lower pH and in oxic environments, As^V is more associated with these oxides compared to As^{III} .

1.3.5.2) Geological settings

The arsenic content of the different rock strata depends on a variety of conditions, including the environmental and depositional settings. Generally, concentrations of arsenic in rocks range from 1.5 mg kg⁻¹ in igneous rocks, about 5 mg kg⁻¹ or less in metamorphic rocks and between 5 – 10 mg kg⁻¹ in sedimentary rocks. Arsenic concentrations are usually lower in igneous rocks

with little variation in this rock type (Akter et al., 2005). This compares to the average crustal abundance of arsenic of 1.5 - 2 mg kg⁻¹ (Plant et al., 2003; Mudhoo et al., 2011). However, it has been noted that arsenic concentrations are higher near areas of volcanic activity (Fodor, 2001). The sedimentary rocks however are the most important sources of arsenic in the environment with argillaceous forms (consisting of clays) having higher averages (13 mg kg⁻¹) compared to arenaceous forms (consisting of sand) (4 mg kg⁻¹) (Dissanayake and Chandrajith, 2009). Marine shales have been observed to be enriched with arsenic which can arise due to the presence of sulphate and pyrite (Dissanayake and Chandrajith, 2009). Though not present as a major component, arsenic tends to be present at varying concentrations in many rock-forming minerals due to its ability to substitute for Si^{IV}, Fe^{III}, Al^{III} and Ti^{IV} (Smedley and Kinniburgh, 2002; Dissanayake and Chandrajith, 2009). Given the similarity in chemistry of arsenic to sulphur, the highest concentrations occur in sulphide minerals (e.g. pyrite, chalcopyrite, galena) (Smedley and Kinniburgh, 2002).

Concentrations of arsenic in metamorphic rocks reflect those of their igneous and sedimentary precursors (Smedley and Kinniburgh, 2013). For the sedimentary rocks sandstones generally have lower concentrations of arsenic, a reflection of the lower concentration in their dominant minerals of quartz and feldspars (Smedley and Kinniburgh, 2013). Black shales are considered an environmental geohazard in relation due to their high arsenic content mainly as a result of a higher pyrite content (Paikaray, 2012). Table 1.3 shows the varying concentrations of arsenic in many materials of the geosphere.

Table 1.3. Typical arsenic concentrations in rocks, sediments, soils and surficial deposits (source: adapted from Smedley and Kinniburgh, 2002 and references therein).

Rock	Average arsenic concentration (mg kg ⁻¹)	Arsenic concentration range (mg kg ⁻¹)
<i>Igneous rocks</i>		
Ultrabasic rocks (peridotite, dunite, kimberlite)	1.5	0.03-15.8
Basic rocks (basalt)	2.3	0.18-113
Basic rocks (gabbro, dolerite)	1.5	0.06-28
Intermediate (andesite, trachyte, latite)	2.7	0.5-5.8
Intermediate (diorite, granodiorite, syenite)	1.0	0.09-13.4
Acidic rocks (rhyolite)	4.3	3.2-5.4
Acidic rocks (granite, aplite)	1.3	0.2-15
Acidic rocks (pitchstone)	1.7	0.5-3.3
Volcanic glasses	5.9	2.2-12.2
<i>Metamorphic rocks</i>		
Quartzite	5.5	2.2-7.6
Hornfels	5.5	0.7-11
Phyllite/slate	18	0.5-143
Schist/gneiss	1.1	<0.1-18.5
Amphibolite and greenstone	6.3	0.4-45
<i>Sedimentary rocks</i>		
Marine shale/mudstone	NA	3-490
Shale (Mid-Atlantic ridge)	174	48-361
Non-marine shale/mudstone	NA	3-12
Sandstone	4.1	0.6-120
Limestone/dolomite	2.6	0.1-20.1
Phosphorite	21	0.4-188

Table 1.3. (continued).

Rock	Average arsenic concentration (mg kg ⁻¹)	Arsenic concentration range (mg kg ⁻¹)
Limestone/dolomite	2.6	0.1-20.1
Phosphorite	21	0.4-188
Iron formations and Fe-rich sediment	NA	1-2900
Evaporites (gypsum/anhydrite)	3.5	0.1-10
<i>Unconsolidated sediments</i>		
Various	3	0.6-50
Alluvial sand (Bangladesh)	2.9	1-6.2
Alluvial mud/clay (Bangladesh)	6.5	2.7-14.7
Glacial till (British Columbia)	9.2	1.9-170
<i>Soils</i>		
Various	7.2	0.1-55
Peaty and bog soils	13	2-36
European agricultural soils ¹	5.69 (median)	<0.1-666
European grazing land soils ¹	5.75 (median)	<0.1-292
Soil Ireland ²	7.25 (median)	<0.2-173

¹Tarvainen et al., 2013

²Zhang et al., 2008^a

1.3.5.3) Arsenic in bedrock aquifers

Most of the research focused on arsenic in groundwater has focused in unconsolidated sediments aquifers in alluvial plains and deltas (Bondu et al., 2016). However research has shown that elevated arsenic in groundwater is present in fractured bedrock aquifers in a variety of geological settings (Ravenscroft et al., 2009). For example, fractured bedrocks frequently consist of metavolcanic and metasedimentary rocks intruded by granitoids that have been sporadically overlain by younger deposits, i.e. glacial sediments (Bondu et al., 2016). These fractured bedrock aquifers give rise to elevated concentrations of arsenic in groundwaters have been observed in many regions of the world including USA (Ayotte et al., 2003; Peters, 2008; Verplanck et al., 2008; Yang et al., 2009; Ryan et al., 2011, 2013 and 2015; O'Shea et al., 2015; Andy et al., 2017), Canada (Klassen et al., 2009; Drummer et al., 2015; Bondu et al., 2017a), Africa (Smedley et al., 2007), Finland (Parviainen et al., 2015), France (Tisserand et al., 2014), Italy (Reyes et al., 2015), Greece (Zkeri et al., 2015), and certain regions in Asia (Shukla et al., 2010; Kim et al., 2012; Ahn and Cho, 2013). Additionally arsenic can be observed in glaciated bedrock aquifers in North America (especially Midwestern USA) (Ravenscroft et al., 2009) including New England, Illinois, Minnesota and Nova Scotia (Warner, 2001; Thomas, 2003; Ayotte et al., 2006; Erickson and Barnes, 2005a and 2005b; Ravenscroft et al., 2009; Nicholas et al., 2017).

1.3.6) Arsenic mobilisation mechanisms

Aqueous arsenic concentrations and other elements of geogenic origin are controlled by three important factors: i) the source of arsenic, ii) its solubility and attenuation, and iii) its

subsequent transportation and distribution (Smedley and Kinniburgh, 2002 and 2013). Several arsenic mobilisation mechanisms and their geochemical processes have been reported in the literature (Neil et al., 2012). Changes in the physiochemical behaviours of aquifers and water-sediment (rock) interactions (dissociation, association, adsorption, desorption, dissolution, etc) in addition to abiotic and biotic processes cause the mobilisation of arsenic into groundwater (Sar et al., 2014).

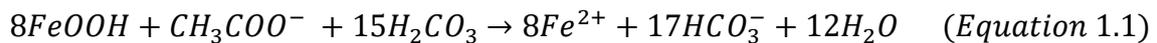
Generally, there are four mechanisms for arsenic mobilisation in the environment. Each mechanism is generally associated with predictable geological and climatic environmental settings (Ravenscroft et al., 2009). These mechanisms are (in order of decreasing importance): reductive dissolution, alkali desorption, sulphate oxidation and geothermal. Table 1.4 shows the summary of documented high-arsenic groundwater provinces and their typical hydrogeological and geochemical characteristics in addition to the groundwater environment of these mobilisation mechanisms.

Table 1.4. General summary of the documented high-arsenic groundwater provinces and their typical hydrogeological and geochemical characteristics and illustration of the key arsenic mobilisation mechanisms: reductive dissolution, alkali desorption, sulphate oxidation and geothermal waters (source: adapted from Smedley and Kinniburgh, 2013)

Groundwater environment/ aquifer type	Examples	Typical conditions	aquifer	Typical geochemical features of high-arsenic groundwaters	Likely mechanisms of arsenic mobilisation
Strongly reducing groundwater	Alluvial/ deltaic aquifers BGM, Mekong delta, northern China, Taiwan, Great Hungarian Plain	Quaternary sediments, often slow groundwater flow, low-lying parts of aquifers, rapidly accumulated sediments		High Fe (>1 mg L ⁻¹), Mn (>0.5 mg L ⁻¹), NH ₄ -N (>1 mg L ⁻¹), high HCO ₃ (>500 mg L ⁻¹); low NO ₃ -N (<1 mg L ⁻¹), low SO ₄ (<5 mg L ⁻¹). Often high P (>0.5 mg L ⁻¹). Sometimes high concentrations of dissolved organic matter, including humic acid. Arsenic dominated by As ^{III}	Reductive desorption of arsenic from metal oxides and reductive dissolution of Fe oxides. Competition between arsenic and other anionic species (especially P)
Geothermally influenced groundwater	Parts of Kamchatka, Chile, Argentina, Equador, western USA, Japan, New Zealand	Any aquifers affected by geothermal inputs, especially in rift zones		High Si, B, Li, often high salinity (Na, Cl); high pH (>7); increased groundwater temperature; arsenic speciation variable	Mixing of fresh groundwater with geothermal solutions
Oxic (aerobic) groundwater, high pH	Island basins or closed basins (arid and semi-arid areas): Argentina, Mexico, parts of Nicaragua, western USA, Chile, Spain	Quaternary sediments, slow groundwater flow, low-lying parts of aquifers; often (not always) volcanic components present		pH typically >8, high HCO ₃ (>500 mg L ⁻¹), low Fe, Mn, often correspondingly high F, U, B, V, Mo, Se. some groundwaters have high salinity due to evaporation. Arsenic dominated by As ^V	Desorption of arsenic and other oxyanion-forming elements from metal oxides, especially Fe and Mn; volcanic ash may be ultimate source for some locations
Groundwater from sulphide mineralised/mining areas	Parts of Burkina Faso, Canada, USA, Thailand, Korea, Poland, Greece, Ghana, Zimbabwe, England	Groundwater in fractures in crystalline rocks or alluvial placer deposits		Oxidising or mildly reducing conditions possible; high SO ₄ concentrations (typically hundreds of mg L ⁻¹ or higher); often increased concentrations of other trace elements (Ni, Pb, Zn, Cu, Cd). Arsenic speciation variable but mainly As ^V	Oxidation of sulphide minerals

1.3.6.1) Reductive dissolution

The occurrence of this mechanism is most prevalent in areas of the South and Southeast Asian Arsenic Belt (SSAAB). This process occurs when iron oxides which arsenic is adsorbed (oxides are coatings on aquifer sands) onto, dissolved via decaying organic matter (consumes oxygen) (Ravenscroft, 2007; Ravenscroft et al., 2009). This process liberates arsenic and other trace elements present on the mineral phases. This dissolution processes is generally microbial-mediated and produces groundwaters that are near-neutral-reducing (NNR) which is characterised by a pH of 6.7-7.5 (Ravenscroft, 2007). Indicator of reducing conditions present include high concentrations of iron, manganese, ammonium, methane gas and bicarbonate in the absence of oxidised species such as nitrate, dissolved oxygen (O₂) and sulphate (Ravenscroft, 2009; Ravenscroft et al., 2009). The dominant arsenic species is the reduced inorganic species arsenite, As^{III}. Equation 1.1 shows the reduction of iron (arsenic bearing ferrihydrite) by microorganisms in the presence of organic matter (McArthur et al., 2001). Ba can also be present in this mechanism.



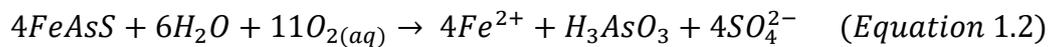
1.3.6.2) Alkali desorption

This mobilisation mechanism occurs at high pH (≥ 8) in the presence of dissolved oxygen, nitrate or sulphate. These waters are generally termed as alkali-oxic and have low concentrations of iron and manganese (Ravenscroft et al., 2009). These alkali-oxic waters are dominated by inorganic As^V. The increased pH leads to a set of biogeochemical processes that promotes desorption of arsenic adsorbed onto iron, manganese and aluminium oxides and clay minerals (Ravenscroft et al., 2009). Conversely, at aerobic and near-neutral conditions arsenic will stay adsorbed onto these oxide minerals (Smedley and Kinniburgh, 2013). However, in alkali-oxic waters other factors such as evaporation, residence time and weathering can independently cause increases in pH and arsenic when compared to the desorption processes (McArthur et al., 2004). However, depending on the mineralogy present the adsorption of arsenate onto most oxides and clays decreases significantly pH ≥ 8 (particularly at pH ≥ 8.5) (Ravenscroft et al., 2009). This desorption process increases the aqueous concentration of arsenic and this affect is intensified by the high solid-to-solution ratios that are typical of aquifers (Smedley and Kinniburgh, 2013). For iron oxides this occurs steadily from subneutral pH and in the region of pH 6-8 for aluminium oxides. The variability in desorption in alkaline waters can be explained through these differences in oxide and clay mineralogy (Ravenscroft

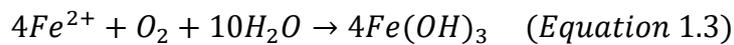
et al., 2009). These processes can also cause desorption of other oxyanions such as phosphate, vanadate, uranyl, borate and molybdate (Smedley and Kinniburgh, 2013).

1.3.6.3) Sulphate oxidation

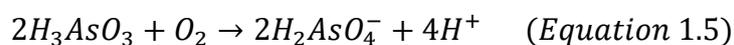
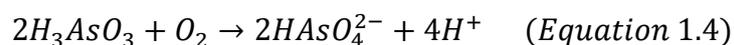
Sulphide minerals such as pyrite or arsenopyrite can be oxidised via oxygen (as dissolved oxygen) or ferric iron (often at the water table) which in turn produce waters that are slightly to strongly acidic (pH 1 – 6) and sulphate-rich (Ravenscroft et al., 2009). Pyrite oxidation produces a low acidity, but carbonate minerals present can neutralise this (Ravenscroft et al., 2009). In areas of crystalline basement this acidity may become persistent (Ravenscroft et al., 2009). Generally, these processes occur when the water table fluctuates over a sulphide-rich layer (Ravenscroft, 2007). These acid-sulphate waters are not necessarily high in iron, but can be. Other trace elements that may be present as a result of this process include Co, Cr, Ni and Zn. Arsenopyrite is of more concern compared to pyrite due to the high content of arsenic in this mineral. Arsenopyrite can be oxidised by molecular oxygen at near-neutral pH where As^{III} is released as the uncharged anion H₃AsO₃ from the following mechanism in Equation 1.2 (Walker et al., 2006).



While this reaction (Equation 1.2) does not produce acidity, subsequent secondary reactions will yield protons into solution. The oxidation of ferrous iron from Equation 1.2 will form iron oxyhydroxides (Equation 1.3).



Arsenite liberated from Equation 1.2 can be oxidised to arsenate. At near-neutral pH, the pK_{a2} fo As^V is 6.98 which yields HAsO₄²⁻ and H₂AsO₄⁻ in equal proportions from arsenite oxidation (Equation 1.4 and 1.5) (Walker et al., 2006).



1.3.6.4) Geothermal

Waters from deep, oftentimes volcanic, sources release arsenic from the lithology (Ravenscroft et al., 2009). These waters can be distinguished from other mobilisation processes by elevated temperature in addition to a correlation of arsenic with chloride. Geothermal arsenic usually occurs in three tectonic settings: i) colliding plate boundaries (subduction zones, continental sutures), ii) intraplate hot-spots (magma chambers, e.g. Yellowstone), iii) along rift zones (Ravenscroft et al., 2009).

1.3.7) Aqueous speciation

Speciation deals with the individual oxidation states that make up an element. This is an important environmental and health consideration as different oxidation states of the same element may have differing mobilities and toxicities. For example, trivalent chromium (chromate, Cr^{III}) is an essential element, whereas hexavalent chromium (chromate, Cr^{VI}) is highly toxic. A key reason why arsenic is so persistent in the environment is that, compared to other oxyanion forming elements, such as Se, Sb, Mo, V, Cr and U, arsenic is mobile under a wide range of aqueous redox conditions (Smedley and Kinniburgh, 2002; Campbell and Nordstrom, 2014). Under oxidising conditions, the oxyanion selenate (SeO_4^{2-}) is mobile whereas the oxyanion, selenite (SeO_3^{2-}) is immobilised under reducing conditions. Similarly, the mobility of molybdate (MoO_4^{2-}), vanadate (VO_4^{3-}) and uranyl (UO_2^{2+}) are less mobile under reducing conditions (Smedley and Kinniburgh, 2002).

1.3.7.1) Aqueous arsenic speciation

Arsenic, a metalloid can be present as four oxidation states, or physiochemical forms, which include arsenate (As^{V}), arsenite (As^{III}), elemental (As^0) and arsenide ($\text{As}^{-\text{III}}$) (Hung et al., 2004; Stolz et al., 2006). Arsines occur as highly toxic gases in the form of arsine (H_3As) and trimethylarsine ($(\text{CH}_3)_3\text{As}$), however very little is known about the biogeochemical cycles of both these compounds as they are found in the environment in low concentrations (Oremland and Stolz, 2005; Mestrot et al., 2013). Elemental arsenic is rarely encountered while arsines have been identified in strongly reducing environments (Campbell and Nordstrom, 2014).

In the environment arsenic can be present as either inorganic (i-As) or organic (o-As) (organoarsenials) forms and generally in the trivalent and pentavalent form (Fig. 1.1a and b). These methylated organic arsenic species can be formed through biomethylation by microorganisms (Cullen and Reimer, 1989). The presence of MA^{V} and DMA^{V} in the environment are as stable methylated mammalian metabolites (Villaescusa and Bollinger,

2008). However, DMA^{V} and the sodium salts of MA^{V} can also be present in the environment due to their use as herbicides (Hughes, 2002). However, the concentrations of these methylated forms of arsenate and arsenite are low in the environment (Hung et al., 2004; Oremland and Stolz, 2005). The toxicity of the species generally follows the following pattern: arsenite > arsenate > MA^{V} > DMA^{V} . Previously, it was considered that the methylation of inorganic arsenic species was a mechanism of the detoxification process; however recently it has been shown that some methylated products show similar toxicities to the inorganic forms of arsenic (Stolz et al., 2006). While the toxicity of the trivalent methylated species are much higher than the pentavalent forms, they are not readily encountered in the environment as stable species unless strong reducing conditions in addition to high concentrations of arsenic are present. Recently a study found high concentrations of MA^{III} (with minor amounts of MA^{V} , As^{III} , As^{V} and DMA^{V}) ($3.10\text{-}743.8 \text{ mg L}^{-1}$ for sum of arsenic species) in groundwater near a former herbicide manufacturing plant (McKnight-Whitford et al., 2010). Generally, arsenite (As^{III}) is present in anoxic reducing environments while arsenate (As^{V}) is present in more oxidising environments (Cullen and Reimer, 1989; Duker et al., 2004).

1.3.7.2) Inorganic arsenic speciation

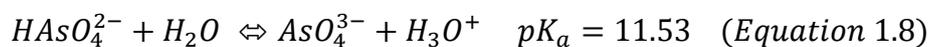
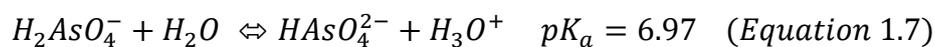
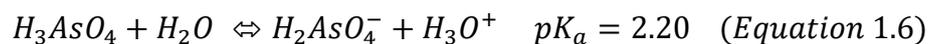
In natural water the most commonly encountered species are the inorganic forms of arsenate (As^{V}) and arsenite (As^{III}), or HAsO_4^{2-} and HAsO_2^- (Smedley and Kinniburgh, 2002; Oremland et al., 2009). In the environment arsenite has a greater hydrologic mobility compared to arsenate. The rate of sorption onto minerals surfaces for arsenate is higher making it less mobile (Oremland et al., 2009). Fig. 1.4 shows the Eh-pH (Pourbaix) diagram of arsenic in natural waters while the distribution of As^{III} and As^{V} in natural waters is illustrated in Fig. 1.5. The relative acidic and basic properties of arsenite and arsenate (arsenic and arsenous acid) will dictate their environmental and analytical behaviours (Prohaska and Stinger, 2005). At different acid dissociation constant (pK_a) values the species will dissociate. For arsenic acid (As^{III}) the species $\text{As}(\text{OH})_3$ readily dissociates sequentially in Equations 1.6, 1.7 and 1.8. At neutral pH, the dominant form of As^{III} is $\text{As}(\text{OH})_3$ while $\text{As}(\text{OH})_2\text{O}^-$ remains a small fraction (<1%) (Sharma and Sohn, 2009). The contributions from $\text{As}(\text{OH})\text{O}_2^-$ and AsO_3^- is negligible.

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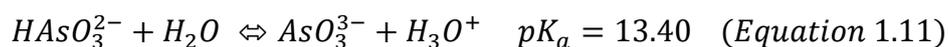
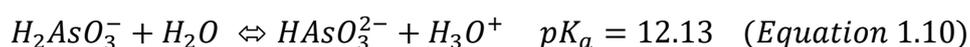
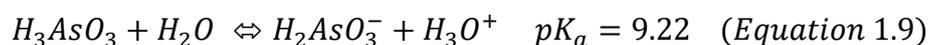
Fig. 1.4. Eh-pH diagram for aqueous arsenic species in the As-O₂-H₂O system at 25°C at a pressure of 1 bar (source: adapted from Smedley and Kinniburgh, 2002).

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Fig. 1.5. Distribution of As^{III} and As^V in natural waters as a function of pH (source: adapted from Meng et al., 2000).



In comparison, As^V is a triprotic acid. At a pH of 7 As^V will exist in equivalent amounts as AsO₂(OH)₂⁻ and AsO₃(OH)₂⁻ (Sharma and Sohn, 2009). The stepwise sequential dissociation of arsenous acid (As^V) are illustrated in Equations 1.9, 1.10 and 1.11.

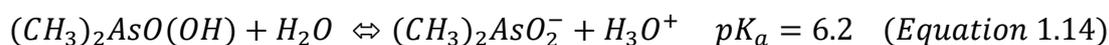
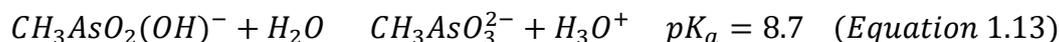
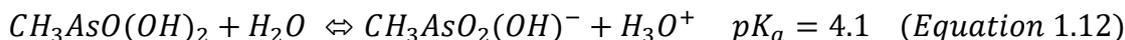


In natural waters, the major controls of arsenic speciation and thus mobility are pH and Eh (Plant et al., 2005; Smedley and Kinniburgh, 2013). Other minor controls of arsenic speciation include temperature, surface properties of solids, abundance of potential ligands, biological activity, major cations and anions, the presence or absence of dissolved and/or particulate organic matter (Plant et al., 2005). While changes in the oxidation state of arsenic will affect solution chemistry, changes in pH have control of dissolution reactions including hydrolysis, inorganic complexation and sorption/desorption (Plant et al., 2005). In oxidising conditions (high Eh values) inorganic arsenic is seen predominantly as the form H₃AsO₄ (As^V) at pH <2 while both H₂AsO₄⁻ and HAsO₄²⁻ exist across the pH range of 2-11 (Sharma and Sohn, 2009). In comparison, at low Eh values, i.e. reducing conditions, favours H₃AsO₃ (As^{III}) as the thermodynamically stable species. While arsenic compounds such as As₂S₂ can be formed in the presence of sulphur and hydrogen sulphide if the Eh value falls below -250 mV. However, these conditions are not environmentally relevant. In sulfidic environments the speciation of arsenic can be dominated by thioarsenic species (i.e thioarsenates, H₃AsS₄ and thioarsenites, H₃AsS₃) in which the oxygen atoms bound to arsenic are replaced by sulphur (Cambell and Nordstrom, 2014). These species are of consideration where there is abundant reduced sulphur which can be present in organic-rich groundwaters, hydrocarbon plumes, lacustrine and marine sediments and in geothermal waters.

1.3.7.3) Organic arsenic speciation

MA^V and DMA^V are diprotic and monoprotic acids respectively and their dissociations can be seen in Equations 1.12, 1.13 (MA^V) and 1.14 (DMA^V). At pH 7, MA^V will exist predominantly as the species CH₃AsO₂(OH)⁻ with minor amounts of CH₃AsO₃²⁻ present (Sharma and Sohn,

2009). DMA^V will exist as (CH₃)₂AsO(OH) and (CH₃)₂AsO₂⁻ at a neutral pH (Sharma and Sohn, 2009).



1.3.7.4) Groundwater arsenic ratios

In groundwaters the ratio of As^{III} to As^V (As^{III}/As^V) can vary due to the activity of microorganisms, abundance of redox-active solids, redox state of aquifer and the extent of convection and diffusion of O₂ from the atmosphere (Smedley and Kinniburgh, 2002 and 2013). The redox state of the aquifer is controlled by the abundance of redox-active solids (especially organic carbon) and the flux of potential oxidants including oxygen, nitrate and sulphate (Smedley and Kinniburgh, 2013). The ratio of As^{III} is greater in reducing groundwaters (i.e. Fe^{III}-and SO₄²⁻-reducing aquifers) while this compares to As^V which is more abundant in oxidising groundwaters. Ratios of As^{III}/As_T (total arsenic) vary from 0.1 to 0.9 but generally seen about the value 0.5-0.6 (Smedley and Kinniburgh, 2002). It has been noted that in hyperacidic geothermal waters with a high Eh value (>500 mV) arsenate will be the dominant species (Farnfield et al., 2012). The As^{III}/As^V couple has a redox potential of 130 mV, a stronger oxidant compared to the sulfate/sulfide (SO₄²⁻/S²⁻) couple (-220 mV), but less than the nitrate/nitrite (NO₃⁻/NO₂⁻) couple (440 mV) or oxygen/water (O₂/H₂O) couple (818 mV) (Oremland et al., 2009). Table 1.5 shows the presence of both dominant and minor arsenic species in difference geochemical groundwater conditions. When detected both DMA^V and MA^V occur in minor amounts.

Table 1.5. Comparison of both major and minor arsenic species as a function of groundwater geochemical conditions at differing arsenic concentrations

Geochemical conditions	Total arsenic concentrations (µg L ⁻¹)	Dominate arsenic species	Minor arsenic species	Reference
NA	High	As ^{III} and As ^V	DMA ^V and MA ^V	Bednar et al., 2004 ^a
Acidic to neutral pH	19 – 9080	As ^{III} and to a lesser degree As ^V	DMA ^V and MA ^V	Lord et al., 2012 ^b
Mildly reducing	<0.2 – 326.4	As ^{III} and to a lesser degree As ^V	DMA ^V and MA ^V	Bondu et al., 2017a ^b
Oxidising	7.2 – 210.3	As ^V and to a lesser degree As ^{III}	No DMA ^V or MA ^V present	Sugár et al., 2013 ^b

Table 1.5. (continued).

Geochemical conditions	Total arsenic concentrations ($\mu\text{g L}^{-1}$) ^{b)}	Dominate arsenic species	Minor arsenic species	Reference
Oxidising	0.3 – 1326	As ^{III}	As ^V , DMA ^V and MA ^V	O'Reilly et al., 2010 ^c
Acidic AMD	11 – 4592	As ^V , As ^{III} and DMA ^V	MA ^V	Watts et al., 2010 ^c
Oxidising	133 – 305	As ^{III} and As ^V	MA ^V	Watts et al., 2010 ^c
Oxidising	3.3 – 59.8	As ^V and to a lesser degree As ^{III}	MA ^V (no DMA ^V detected)	Christodoulidou et al., 2012 ^b
Mixed reducing and oxidising conditions	3.0 – 74.6	As ^{III} and to a lesser degree As ^V (inferred)	NA	Katsoyiannis et al., 2007 ^b
Hyperacidic waters (pH 0.82-1.08)	<0.2 – 3783	As ^{III} and to a lesser extent As ^V	MA ^V and to a lesser extent DMA ^V	Farnfield et al., 2012 ^b
Neutral to basic pH	0.5 – 117	As ^{III}	As ^V	Munk et al., 2011 ^b
Acidic to neutral pH with oxic to sub-oxic	<3 – 1160	As ^{III} and to a lesser extent As ^V	NA	Verplanck et al., 2008 ^b
NA	1.27 – 752.5	As ^{III} and to a lesser extent As ^V	NA	Torrance et al., 2012 ^b
NA	7 – 33	As ^V and to a lesser extent As ^{III}	DMA ^V	Donner et al., 2017 ^a
Circum-neutral pH	Low	As ^{III} and to a lesser extent As ^V	NA	Simpson et al., 2011 ^b
NA	Low	As ^V and As ^{III}	NA	Yalçin and Le, 2002 ^b
NA	Low	As ^{III} and As ^V	NA	Murakami et al., 2016 ^b

^a chromatographic laboratory-based speciation and solid phase extraction speciation

^b field or laboratory based solid phase extraction speciation

^c chromatographic laboratory-based speciation

1.3.7.5) Other organic arsenic species

Other organic arsenic species exist predominantly in foodstuffs like marine derived foodstuffs where 85% of the total arsenic concentration is composed of these relatively non-toxic organoarsenicals (Feldmann and Krupp, 2011). A common class of organoarsenicals found in seaweed are the arsenic-containing ribofuranosides or arsenosugars (Feldmann and Krupp, 2011). Over 50 naturally occurring arsenicals have been documented in marine organisms (Francesconi, 2010).

1.3.8) Role of microbial communities and microbial biomethylation

Recently, it has been shown that microbes play a key role in the speciation and release of arsenic in the environment, especially in the BGM area of Asia. They can act as catalysts for the oxidation of arsenite, reduction of arsenate, and in the methylation and volatilization of arsenic species (Smedley and Kinniburgh, 2013). These microbiological transformations in the

environment can i) provide sources of energy or ii) act as a detoxifying mechanism (Smedley and Kinniburgh, 2013). Microbial processes play a pivotal role in the biogeochemical cycling of arsenic in the environment. In the natural environment, mobilisation of arsenic is predominately driven by microbially mediated biogeochemical interactions.

Indeed, in groundwaters of high microbial activity, microorganisms can be responsible for the lack of redox equilibrium between the arsenic species (Smedley and Kinniburgh, 2013). While microbial activity is generally low in groundwaters, this fact is compensated due to the long-time scales involved in groundwater flow (Oremland and Stolz, 2003 and 2005; Lloyd and Oremland 2006).

In these natural environments, bacteria can replace the hydroxyl groups on the inorganic species arsenite and arsenate with methyl ($-\text{CH}_3$) groups (Bissen and Frimmel, 2003). Numerous studies have demonstrated that arsenic is toxic to many bacteria and archaea (Stolz et al., 2006). However, some microorganisms in the environment can tolerate these high concentrations of arsenic (as arsenate and arsenite) and others have the molecular machinery to manage the toxicology of arsenic. In high concentrations, arsenic has been observed to support a wide diversity of microbial life including extremes of pH, salt and metal concentrations (Campbell and Nordstrom, 2014; Oremland et al., 2009). Microbes have dynamic mechanisms in which to cope with elevated concentrations of metals, i.e. arsenic in their surroundings. Microorganisms exhibit a wide phylogenetic diversity of As^{III} -oxidising and As^{V} -reducing bacteria and archaea (Oremland and Stolz, 2003). Indeed, the oxidation of arsenite is one of the protective mechanisms that microbes possess (Cullen and Reimer, 1989).

1.4) Commonly encountered trace elements in groundwater

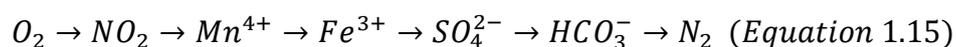
In studies focusing on arsenic within the groundwater system co-contaminants can be commonly reported such as Fe, Mn, Se, U and F which are dependent on the mobilisation mechanism (Smedley and Kinniburgh, 2013; Bacquart et al., 2015; Guo et al., 2016; Etim, 2017). There is a variation in the reported co-contaminants occurring alongside arsenic with differing groundwater geochemistry. For example, oxyanions such as B, S, V and Mo can commonly occur with arsenic through alkali desorption (oxidative desorption) processes, while higher concentrations of iron and manganese can be observed through the mobilisation of arsenic via reductive dissolution (Polya and Middleton, 2017). Due to mineralisation processes arsenic can be found in close association with iron, copper, cadmium, lead, gold, silver, tungsten and molybdenum in many regions of the world (Cullen, 2008). These trace elements are of environmental concern within the groundwater system and can be mobilised by many

important factors such as water chemistry, rock geochemistry and microbiological activity. Several trace elements that occur naturally in groundwater are associated with certain health effects, including arsenic, manganese and uranium (Mitchell et al., 2011).

1.4.1) Iron (Fe) and manganese (Mn)

Regarding the chemistry of arsenic in the environment, both iron and manganese play a critical role. Both Fe and Mn are the two most abundant transition elements in the environment. Manganese is present in differing oxidation states, but the most environmentally relevant forms are soluble Mn^{II} when under reducing conditions and insoluble Mn^{IV} under oxidising conditions (Homoncik et al., 2010). Microorganisms, either directly or indirectly, act as the major catalysts for the biogeochemical cycling of manganese in the environment (Gounot, 1994). Manganese is an essential trace element and is directly involved in many enzymatic reactions, especially those associated with oxygen. Manganese is widely distributed in igneous, metamorphic and sedimentary rocks due to its similar ionic size to magnesium and calcium (Adriano, 2001). For this reason, it can substitute for both these trace elements in silicate structures (Adriano, 2001). While the concentrations of manganese in different rocks can vary, certain rock types (e.g. mafic and ultramafic rocks, igneous rocks, greywacke, shale and limestone) contain higher concentrations which can lead to elevated concentrations in soils and sediments (Adriano, 2001; Homoncik et al., 2010). Lower concentrations are reported in sandstone (Adriano, 2001). Aqueous geochemical parameters such as pH, Eh (redox potential), dissolved oxygen ($d-O_2$) and dissolved organic carbon (DOC) play a critical role in the mobilisation and speciation of manganese (Homoncik et al., 2010).

The chemistry of manganese in the environment closely follows that of iron. While iron is present in two oxidation states of divalent (ferrous) and trivalent iron (ferric) (Fe^{II} , Fe^{III}), manganese is found in three oxidation states (Adriano, 2001). Both iron and manganese are involved in redox reactions within the groundwater system. Compounds are reduced in order of liberating the largest amount of energy first. Sequential reduction reactions can then occur in the following order (Equation 1.15) (Gounot, 1994).



While iron is a common constituent within the groundwater system, there are no health-based guidelines for its concentration in groundwater (Sharma et al., 2005). Rather it is undesirable (like manganese) in that it can cause several aesthetic and operational problems including

discolouration, bad taste, staining, and deposition in distribution systems leading to after growth and instances of high turbidity (Sharma et al., 2005).

1.4.2 Uranium (U) and selenium (Se)

Both uranium and selenium have been demonstrated to cause adverse effects in humans through exposure via drinking water (Fawell and Nieuwenhuijsen, 2003). However, selenium is considered an essential for certain cellular and enzymatic processes, but it can become harmful at greater concentrations (Stolz et al., 2006). Relevant environmental forms of selenium include selenides ($\text{Se}^{-\text{II}}$), elemental (Se^0), selenites (Se^{IV}) and selenates (Se^{VI}) (Bailey, 2017). Because selenium is a metalloid, like arsenic, it has similar chemistry to sulphur, with selenium compounds having important biological roles (Dissanayake and Chandrajith, 2009). Selenium can be found in low concentrations in igneous rocks while in sedimentary rocks selenium is usually associated with the clay fraction and as a result is more abundant in shale when compared to limestone or sandstone (Dissanayake and Chandrajith, 2009; Bailey, 2017). As selenium is a chalcophile element, it can substitute for sulphur in ore minerals such as pyrite and chalcopyrite (Phoon et al., 2012). Like arsenic, selenium can undergo microbial transformations in the environment including dissimilatory and assimilatory reduction processes. As a result of the chronic toxicology of selenium, the condition, selenosis, occurs when excess selenium is ingested (Bailey, 2017). In comparison uranium is a renal toxin that is commonly detected in groundwater associated with granitic rocks and other mineral deposits (Fawell and Nieuwenhuijsen, 2003). Uranium can be found in five oxidation states in natural waters, but hexavalent (U^{VI}) and tetravalent (U^{IV}) uranium are the main forms.

1.4.3 Fluorine (F)

Fluorine, a highly reactive element, due to its high electronegativity, is usually not found in its elemental state, but bound as inorganic fluoride in the environment. In the lithosphere, fluorine can be found in rocks of volcanic origin and enters the environment through volcanic eruptions, rock dissolution and anthropogenic activities (i.e. coal burning) (Kanduti et al., 2016). It is an essential element with concentrations in drinking water around 1 mg L^{-1} thought to be optimal for health, but concentrations $> 1.5 \text{ mg L}^{-1}$ can be considered adverse to health (Edmunds and Smedley, 2005). The presence of elevated concentrations of fluoride in groundwater poses a potential health threat to many people around the world in the form of fluorosis (Amini et al., 2008b). Many of the areas where high levels of fluoride are found are underlain by crystalline igneous and metamorphic lithology (e.g. South Africa and Scandinavia) or in areas of volcanic

and associated hydrothermal activity (Ozsvath, 2009). Indeed, shales, volcano-clastics and bentonites are the most fluoride-rich sedimentary rocks with lower concentrations in sandstones, greywackes, dolomite and limestone (Dissanayake and Chandrajith, 2009). It has been shown that the total fluoride content of clays that are associated with clastic rocks, approximately 80-90% is found in the mica group of minerals (Dissanayake and Chandrajith, 2009). Fluoride is released preferentially from primary minerals (e.g. biotites and amphiboles) (Edmunds and Smedley, 2005). These minerals are generally abundant in granites which can give rise to fluorine within the groundwater system. In most natural waters, F^- (fluoride, F^- , is the ionic form of fluorine) is the most dominant form with minor concentrations of complexes with other major cations (calcium, magnesium and sodium) (Edmunds and Smedley, 2005). Fluoride mobilisation can be enhanced if other elements that it forms complexes with (i.e. Al, B, Be, V, U, Si and ferric iron) are present in significant quantities (Edmunds and Smedley, 2005). Both the water-rock interactions (and soil-water) and the residence time of fluoride are critical factors that determine its concentration in natural waters (Dissanayake and Chandrajith, 2009). Generally, fluoride is found in higher concentrations in deep wells (compared to shallow wells) because of the enhanced water-rock interaction due to longer residence times (Dissanayake and Chandrajith, 2009).

1.5) Less commonly encountered trace elements in groundwater

1.5.1) Chromium (Cr), copper (Cu) and zinc (Zn)

Chromium a lithophile metallic element present in the environment mainly as an essential element as trivalent chromium (Cr^{III}) and as the much more toxic hexavalent form (Cr^{VI}). Sources of Cr^{VI} in the environment are mainly due to anthropogenic rather than geogenic activity. During weathering processes, it can accumulate in detrital materials or in secondary oxides and clays, because the valance and ionic radius of Cr^{III} is similar to both Fe^{III} and Al^{III} (Phoon et al., 2012). The highest concentrations are found in ultrabasic igneous rocks (lower concentrations in basalts, especially granites) with lower values seen in the sedimentary rocks of shale and sandstone (Phoon et al., 2012). The lowest values are seen in limestones. Copper, a chalcophile metallic element, is found in the igneous rocks of basalts and granites at higher concentrations (Phoon et al., 2012). Gabbros usually contain less with lower proportions being found in shales, sandstones and limestone (Phoon et al. 2012). Zinc, another chalcophile element usually exists as the divalent oxidation state in most minerals and is readily partitioned into oxide and silicate minerals by substitution for Fe^{II} and Mg^{II} due to similar ionic radii to

Zn^{II} (Phoon et al., 2012). As a result, it is often found as a trace constituent of minerals such as mica, garnet, magnetite, amphibole and pyroxene (Phoon et al., 2012). Higher concentrations are found in basaltic and granitic igneous rocks in addition to shales with lower concentrations found in sandstone and limestones (Phoon et al., 2012). These three elements have a variety of anthropogenic sources due to their widespread use. Principle minerals of these elements include: Cr, chromite (FeOCr₂O₃), chromatite (CaCr₂O₂) and zinccochromite (ZnCr₂O₄); Cu, chalcocite (Cu₂S), cuprite (Cu₂O), malachite (Cu₂CO₃(OH)₂), chalcopyrite (CuFeS₂); Zn sphalerite (ZnS), willemite (Zn₂SiO₄), and hemimorphite (Zn₄Si₂O₇(OH)₂H₂O) (Phoon et al., 2012).

1.5.2 Molybdenum (Mo)

Molybdenum occurs in natural waters in several oxidation states, but the most environmentally relevant forms include the tetravalent (Mo^{IV}) and hexavalent (Mo^{VI}) states (Smedley et al., 2014). As a chalcophile it occurs in many sulphide-based minerals including molybdenite (MoS₂) (Smedley and Kinniburgh, 2017). The relative concentrations of Mo in rocks (highest to lowest) is shale (black shales have highest concentrations), phosphorite, sandstone, limestone, granitic igneous and basaltic igneous (Adriano, 2001). However, it tends to be uniformly distributed in the environment as Mo can substitute for Fe, Ti and Al in silicate lattice structures. In oxidising environments Mo^{VI} is the dominant oxidation state (MoO₄²⁻) while in reducing environments Mo^V or Mo^{IV} is the dominant form. Typically, concentrations of Mo in groundwater are as low as a few µg L⁻¹, but some hydrogeological conditions can lead to higher concentrations (Smedley and Kinniburgh, 2017)

1.5.3 Mercury (Hg) and lead (Pb)

Mercury can be found in the environment as element, inorganic and organic forms, most notably as methylmercury (CH₃Hg). Due to its toxicity it is deemed a priority pollutant. Lead can be found in mineralised rocks as the minerals galena (PbS), anglesite (PbSO₄) and cerussite (PbCO₃) and is found in many other minerals (Pan et al., 2012). It is found in higher concentrations in granites, shale, schist and lower concentrations in limestones and basalt (Pan et al., 2012). In waters it occurs as the divalent ion (Pb^{II}) (Pan et al., 2012). The toxicants of both Hg and Pb are well established as potent environment contaminants.

1.6 Mobilities of trace elements in the environment

The relative mobilities of these trace elements depend on their environment settings (i.e. oxidising, acid, neutral-alkaline and reducing). For example, the relative mobilities of Mo, U,

Se, F and Zn are high in oxidising and acidic waters (Phoon et al., 2012). This can be seen in Table 1.6 where the pH and Eh are the two most important factors that are directly involved in controlling mobility and solubility (Plant et al., 1996). At high pH conditions anions and oxyanions (e.g. Te, Se, Mo, U, As, P and B) are more mobile than most cations (e.g. Cu, Pb, Cd and Hg) which are less mobile (Plant et al., 1996). However, at lower pH conditions the reverse is true (Plant et al., 1996).

Table 1.6. Mobility of selected elements (essential and potentially toxic elements) in different pH and Eh conditions (source: adapted from Plant et al., 1996).

Relative mobility	Environmental conditions			
	Oxidising	Acid	Neutral-alkaline	Reducing
Very high	I	I	I, Mo, U, Se	I
High	Mo, U, Se, F, Zn	Mo, U, Se, F, Zn, Cu, Co, Ni, Hg	F	F
Medium	Cu, Co, Ni, Hg, As, Cd	As, Cd	As, Cd	
Low	Pb, Be, Bi, Sb, Tl	Pb, Be, Bi, Sb, Tl, Fe, Mn	Pb, Be, Bi, Sb, Tl, Fe, Mn	Fe, Mn
Very low to immobile	Fe, Mn, Al, Cr	Al, Cr	Al, Cr, Zn, Cu, Co, Ni, Hg	Al, Cr, Mo, U, Se, Zn, Co, Cu, Ni, Hg, As, Cd, Pb, Be, Bi, Sb, Tl

1.7) Dissertation objectives and general structure

The following section presents an overview of the general aims and specific objectives of the present study which is followed by a brief overview of the dissertation structure.

1.7.1) General research aims and objectives

Overall, the aim of this present work was to investigate the occurrence and speciation of arsenic on a national, regional and local-scale in Ireland. This was completed through the following specific objectives;

- 1) Develop a statistical methodology to account for multiple censored data of environmental groundwater data (Chapter 3, 4 and 5).
- 2) Investigate the presence of arsenic in groundwater at a national-scale by focusing on its spatial distribution (Chapter 3).
- 3) Investigate the occurrence of arsenic in groundwater at a regional-scale (Chapter 4 and 5).
- 4) Determine the potential controlling factors of arsenic using geological, hydrogeological and land-use data (Chapter 3 and 4).

- 5) Investigate the presence of trace elements, nutrients and microbiology during a groundwater monitoring programme collected as part of a road construction project (Chapter 5).
- 6) Implement a field-based arsenic speciation analytical methodology (Chapter 6).
- 7) Investigate the occurrence and geochemical processes of arsenic at a local-scale in metasedimentary lithology using detailed aqueous geochemistry and arsenic speciation studies (Chapter 6).

These aims and objectives were completed using a combined methodology of analytical chemistry, hydrogeological and statistical techniques which are elaborated on more detail in their respective chapters.

1.7.2) Dissertation structure

This dissertation can be broadly divided into three parts. Firstly, an overview of arsenic in the environment is provided (Chapter 1) in addition to a methodological and analytical background for measuring trace elements at trace levels which includes a rationale for its use in this present work (Chapter 2). This is an important consideration as contamination along the analytical pathway can affect the results and thus their meaningful interpretation especially at the low levels encountered in this study. Groundwater related environmental data contains multiple dimensions (e.g. contaminant, time, depth, other variables, etc) which leads to the generation of vast quantities of data (Edwards et al., 2015; Suthersan et al., 2017). Recently the use of “big data” (especially “environmental big data”) utilises these datasets (e.g. groundwater chemistry, geological and hydrogeological datasets) to extract new insights and create new forms of value (Suthersan et al., 2017). A classic environmental “big data” dataset includes groundwater chemistry data collected over many decades (Edwards et al., 2015). Secondly, using these big data concepts (or environmental informatics), exploratory data analysis was undertaken on datasets to investigate the associations of arsenic in groundwater relating it to geological and hydrogeological classifications. This was completed at both national (Chapter 3) and regional-scales (Chapter 4). Additionally, statistical analysis was conducted in Louth using a historical dataset (4 years of samples) (Chapter 5). These three chapters all use the techniques of censored data analysis. The third part of this dissertation involved combined hydrogeochemical and speciation studies of arsenic in groundwater based in a fractured bedrock aquifer (Chapter 6). Finally, a summary discussion and conclusions chapter are presented (Chapter 7) to synthesise main conclusions of all the chapters and makes recommendations and identification of further research needs in this area based on results obtained.

Chapter 2

Methodological approach and experimental rationale

2.0) Trace element geochemistry

When information is sought at the ppb to sub-ppb level important considerations must be explored if accurate and meaningful results as part of a geochemical survey can be achieved. The concept of trace metal (element) clean techniques for environmental analysis was pioneered by Claire C. Patterson (USEPA, 1996) in which he demonstrated that environmental concentrations of lead were often erroneously high due to lead contamination of the sample (Patterson, 1965).

Clean rooms are now an important component for trace element geochemistry, especially at the ultra-trace levels. Clean rooms facilitate the removal of particulates (which can contain trace elements) by the presence of high efficiency particle attenuation (HEPA) filters with the number of particulates present after filtration depending on the class of cleanroom. Clean techniques are important to reduce the level of contamination artefacts during collection, handling, storage and analysis of waters. These techniques, when completed in clean room facilitates, lead to trace elements measured in blank samples at the ultra-trace level.

In order to process samples for this present work, all sampling handling and analysis was conducted within clean room facilities at the Chemical Monitoring Facility (CMF) of the Ryan Institute. This facility is separated as an ISO 7 sample preparation facility (with ISO 5 laminar flow hood) and an ISO 6 analytical facility, equivalent to the federal standard FED-STD-209E Class 10000 and Class 1000, respectively. Analytical instrumentation housed within this dedicated trace element clean room facility can be observed in Fig. 2.1.



Fig. 2.1. ISO 6 analytical facility at the CMF: **a)** Perkin Elmer ICP-MS DRC-e, **b)** Perkin Elmer AS 93 Plus autosampler, and **c)** Perkin Elmer Series 200 HPLC system (source: authors own image).

2.1) Sample bottle decontamination

Sample containers and their decontamination are an important aspect of sampling as the sample matrix can interact with the storage container which can cause inconsistent results. Thus, washing of bottles is an important feature of trace elements analysis.

In a study by Reimann et al. (1999) different bottle types and acid-washing procedures were investigated to see if these parameters influence trace element analysis. High density polyethylene (HDPE) bottles were found to not affect trace element concentrations. However, for more accurate analysis, the bottles made from fluorinated ethane propene copolymer (FEP) and perfluoroalkoxy polymer (PFA) were found to be better for most trace elements, especially Cr. However, the disadvantages of using fluorinated bottles is that they are much more expensive compared to HDPE bottles, especially for routine monitoring. In comparison, Gasparon (1998) found that properly treated HDPE bottles were comparable to Teflon[®] (polytetrafluoroethylene – PTFE) bottles. However, irrespective of the different type of container used in a study, all phases of sampling and analytical determination must be performed under strict specifications and tested for contamination throughout the process (Gasparon, 1998).

The washing of bottles may introduce contamination. If a strong acid is used, then potential damage to the interior of the bottle may occur, thus increasing the sorptive capacity of the bottle and potentially leaching trace elements into the sample. In a study by Reimann et al. (2007), acid washing caused significant leaching of trace elements (particularly Ba and Zn) from white HDPE bottles. There are several acids to choose from when initiating a decontamination campaign. Both HCl and HNO₃ are recommended for cleaning bottles (Moody and Lindstrom, 1977). In this study, HCl was used as the acid first as traces of chloride would interfere with spectroscopic determination. In this work, the following washing procedure was used sample bottle decontamination which was modified from a GEOTRACES protocol (Cutter et al., 2010).

- 1) LDPE bottles (60, 125, 250, 500 and 1000 cm³, Fisher Scientific, Dublin) were rinsed out three times with ultrapure water (18 MΩ, Millipore Elix and Milli-Q, Ireland) and left in 1% detergent solution (Citronrox, Lennox, Ireland) for 24 hours.
- 2) Bottles were rinsed out of detergent several times to remove traces of detergent. Bottles were then left soaked in 40% (v/v) HCl (TraceMetal[™] grade, Fisher Chemical, Fisher Scientific, Ireland) for a week.

- 3) Bottles were then emptied of HCl and rinsed to remove traces of acid. Following this, 40% (v/v) of HNO₃ (TraceMetal™ grade, Fisher Chemical, Fisher Scientific, Ireland) was soaked in the bottles for a week and then removed and rinsed.
- 4) Finally bottles were soaked in 2% ultrapure HNO₃ (v/v) (Optima™, Fisher Chemical, Fisher Scientific, Ireland) for 48 hours and rinsed.
- 5) Bottles were then filled with Milli-Q water (18 MΩ) and stored in bags (Bryson Packaging™ Minigrip™ PE Bags, Fisher Scientific, Ireland) until sampling occurred.
- 6) Washings of water along the cleaning procedure were collected and analysed for trace element concentrations.

2.2) Groundwater sampling

The collection of groundwater samples is a routine aspect of hydrogeochemical investigations in order to understand the groundwater chemistry for a specific research, remediation, or industry question(s). However, the collection of groundwater from the formation (i.e. representative samples) without changing it in any way during the sampling process presents several difficulties. In order for groundwater samples to be representative of the surrounding formation, then the removal of stagnant water must be completed before sampling can be initiated. The requirement for purging a groundwater well is needed based on the assumption that stagnant water in the well has different chemical characterises than groundwater within the aquifer (or formation) (Daughney et al., 2007).

2.2.1) Traditional purging

Traditionally, three to five well volumes were considered adequate to provide purging conditions that would generate samples that are truly representative of formation water. This methodology was developed in the late 1970s (Ritchey, 2002). In addition, this practice would re-suspend sediments which had settled at the bottom of the well and the acid preservative would leach out any metals present in the suspended sediment, thus potentially overestimating the metal content of the groundwater (Ritchey, 2002). However, due to high cost associated with these high purging volumes and appropriate hazard waste disposal, alternative methods were investigated.

2.2.2) Low-flow purging

Low-flow purging is an alternative method of groundwater purging that involves the extraction of groundwater at rates comparable to ambient groundwater flow rates in an effort to minimize

drawdown and also to limit the mixing of stagnant water in the well casing (Gray et al., 1996; Richey, 2002). This method facilitates the equilibration with the surrounding formation water (i.e. through the stabilisation of groundwater parameters) which results in samples that are most representative of the formation water (Gray et al., 1996). Only the water in the well immediate around the pump must be purged before sampling can be initiated. This method does not remove stagnant water in the well and the turbidity is minimised. Typically flow rates are of the order of 0.1 to 0.5 L min⁻¹, but these can vary due to site and well specific factors (Ritchey, 2002). When indicator parameters are stable after purging, then groundwater samples can be collected with indicator parameters still monitored during the sampling.

Overall, low-flow purging has led to improved sample quality, improved sample accuracy and precision, minimal turbidity, reduced sample variability, and reduced sample degassing in addition to improved sample consistency (Ritchey, 2002). A comparison of traditional versus low-flow purging can be viewed in Fig. 2.2.

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Fig. 2.2. Comparison of traditional purging versus low-flow purging. Low-flow purging extracts much less groundwater in comparison to traditional purging (source: adapted from Ritchey, 2002).

2.2.3) Sampling indicator parameters

Groundwater indicator parameters are usually monitored in either a flow cell or a bucket. However, the use of the latter means that contact with the atmosphere can affect the

measurement of redox sensitive parameters. The use of flow-through cell should be used to isolate flowing groundwater from the atmosphere with indicator parameters recorded at regular intervals (Trick et al., 2008). Air bubbles should be expelled from the flow-through cell in order to prevent anomalous readings in addition to keeping the flow constant (Trick et al., 2008). Small volume flow cells are preferable (i.e. < 250 cm³) as they facilitate in observing the presence of air bubbles and sediment build up which can interfere with the electrochemical probes during groundwater parameter stabilisation (Table 2.1). Another advantage of small volume flowcells is that they offer a high turnover of water between measurements of groundwater parameters during stabilisation.

Table 2.1. Ranges for stable parameters for groundwater purging (percent differences based on at least two subsequent measurements during the stabilisation process).

pH (units)	Conductivity	Temperature	d-O ₂	Eh	Reference
± 0.1 units	± 3%	± 0.2°C	-	-	Daughney et al., 2007
± 0.2 units	±3 %	±0.2°C	±10% or ± 0.2 mg L ⁻¹ *	±20 mV	Thornton and Wilson, 2008
± 0.2 units	±3 %	±0.2°C	±10% or ± 0.2 mg L ⁻¹ *	±20 mV	Nielson and Nielson, 2006

* whichever greater

2.2.4) Sampling pumps

Groundwater sampling pumps can be either dedicated or portable which can be fabricated from a variety of materials (polyvinyl chloride (PVC), polytetrafluorethylene (PTFE), glass, fluoroelastomers, polyethylene (PE), polypropylene (PP), HDPE, polyvinylidene fluoride (PVDF) and stainless steel) and their use depends on budget, analyte(s) required and sampling frequency (Nielson and Nielson, 2006). For example, Stainless Steel is an ideal material for a portable pump as it is easy to decontaminate between sampling locations, however it is expensive. Some materials (e.g. PVC) may be unsuitable for trace element groundwater chemistry sampling due to the presence of filler materials (e.g. zinc compounds) used in the extrusion or moulding process. In order to quantify the potential of cross-contamination in portable sampling systems, it is recommended that deionised water should be passed through the sampling system and collected for analyses. Indeed, background wells (or wells with low levels of contamination) should be collected first, then increasing on the contamination level. A comparison of the different types of groundwater sampling devices showing their advantages and disadvantages are illustrated in Table 2.2.

Table 2.2. Comparison of the advantages and disadvantages on the different types of groundwater sampling devices (data compiled from Nielsen and Nielsen (2006), Sundaram et al., (2009), Thornton and Wilson (2008) and Trick et al., (2008))

Technique	Advantages	Disadvantage
Bladder pump (gas operated)	I) portable, II) range of different lengths and diameters suitable for different applications, III) minimal effect on water chemistry because of non-contact, IV) can be made from inert materials, V) pumping rates can be precisely controlled for high flow rate and low flow rate purging and sampling, VI) controlled discharge rates	I) non-continuous (cyclic) flow II) lift capacity ~60m, (III) expensive compared to comparable devices, IV) check-valve malfunctions due to sediment build up.
Bailer	I) Various size to suit monitoring point, II) inexpensive, III) easy transportation, IV) no external power needed, V) easy to decontaminate, VI) readily available, VII) sample any depth of borehole	I) Increases turbidity, II) aerates sample, III) disturbance of water column, IV) time consuming, V) non-continuous flow, VI) difficulty in determining the point in the water column that the sample represents, VII) long sampling handling in deep boreholes which can affect redox and air sensitive parameters, VIII) causes considerable disturbance of water column, IX) inefficient bailer value, X) mixing of stagnant and dynamic water via surging XI) high operator error (lower sampling precision, XII) unreliable in collecting samples that are representative of formation water
Inertial-lift pumps	I) Low cost, low maintenance and easy to clean, II) no pressure changes during sampling, III) can operate with silt present, IV) if dedicated, it can avoid cross-contamination	I) Disturbance of water column, II) sample degassing, III) increased turbidity
Vacuum pump	I) relatively portable and inexpensive, II) dedicated tubing left in well	I) Sample degassing, II) limited to water tables <9m, III) not suitable for detailed chemical analyses or pH sensitivity applications, IV) inert gas needed due to oxygenation,
Peristaltic	I) highly portable, II) inexpensive, III) flow rate is easily controlled, IV) dedicated tubing can be left in well, V) sample only in contact with tubing	I) limited sampling depth (8-10 m), II) sample degassing

For this study, a bladder pump was used in the field site in Co Louth due to the deeper groundwater sources. A bladder pump is gas-driven pump that uses compressed air to expand and compress flexible bladder in order to retrieve the sample (Sundaram et al., 2009). Bladder pumpers are generally regarded as one of the best groundwater sampling pumps and provide representative samples under a wide range of field conditions (Nielsen and Nielsen, 2006; Trick et al., 2008). While a disadvantage of this pump is that it has a low flow rate, this is a suitable requirement for low-flow sampling. While a bladder pump may have a maximum lift capacity of approximately 60 m, this operational depth can be increased to any depth the sampler requires due to an adapter kit. The only requirement is that the bladder pump is below the static water level of the monitoring location. Because bladder pumps are easily disassembled, they are an ideal choice for a portable sampling device in order to avoid cross contamination. The bladder pump used in this study was a 42 mm (diameter) Geotch Geocontrol Pro™ (Fig. 2.3) which was controlled by a PCU ProPlus control unit (maximum operating limit of 100 psi). An advantage of this unit over other commercial bladder pumps is that it has a built in air compressor, thus avoiding the need to carry a separate air compressor and fuel.



Fig. 2.3. Groundwater sampling set up for trace element sampling in Louth (BH-24) with the following equipment: **a)** controller unit, **b)** dip meter, **c)** safety cable **d)** electrochemistry probes and **e)** flow-through cell. Image insert showing the bladder pump unit with air and sample tubing with a safety line (Dyneema®) attached (source: authors own image).

2.3) Speciation

Speciation is a relatively new analytical technique applied to the area of environmental analytical chemistry. The speciation of an element comprises all the different chemical forms which make up a total metal concentration and thus the physicochemical forms of the trace element in question can be elucidated (Bose et al., 2011). Total element concentrations do not furnish information regarding the various physicochemical forms so that information regarding metabolism, biotransformation, biogeochemical cycling, toxicity, and potential mobility in the environment are unknown (Cullen and Reimer, 1989; Fodor, 2001; Gong et al., 2002; Michalke, 2003; Ali and Jain, 2004).

2.3.1) Laboratory speciation

Analytical techniques used for speciation analysis for arsenic in the environment must be both sensitive and selective (Gong et al., 2002). Arsenic speciation techniques have included high performance liquid chromatography (HPLC), gas chromatography (GC), voltammetry, ion chromatography with atomic spectrometric detection using inductively coupled plasma – mass spectrometry (ICP-MS) (Szpunar et al., 2000; Sarzanini and Bruzzoniti, 2001; Butcher, 2007; Mays and Hussam, 2009; Popp et al., 2010; Ammann, 2011; Komorowicz and Barańkiewicz, 2011; Maher et al., 2012). The increased sensitivity resulting from hyphenation of HPLC and

ICP-MS is the most common laboratory-based speciation techniques and offers low detection limits.

A major disadvantage of laboratory-based speciation is preservation methods to stop species redistribution between sampling and analytical determination. For successful arsenic speciation, species instability during sampling, storage and sample pre-treatment must be critically analysed (Gong et al., 2002). Changes in pH, Eh, microbial activity, photochemical oxidation, metal oxyhydroxide precipitation and adsorption effects, can affect the stability of arsenic species with species redistribution affecting the quality of data (Gong et al., 2002; Leybourne et al., 2014). Sample preservation is best used when a thorough knowledge of the matrix is known.

While there is no universal method for arsenic species preservation (Kumar and Riyazuddin, 2010), the use of ethylenediaminetetraacetic acid (EDTA) as a preserving agent has had success (Gallagher et al., 2001; Bednar et al., 2002; McCleskey et al., 2004; Pandey et al., 2004; Samanta and Clifford, 2005).

2.3.2) Field speciation

A promising alternative to laboratory-based speciation is the development of field speciation by adopting solid phase extraction (SPE) methodologies. By conducting speciation in the field no arsenic species redistribution occurs and gives lower detections limits as it is a preconcentration technique. Several methodologies have been proposed for the field speciation of arsenic in waters (Nath et al., 2008; O'Reilly et al., 2010; Watts et al., 2010; Munk et al., 2011; Simpson et al., 2011; Farnfield et al., 2012; Lord et al., 2012; Sugař et al., 2012).

For the current study, both laboratory-based speciation and field speciation was completed. The field speciation methodology was adapted from O'Reilly et al. (2010) and Watts et al. (2010), which can be seen in Fig. 2.4.

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Fig. 2.4. Methodology of arsenic speciation using SPE (source: adapted from O'Reilly et al., 2010).

2.4) Analytical instrumentation

2.4.1) Analysis by ICP-MS

ICP-MS is a multielement technique that can measure low levels of analytes, from lithium to uranium with a quadrupole mass analyser (Robinson et al., 2005). Unlike other atomic spectroscopic techniques, ICP-MS is capable of analysing aqueous samples based on the elements isotopic composition (Dean, 2014). The ICP is positioned horizontally to the interface of the mass spectrometer so that ions, from the ICP, can be introduced via the sample-skimmer cones directly into the mass spectrometer (Dean, 2014). There are many different ICP-MS designs available, but all share similar components such as nebulizer, spray chamber, and plasma torch (Thomas, 2013). While they can have similar components, they can vary quite significantly in the design of the interface, ion focusing system, mass separation device and vacuum chamber (Thomas, 2013). A simplified block diagram of an ICP-MS can be seen in Fig. 2.5.

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Fig. 2.5. Block diagram of an ICP-MS instrument (source: redrawn from Thomas, 2001a).

The parts of the ICP-MS are described briefly below.

- 1) *Sample introduction system:* introduce the liquid sample into the plasma of the ICP-MS (consists of nebulizer and spray chamber) (Thomas, 2001a).
- 2) *Plasma source:* this consists of the plasma torch and radio frequency (RF) power supply for the ionisation of the sample (Thomas, 2001b).
- 3) *The interface region:* this region transports the ions from a regional at atmospheric pressure to the mass spectrometer analyser region at a vacuum (10^{-6} Torr). This region also contains the sampler and skimmer cones (Thomas, 2001c).
- 4) *Ion focusing system:* the ion optics are placed between the skimmer cone and the mass separation device which consist of one or more electrostatically controlled lens components (Thomas, 2001d).
- 5) *The mass analyser:* the mass analyser (usually a quadrupole, hexapole or octopole) is positioned between the ion optics and the detector and the function of this component is to separate out the ions of interest. A second turbo molecular pump ensures that a vacuum is kept (10^{-6} Torr). A smaller mass analyser can be placed before the main as a reaction cell to remove potential interferences (Thomas, 2001e; Thomas, 2002a).
- 6) *Ion detection:* ion detection is completed using a detector with modern instruments based on a Faraday cup or discrete dynode electron multiplier. The detector converts the ions into an electrical pulse with the magnitude of the pulses corresponding to the number of analyte ions present in the sample (Thomas, 2002b).

2.4.1.1) Interferences in ICP-MS applications

A major disadvantage of ICP-MS is that some elements have poor detection limits due to spectral (isobaric) interferences (May and Wiedmeyer, 1998). These are referred to as polyatomic interferences, which are the most prominent group of interferences in ICP-MS determination and are generated by ions derived by the plasma (e.g. Ar), matrix components, or the acid used and they have the same mass-to-charge ratio (m/z) as the analyte of interest (Thomas, 2013). For example, chloride in the groundwater sample can react with argon from the plasma and interfere with arsenic determination, i.e. $^{35}\text{Cl}^{40}\text{Ar}$ for ^{75}As .

There are several methods with which these polyatomic interferences can be compensated for. Firstly, interferences on the sample can be corrected using mathematical correction equations and can be applied to less severe spectral interferences (Thomas, 2002c). An alternative, and more common approach is to use collision or reaction cells in the instrumentation which use ion-molecule collisions and reactions to remove interferences from the ion beam before they can enter the mass analyser of the instrument (Thomas, 2002c). The reaction cell is usually a small hexapole or quadrupole inserted between the ion optics and mass analyser of the instrument. When polyatomic ions pass through the reaction cell, they are bombarded with gas molecules, which aim to break the polyatomic ions down which greatly reduces their numbers (Robinson et al., 2005). Common reaction gases include helium (He_2), oxygen (O_2), ammonia (NH_3) and methane (CH_4). Proprietary instrumentation from PerkinElmer offers the Dynamic Reaction Cell™ (DRC) which uses specific gas phase chemical reactions to greatly reduce interferences. The DRC, a quadrupole, is placed inside a reaction chamber (Robinson et al., 2005). A list of the interferences encountered in this work and their measured isotopes are seen in Table 2.3.

Other less common interferences in ICP-MS include matrix and physical (Thomas, 2002c). In order to avoid matrix interferences, standards used for calibration should be matrix matched to the sample in composition. Physical interferences can be compensated by using an internal standard which is spiked into standards, blanks and samples to correct for any variations in the response of the elements caused by the matrix (Thomas, 2002c). The internal standard is added to samples being analysed, is grouped in a similar mass range, of similar ionisation potential, analyte elements do not spectrally interfere with internal standard and they do not themselves spectrally interfere with the analytes (Thomas, 2002c). Common internal standards for ICP-MS include ^9Be , ^{45}Sc , ^{59}Co , ^{74}Ge , ^{89}Y , ^{105}Rh , ^{115}In , ^{169}Tm , ^{175}Lu , ^{187}Re and ^{232}Th (Thomas, 2002c). For this present work, ^{115}In was used as the internal standard for ICP-MS determination.

Table 2.3. Common polyatomic interferences encountered in this study and the analyte with which they interfere (m/z) (adapted from May and Weidmeyer (1998) and references therein)

Isotope	Interfering species	Reaction gas
⁷⁵ As	⁴⁰ Ar ³⁵ Cl ⁺ , ⁵⁹ Co ¹⁶ O ⁺ , ³⁸ Ar ³⁸ Ar ¹ H ⁺ , ³⁸ Ar ³⁷ Cl ⁺ , ³⁶ Ar ³⁹ K ⁺ ,	O ₂
⁸⁰ Se	⁴⁰ Ar ₂ ⁺ , ³² S ¹⁶ O ₃ ⁺ ,	CH ₄
⁶⁶ Zn	⁵⁰ Ti ¹⁶ O ⁺ , ³² S ¹⁶ O ₂ ⁺ , ³³ S ¹⁶ O ₂ ¹ H ⁺ ,	CH ₄
⁵⁶ Fe	⁴⁰ Ar ¹⁶ O ⁺ , ⁴⁰ Ca ¹⁶ O ⁺ , ⁴⁰ Ar ¹⁵ N ¹ H ⁺ ,	CH ₄
⁵² Cr	³⁵ Cl ¹⁶ O ¹ H ⁺ , ⁴⁰ Ar ¹² C ⁺ , ³⁶ Ar ¹⁶ O ⁺ ,	CH ₄

2.4.2) Separation science

HPLC is a chromatographic technique that employs a liquid mobile phase and very finely divided solid stationary phase (Skoog et al., 2004). In this technique a liquid sample is carried through a chromatographic column by a liquid mobile phase with separation based by solute/stationary-phase interactions. A typical HPLC system consists of a pump, column, column oven injection valve, and a detector (Dean, 2014) (Fig. 2.6). These are expanded on below.

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Fig. 2.6. Block diagram of a HPLC (source: redrawn from Harvey, 2000).

- 1) *Pump and solvent reservoir:* a key feature of HPLC is the presence of several solvent reservoirs as manipulating the mobile phases polarity can prove vital in improving chromatographic separation (Harvey, 2000). HPLC pumps must be able to withstand high pressure and have pulse-free output (Skoog et al., 2004). The most common type of pump is the reciprocating pump (Skoog et al., 2004). Usually before solvents are pumped, they are treated to remove dissolved gasses such as N₂ and O₂ by either a vacuum pump or by sparging with an inert gas (Harvey, 2000). In order to obtain satisfactory flow rates, however, the liquid mobile phase must be pressurised to several hundred or more pounds per square inch (PSI) (Skoog et al., 2004).
- 2) *Column and column oven:* the stationary phase of the column can be either normal phase (NP) or reserve phase (RP). Reverse-phase chromatography is becoming more

popular. In this type, a non-polar stationary phase is used (C₂, C₈ and C₁₈) with a polar mobile phase which are usually buffers (Ali and Jain, 2004). Separations can be either gradient or isocratic. In an isocratic elution the mobile phase composition is fixed during a run while in a gradient elution, the mobile phase composition can be varied during the HPLC run (Dean, 2014). Typically, in an analytical HPLC system a guard column is usually placed ahead of the analytical column to increase the life of the analytical column by removing particulate matter and contaminants from the solvents (Skoog et al., 2004). They should have a similar packing material to the analytical column used. These are usually connected via inert tubing, i.e. polyether ether ketone (PEEK). The column oven is used to maintain the temperature during an analytical run to a few tenths of a degree for temperature sensitive determinations.

- 3) *Injection valve*: typically, a Rheodyne[®] injector valve (6-port) is used to inject a discrete fixed amount of sample into the flowing mobile phase via a sample loop (Dean, 2014). Many modern HPLC instruments incorporate the use of an autosampler with an automatic injector (Skoog et al., 2004).
- 4) *Detector*: there are many detectors available for HPLC depending on the application which include spectroscopic (UV/Vis, fluorescence), electrochemical (amperometry, voltammetry and conductivity) and mass spectrometers (Harvey, 2000). The hyphenated of HPLC and ICP-MS produces a powerful separation and detection system. Indeed, HPLC-ICP-MS is now the most common method for arsenic speciation analysis (Bose et al., 2011; Gong et al., 2002; Michalke, 2009; Sharma and Sohn, 2009).

2.4.3) Analytical sensitivity

In an analytical determination detection limits (DLs), or limit of detection (LOD) are used to express the smallest concentration that can be reported at a certain level of confidence (Skoog et al., 2004). Where a method uses a calibration series, the detection limit is defined as the analyte concentration that yields a response of a confidence factor k higher than the standard deviation of the blank, s_b , as illustrated in Equation 2.1 (Skoog et al., 2004).

$$DL = \frac{k s_b}{m} \quad (\text{Equation 2.1})$$

where m is the calibration sensitivity. Generally, IUPAC has recommended a value of 3 for k , but recent a value of 2 is used in spectroscopy (Thomsen, 2003). Equation 2.1 can also be used to illustrate the DL (x_L) below from IUPAC in Equation 2.2.

$$X_L = x_{bi} + ks_{bi} \quad (\text{Equation 2.2})$$

where x_{bi} is the mean of the blank measures and s_{bi} is the standard deviation of the blank measures. However, the precision of a measurement at a DL is often in many cases quite poor when compared to the precision at higher concentrations and for this reason another limit, the limit of quantification (LOQ), is defined, which is higher than the LOD and yields better precision (Robinson et al., 2005). For the LOD, it can be said whether an analyte is present or not, however the LOQ is used to describe the beginning of the quantification of an analyte, i.e. 10 times the standard deviation of a blank (Thomsen et al., 2003). As a result, the LOD and LOQ are defined in Equations 2.3 and 2.4.

$$LOD = \bar{x}_{blank} \pm 3\sigma_{blank} \quad (\text{Equation 2.3})$$

$$LOQ = \bar{x}_{blank} \pm 10\sigma_{blank} \quad (\text{Equation 2.4})$$

where \bar{x}_{blank} is the mean of the blank (8-10 replicates) and σ_{blank} is the standard deviation of the blank (8-10 replicates). Usually 2σ (results in LOD with 95% confidence level) is used, but more recently the use of 3σ (results in LOD/LOQ with a 99% confidence level) is being used more. However, any results that are in-between the values of LOD and LOQ for an analyte are only detected, but not quantifiable and remain as estimates (Robinson et al., 2005).

2.5) Quality assurance

Quality assurance (QA) is concerned about obtaining correct results that are representative of the original sample (Dean, 2014). This is a challenging practice in environmental analyses as there is a combination of multiple steps: sampling, treatment and storage, sample preparation and analytical determination (Dean, 2014). High standards of quality assurance can be put in

place (in the form of test samples) to make sure quality is high. Below is a list of QA schemes that were adopted in this study.

2.5.1) Certified reference materials

According to IUPAC a certified reference material (CRM) or standard reference material (SRM) is a substance or mix of substances, the composition of which is known within specified limits, with one or more properties (e.g. concentration of arsenic in groundwater) is sufficiently well established to be used for the calibration of instruments, assessment of measuring method or assigning values to materials (Calvert, 1990). The CRM must have a traceable certificate and be issued by a certifying body (Dean, 2014). Concentrations of constituents within the CRM can be either certified or indicative values. Certified values mean that the concentrations stated on the certificate are reliable. In comparison, the indicative value means that the concentrations stated have an additional level of uncertainty attached to them, mainly due to insufficient number of testing laboratories (Dean, 2014). In this present work, the use of CRMs was used to ensure quality control (QC) by accounting for instrumental drift during the analysis. However, due to a lack of appropriate CRMs for arsenic species in water, no CRM could be used for speciation of arsenic by HPLC-ICP-MS. In this present work six CRMs were used, with varying trace element concentrations to ensure QC along the linear dynamic range of the analyses. CRMs from Community Bureau of Reference (BCR[®]) and Institute for Reference Materials and Measurements (IRMM) include BCR-609 (Trace Elements in Groundwater – Low Level; No. 0271) and BCR-610 (Trace Elements in Groundwater – High Level; No. 0373). CRMs from SCP Science (Québec, Canada) include both the *EnviroMAT*[™] ES-L-2 (Groundwater – Low Level; Lot No. SC6074649) and ES-H-2 (Groundwater – High Level; Lot No. SC6074648). Finally, CRMs from National Institute of Standards and Technology (NIST) include 1643e (Trace Elements in Water) and the recently updated 1643f (Trace Elements in Water). Certified (and indicator) values for these six CRMS are presented in Table 2.4 with the uncertainty presented in either as a standard deviation or a range (depending on manufacturer).

Table 2.4. Certified values of CRMS used in this study with uncertainty (BCR-609, BCR-610, 1643e and 1643f) and confidence intervals (ES-L-2 and ES-H-2; 95% confidence level which is equivalent to 2σ) in parentheses. Indicator values are presented in italics without an uncertainty value associated with them due to the lower number of participating testing laboratories.

Analyte	Units	CRM					
		BCR		SCP Science		NIST	
		BCR-609	BCR-610	ES-L-2	ES-H-2	1643e	1643f
Be	$\mu\text{g L}^{-1}$			20 (19 – 20)	197 (190 – 201)	13.98 (0.17)	13.67 (0.12)
B	$\mu\text{g L}^{-1}$			<i>24</i>	1610 (1560 – 1670)	157.9 (3.9)	152.3 (6.6)
Al	$\mu\text{g L}^{-1}$	47.7 (1.6)	159 (4)	38 (34 – 42)	209 (194 – 224)	141.8 (8.6)	133.8 (1.2)
V	$\mu\text{g L}^{-1}$			5 (4 – 5)	798 (780 – 816)	37.86 (0.59)	36.07 (0.28)
Cr	$\mu\text{g L}^{-1}$			8 (8 – 9)	401 (388 – 414)	20.4 (0.24)	18.5 (0.1)
Mn	$\mu\text{g L}^{-1}$			40 (39 – 41)	318 (310 – 327)	38.97 (0.45)	37.14 (0.60)
Fe	$\mu\text{g L}^{-1}$			10 (7 – 14)	1170 (1120 – 1220)	98.1 (1.4)	93.44 (0.78)
Co	$\mu\text{g L}^{-1}$			20 (20 – 21)	119 (114 – 125)	27.06 (0.32)	25.3 (0.17)
Ni	$\mu\text{g L}^{-1}$	<i>9.11</i>	<i>22.6</i>	4 (4 – 4)	789 (754 – 824)	62.41 (0.69)	59.8 (1.4)
Cu	$\mu\text{g L}^{-1}$	2.48 (0.09)	45.7 (1.5)	9 (8 – 11)	781 (761 – 801)	22.76 (0.31)	21.66 (0.71)
Zn	$\mu\text{g L}^{-1}$			10 (8 – 13)	800 (764 – 836)	78.5 (2.2)	74.4 (1.7)
As	$\mu\text{g L}^{-1}$	1.2 (0.12)	10.8 (0.4)	4 (3 – 5)	404 (391 – 417)	60.45 (0.72)	57.42 (0.38)
Se	$\mu\text{g L}^{-1}$			<i>3</i>	30 (28 – 31)	11.97 (0.14)	11.7 (0.081)
Mo	$\mu\text{g L}^{-1}$			4 (3 – 5)	387 (375 – 398)	121.4 (1.3)	115.3 (1.7)
Ag	$\mu\text{g L}^{-1}$					1.062 (0.075)	0.9703 (0.0055)
Cd	$\mu\text{g L}^{-1}$	0.164 (0.012)	2.94 (0.08)	4 (4 – 4)	200 (194 – 205)	6.568 (0.073)	5.89 (0.13)
Sb	$\mu\text{g L}^{-1}$			2 (2 – 3)	40 (38 – 42)	58.3 (0.61)	55.45 (0.4)
Te	$\mu\text{g L}^{-1}$					1.09 (0.11)	0.977 (0.0084)
Ba	$\mu\text{g L}^{-1}$			20 (20 – 21)	3120 (3030 – 3210)	544.2 (5.8)	518.2 (7.3)
Tl	$\mu\text{g L}^{-1}$			27 (26 – 29)	35 (32 – 39)	7.455 (0.096)	6.892 (0.035)
Pb	$\mu\text{g L}^{-1}$	1.63 (0.04)	7.78 (0.13)	<i>1</i>	102 (97 – 107)	19.63 (0.21)	18.488 (0.084)
Bi	$\mu\text{g L}^{-1}$					14.09 (0.15)	12.62 (0.11)
U	$\mu\text{g L}^{-1}$			<i>19</i>	<i>244</i>		
Mg	mg L^{-1}			0.75 (0.069 – 0.81)	6.11 (5.91 – 6.3)	8.037 (0.098)	7.454 (0.06)

2.5.2) Blanks (field and lab)

Blank samples are the main quality control measurement check used for monitoring contamination, whether in the field or in the lab. Blanks are prepared from analyte-free water and are treated in the same way as samples. For this study blanks were taken in the field (at timed intervals) in order to access the potential contamination and associated performance of the sampling device. These were generally taken after a sample had been taken from a monitoring location. Several litres of Milli-Q water were pumped through the groundwater sampling apparatus (via a HDPE carboy) until the conductivity measurement was low and a sample was taken. Blank samples were also prepared in the laboratory as method blanks and as rinse blanks.

2.5.3) Duplicate samples

In order to show the precision and accuracy of the sampling in the field, field duplicate samples were taken. Precision was then expressed as percentage relative standard deviation (RSD), which is expressed as a percentage (Equation 2.5). The lower the RSD then the data are clustered around the mean whereas if the RSD was a large percentage then there is more variation in the data, and likely some sources of contamination is present. It must be noted though, at low concentrations, duplicate samples may show large variation where the sensitivity of the method is insufficient (Appelo and Postma, 2005).

$$RSD = \frac{s}{\bar{x}} \cdot 100 \quad (\text{Equation 2.5})$$

where s is the sample standard deviation and \bar{x} is the sample mean.

2.5.4) Chemical analyses accuracy

There are generally two types of errors associated with a chemical analysis.

- 1) *Precision (or statistical errors)*: these errors reflect the random fluctuations in the analytical procedure (Appelo and Postma, 2005).
- 2) *Accuracy (or systematic errors)*: these errors display systematic deviation due to faulty procedures or interferences during analysis (Appelo and Postma, 2005).

The precision can be checked on duplicate samples (Section 2.5.3). Systematic errors can be eliminated by including CRMs as part of the analytical procedure (Section 2.5.1). The accuracy of the analyses can be assessed for major ions from the electrical balance (EB) or charge balance (CB) since the sum of positive and negative charges in water should be equal (Appelo and Postma, 2005). This is illustrated in Equation 2.6.

$$EB, \% = \frac{(\sum \text{Cations} + \sum \text{Anions})}{(\sum \text{Cations} - \sum \text{Anions})} \times 100 \quad (\text{Eq. 2.6})$$

Where cations and anions are expressed in terms of milliequivalents per litre (mEq L⁻¹). An error of ±5-10% in the CB is often used (Nielson and Nielson, 2006). There are a variety of common causes for an imbalance of the CB which include incomplete chemical analysis, choice of method, errors in the analysis of individual species, and groundwater sampling processes (field measurements and preservation methods) (Thornton and Wilson, 2008).

2.6) Statistical methods

Different statistical methods were adopted in this study to help answer the research questions in relation to the arsenic within groundwater. Some techniques are based on the spatial distribution and association while others are concerned about appropriate handling of data. Some of these methods are outline briefly below.

2.6.1) General statistics

Exploratory data analysis (EDA) is a statistical technique used for the purpose of analysing geochemical data in order to detect trends or structures in the data to provide insight into the geochemical processes being studied (Grunsky, 2010).

2.6.2) Censored data analysis

The use of censored data analysis in environmental science arose from the use of survival analysis from medical statistics. Survival analysis is a branch of statistics that contains a collection of statistical procedures for data analysis, for which the outcome variable of interest is time until an event occurs, i.e. time until onset of disease (Singh and Mukhopadhyay, 2011; Zwiener et al., 2011). A key feature of survival analysis is its ability to handle censoring of data (including left, interval or right-censored data) (Singh and Mukhopadhyay, 2011).

In environmental science, as part of an analytical procedure, some analytical results may be reported as non-detects (NDs) or left-censored data, which indicates that results are below the reportable detection limit (DL) of the analytical technique (sometimes defined as reporting limit in USA). This is usually expressed as $<x \mu\text{g L}^{-1}$, where x is a numerical value (Grunsky, 2010). Data below a DL, i.e. left-censored data has been termed type I censoring to the left (Haas and Scheff, 1990). Problems exist on the interpretation of datasets which contain data of this type.

Two of the most simplistic methods to deal with non-detects is to firstly ignore them, or secondly set them to a value of 0 with both methods resulting in a bias in estimating the mean concentration (Hornung and Reed, 1990; Lubin et al., 2004). Although not recommended, it is still common practice to discard censored data prior to statistical analysis (Haslauer et al., 2017). By ignoring (or omitting) non-detect values from calculations, the estimate of the mean can be biased too high while setting non-detects equal to 0, the estimated mean is too low in addition to underestimating the variation (Hoffman and Johnson, 2014). Another method (as suggested by Nehls and Akland, 1973) is to insert a constant equal to one-half of the minimum detectable limit for each method and analysis technique. However, this is

an ad hoc approach and is generally very simple to use and is the most commonly encountered technique (Hornung and Reed, 1990; Orten et al., 2009). However, a basic assumption of this method is that data below the LOD follow a uniform distribution, i.e. every value between 0 and LOD has an equal probability of occurring (Hornung and Reed, 1990). This range has a mean value of one half of the maximum value, i.e. LOD/2 (Cohen and Ryan, 1989). In some cases, data below LOD can be removed from dataset, i.e. (Lahvis et al., 2013). This substitution method of $\frac{1}{2}$ DL has been historically advocated as method of choice by the USEPA as an approach to handle non-detect data for environmental measurements (Gibbons et al., 2009). Within air chemistry, the commonly substituted value for a DL is $\frac{1}{\sqrt{2}}$ or 0.7 times the DL (Helsel, 2012). This method has been previously used for arsenic, molybdenum, nitrate and uranium in groundwater (Sanders et al., 2012; Gong et al., 2014; Nolan and Weber, 2015; Harkness et al., 2017).

Another method to deal with censored values is with imputation, i.e. finding suitable replacement values. For this method, if the nature of the distribution can be assumed to be normal, than the replacement value of the censored data below the LOD and parameters of the distribution (i.e. mean, variance) can be estimated based on the portion of the distribution that is above the DL or non-censored data (Grunsky, 2010).

However, according to the Groundwater Directive (Annex IV), data that are below the quantification limit (except for pesticides) should be arbitrarily set at a value of $\frac{1}{2}$ in order to avoid bias in trend identification (EC, 2006). The USEPA recommends using this $\frac{1}{2}$ DL, DL or small number only when 15% of samples are below the DL (USEPA, 2000). However, in comparison, the United States Geological Survey (USGS) recommends that these substitution methods are not used (Helsel and Hirsch, 2002). As can be seen, there is ambiguity in the literature on how best to deal with these data for the generation of meaningful results and to reconcile these differences in statistical methodologies.

However, as suggested by Helsel (2012), there are generally three common alternative approaches that can be adopted as an alternative to substitution methods for censored data.

- 1) *Nonparametric methods after censoring at the highest reporting limit*: these nonparametric methods deal with ranks (or percentiles) of the data and distribution-free methods (i.e. data are not assumed to follow a particular distribution). Examples of nonparametric methods includes binary approaches (data classified into one of two classes, above or below the reporting limit) and ordinal methods (first censoring at the

highest reporting limit) which includes both the Mann-Whitney and Kruskal-Wallis tests (Helsel, 2012).

- 2) *Maximum likelihood estimation*: maximum likelihood estimation (MLE) is a parametric method that is used to estimate summary statistics with censored data. Maximum likelihood estimation needs three important pieces of information for computation: i) numerical values above reporting limit, ii) proportion of data below each reporting limit, and, iii) mathematical formula for an assumed distribution (Helsel, 2012). For MLE, a likelihood equation is solved to estimate the values for mean and standard deviation that are most likely to have produced both non-detect and detected data (Helsel, 2005). Maximum likelihood estimation remains the method of choice when the censoring rate is low and there are at least 50 observations.
- 3) *Nonparametric survival analysis procedures*: these methods generally do not compute summary statistics, but rather use the relative ranks of data (a reflection of the data's percentile) (Helsel, 2012). These methods are very popular as they use all the available information. Censored values are known to be lower than values above the reporting limit and thus are ranked lower (Helsel, 2012). Examples include score tests and Kaplan-Meier method. An advantage of the Kaplan-Meier method is its ability to handle multiple detection limits in addition to not specifying an assumed distribution (Helsel, 2005). The usefulness of nonparametric procedures for censored environmental data has been previously demonstrated (Helsel and Hirsch, 2002).

In this present work, the procedures of Lee (2013) based upon the work of Helsel (2012), from the R package NADA (Nondetects and Data Analysis for environmental data) were used to handle censored statistics. Specific examples of functions that were used are detailed in the following section.

- *Statistical testing* – In order to test the statistical relationship between censored geochemical data with explanatory variables, the empirical cumulative distribution function (ECDF) using the Kaplan-Meier method was used (namely the *cenfit* function). Score tests (*cenDiff*) were used to compare the distribution functions as these can be used to incorporate all information arising from multiple DLs (Helsel, 2012). The Peto-Prentice version of the generalized Wilcoxon test is computed using the *cenDiff* command (Helsel, 2012). If the null hypothesis is rejected, pairwise comparisons using a Bonferroni correction were performed to see where differences in ECDFs occurred. The Bonferroni correction will adjust the p-value due to the increased risk of a type I error associated with multiple statistical tests (Armstrong, 2014).

- *Correlation* – Often in statistical analysis, correlation is a tool that is routinely used for environmental data to assist within linking potential relationships with similar parameters. For example, a strong correlation between arsenic and pH in groundwater may offer more information on the geochemical processes linking these two parameters. In this study, 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 *cenken* function (Helsel and Hirsch, 2002; Helsel, 2012). This method can account for one censored value (singly censored) or both values in the observation pair are censored (doubly censored) (Helsel, 2012). A major advantage of Kendall’s tau is that it can successfully account for multiple DLs in a dataset. 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). In some instances, a non-parametric regression line associated with Kendall’s tau, the Akrita-Theil-Sen (ATS) line, was used to compute a linear regression for censored data to compare both total and dissolved arsenic (Chapter 6).
- *Summary statistics* – Due to presence of censored data in Chapter 6, censored data analysis was used to compute summary statistics such as mean, standard deviation, minimum, maximum, median, quartile 1 (Q1) and quartile 3 (Q3). Several methods can be used to calculate these summary statistics including maximum likelihood estimation, Kaplan-Meier, and regression on order statistics (Helsel, 2012). The Kaplan-Meier technique is a distribution-free procedure with a long history in medical statistics, and works well for multiple DLs in a dataset, however, when used on a dataset with a single DL, it can introduce a positive bias (Helsel, 2009). In comparison, a condition for regression on order statistics is for data to follow a lognormal distribution, which can be tested using a probability plot correlation coefficient (PPCC) (Helsel, 2012). An advantage of this technique is that it can work for a single DL in a dataset, which is the main reason why it was chosen. However, to avoid transformation bias, the summary statistics are computed by imputing numbers for the censored observations based on a parametric model, i.e. “robust” regression on order statistics (Helsel, 2012).
- *Multivariate methods* – By harnessing the power of multivariate procedures, groundwater datasets containing multiple types of parameters (such as chemical, biological, and physical) can be reduced into a smaller dimension. However, for

multivariate methods to be used, censored data needs to be successfully accounted for, which is dependent on the research question and type of non-detects. Broadly, three different types of procedures can be carried out prior to using multivariate methods: binomial methods (presence/absence), ordinal methods (ranks of data), and Wilcoxon-type methods (u-scores) (Helsel, 2012). Using the binary method, data is recensored into two resulting groups, below versus greater than or equal to the highest DL (Helsel, 2012). While this method can account for censored data, a lot of information is lost in the process. Both ordinal and Wilcoxon-type methods aim to rank the data, with the latter being a simple, but powerful procedure prior to MSA of censored data. Ordinal based methods can be used for data with one DL present (i.e. Chapter 6), while data with multiple DLs present (i.e. Chapter 5) need to be ranked using Wilcoxon-type methods.

2.6.3) GIS and spatial prediction methods

The use of geographic information systems (GIS) in combination with spatial geostatistical methods has increasingly been used to evaluate the presence of trace elements within the groundwater system. This has become abundantly evident for arsenic in groundwater due to the associated health risks which this can be seen at regional (Goovaerts et al., 2005; Ayotte et al., 2006 and 2016; Kim et al., 2011; Yang et al., 2012; Zhang et al., 2012 and 2013; Gong et al., 2014), national (Focazio et al., 2000; Winkel et al., 2008b; Rodríguez-Lado et al., 2013; Dokou et al., 2015; Andy et al., 2017; Ayotte et al., 2017), and international (Ravenscroft, 2007; Amini et al., 2008a) scales. Interpolation methods have also been utilised to predict the spatial distribution of arsenic in unsampled locations (Gong et al., 2014). However, the temporal variability of arsenic in groundwater is often reported as affecting a small number of wells, but it may be a larger issue which has been masked in datasets with large numbers of non-detects (Ayotte et al., 2015).

Chapter 3

Arsenic contamination of drinking water in Ireland: a spatial analysis of occurrence and potential risk

The work outlined in this chapter was published in:

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Abstract

The presence of arsenic in groundwater has become a global concern due to the health risks from drinking water with elevated concentrations. The Water Framework Directive (WFD) of the European Union (EU) calls for drinking water risk assessment for member states. The present study amalgamates readily available national and sub-national-scale datasets on arsenic in groundwater in the Republic of Ireland. However, due to the presence of high levels of left censoring (i.e. arsenic values below an analytical detection limit) and changes in detection limits over time, the application of conventional statistical methods would inhibit the generation of meaningful results. In order to handle these issues several arsenic databases were integrated, and the data modelled using statistical methods appropriate for non-detect data. In addition, geostatistical methods were used to assess principal risk components of elevated arsenic related to lithology, aquifer type and groundwater vulnerability. Geographic statistical methods were used to overcome some of the geographical limitations of the Irish Environmental Protection Agency (EPA) sample database. Nearest-neighbour inverse distance weighting (IDW) and local indicator of spatial association (LISA) methods were used to estimate risk in non-sampled areas. Significant differences were also noted between different aquifer lithologies, indicating that Rhyolite, Sandstone and Shale (Greywackes), and Impure Limestone potentially presented a greater risk of elevated arsenic in groundwaters. Significant differences also occurred among aquifer types with poorly productive aquifers, locally important fractured bedrock aquifers and regionally important fissured bedrock aquifers presenting the highest potential risk of elevated arsenic. No significant differences were detected among different groundwater vulnerability groups as defined by the Geological Survey of Ireland. This research will assist management and future policy directions of groundwater resources at EU level and guide future research focused on understanding arsenic mobilisation processes to facilitate in guiding future development, testing and treatment requirements of groundwater resources.

Keywords: arsenic, geostatistics groundwater, WFD, Ireland, geology

3.0) Introduction

Arsenic exposure via drinking water and food consumption has to date been reported in 105 countries affecting approximately 226 million people worldwide (Murcott, 2012). The chronic toxicological effects of arsenic are well documented (Kapaj et al., 2006; Naujokas et al., 2013). However, recent studies have provided evidence to suggest that long-term, low-dose arsenic exposure can induce varying chronic health effects (Moon et al., 2012; Bräuner et al., 2014; Stea et al., 2014; Tsuji et al., 2014). Although arsenic is abundant in both the solid and aqueous environment, its presence within groundwater has received much attention as groundwater represents a major drinking water resource (Smedley and Kinniburgh, 2002; Naujokas et al., 2013; Ng et al., 2003). Arsenic concentrations are greater in groundwater compared to surface water, because of the higher solid-to-solution ratio within the groundwater system, longer residence times and also the oxidising conditions present in many surface environments (Aker et al., 2005; Smedley and Kinniburgh, 2005; Brusseau and Tick, 2006). The geology, hydrogeology and geochemistry of the aquifer system remain important controls of arsenic speciation and mobility within the solid-aqueous environment (Garelick et al., 2009).

In Asia (and to some extent in South and North America), areas of high-arsenic groundwater are generally associated with Quaternary unconsolidated sediments, with geochemical and hydrogeological conditions favouring the mobilisation of arsenic (Ravenscroft et al., 2005; The World Bank, 2005; Bemmer and Fendorf, 2010; Ryan et al., 2011; Blake and Peters, 2015). By contrast, arsenic occurrence within European groundwater is complex with no definitive characteristic pattern observed (Ravenscroft et al., 2009). Arsenic contamination of groundwater has been identified in a number of countries, including United Kingdom, Hungary, Croatia, Italy, Spain, Greece, Sweden, Romania and Slovakia (van Halem et al., 2009; Selinus et al., 2010; Katsoyiannis et al., 2014), with the Danube Basin being described as potentially the most affected European region (via a geogenic source) (Ravenscroft et al., 2009). The greater intensity of monitoring within the EU because of the WFD, in addition to a good analytical infrastructure, has given rise to the availability of a greater number of data. In many developing countries, the arsenic standard of $50 \mu\text{g L}^{-1}$ in drinking water is still used and, as a result, many potential instances of arsenic contamination may remain unreported (Kinniburgh and Smedley, 2001; Thakur et al., 2011). This is the case in the Republic of Ireland (hereafter referred to as Ireland), where elevated arsenic concentrations have been recently observed as a result of non-routine monitoring of drinking water supplies as part of local government public health investigations around Ireland. In

comparison, arsenic is routinely measured for public water supplies. However, these data have not been collated or analysed before and remains unreported in the literature.

These water chemistry data for arsenic has been systematically collected over a period of 20 years (1993-2012) by the Environmental Protection Agency (EPA). Methods and detection limits have improved over time. An issue of harnessing extensive and valuable but methodologically inconsistent or incomplete geochemical data on groundwater contaminants occurs in many regions around the world. For example, testing and reporting requirements for public and private wells in the United States vary from state to state, and reconciling these data presents a challenge for assessing risk from arsenic (Erickson and Barnes, 2005a and 2005b). Cambodia offers an example of a smaller country in the developing world with a similar problem. Cambodia had no policy on arsenic in groundwater in place before 2001 (Feldman et al., 2007) and the definitions and guidelines for safe drinking water sources vary from agency to agency, making it difficult to compare the results of different studies (Levisay and Sameth, 2006). These “flawed” datasets are common. This approach is relevant not only for arsenic, but to the study of emerging contaminants, because the method permits the exploration of old data sets for chemical species that were initially of secondary interest but have since been shown to have detrimental health effects (eg. Mn, F and V).

A global compendium of arsenic groundwater contamination suggests that the primary source of arsenic in Ireland may be anthropogenic in origin (e.g. burning coals), although, mineralisation associated with zinc and lead sulphide deposits are also considered potential sources (Murcott, 2012). The World Health Organisation (WHO) and EU have set the maximum concentration of arsenic in drinking waters at $10 \mu\text{g L}^{-1}$ (EC, 2007; WHO, 2011) and in Ireland, a lower arsenic concentration of $7.5 \mu\text{g L}^{-1}$ is set as the groundwater threshold value (GTV), i.e. 75% of the Irish legal limit for arsenic in drinking water at $10 \mu\text{g L}^{-1}$ (Craig and Daly, 2010; EC, 2010). For the purposes of clarity, elevated arsenic refers to concentrations $\geq 7.5 \mu\text{g L}^{-1}$ within this study.

In Ireland 25% of public drinking water is derived from groundwater sources (Daly, 2009) rising to 100% in certain localities (McGarrigle et al., 2010). Within Europe this figure rises to 75% and 51% in the United States (Sampat, 2000; Daly, 2009). There are an estimated 200000 private domestic and farm boreholes in Ireland (Wright, 1999; CSO, 2012). Public and other regulated water supplies are regularly tested to ensure compliance with Drinking Water Regulations (EC, 2014). If they do not, water quality is remediated through treatment or blending where the concentration of a water quality parameter is brought below the regulatory value, or the supplies are suspended or decommissioned. Exempted supplies such as individual

private boreholes, are not tested as a matter of course, and it is the responsibility of the owner or user of the supply to organise testing to ensure potability.

Studies conducted in the USA (Focazio et al., 1999; Welch et al., 2000), Canada (Wang & Mulligan, 2006; McGuigan et al., 2010) and China (He and Charlet, 2013) have assessed the spatial distribution of arsenic in groundwater with the aim of leading to better management practices for drinking water supplies. Other geostatistical studies (Ayotte et al., 2006; Amini et al., 2008a; Winkel et al., 2008a; Kim et al., 2011b; Zhang et al., 2012; Gross and Low, 2013; Rodríguez-Lado et al., 2013; Zhang et al., 2013; Gong et al., 2014; Yang et al., 2014) have predicted arsenic occurrence for improved risk assessment and groundwater management. No similar study exists within any EU member state.

In this contribution a novel combination of spatial and geostatistical methods that relate elevated concentrations of aqueous arsenic in drinking water to lithology and aquifer type as applied to datasets from water abstracted from public groundwater sources in Ireland is presented. This is the first national geostatistical assessment of geogenic arsenic contamination in the European Union. The objectives of this study were to i) develop a combined statistical and geostatistical method for the most appropriate interpretation of a non-detect dataset at a national-scale, ii) explore if statistically significant differences existed between arsenic levels across different geological and hydrogeological classifications in Ireland, and, iii) examine the spatial distribution of arsenic in groundwater around Ireland in order to identify potential arsenic clusters through spatial mapping techniques. The utilisation of a highly left-censored dataset with multiple detection limits can potentially provide a combined framework of statistical and geostatistical evaluation of the spatial distribution of arsenic within groundwater which could be implemented by other states with similar databases.

3.1) Materials and Methods

A national collaboration was established between local government, the Geological Survey of Ireland (GSI), the Environmental Protection Agency (EPA) and the Health Service Executive (HSE) in order to collate arsenic concentrations in existing groundwater samples collected across Ireland. The EPA is responsible for a national monitoring network for public drinking water supplies, while the HSE and local government monitor private drinking water sources in an ad hoc system for public health investigations.

3.1.1) EPA database

As part of the implementation of the Water Framework Directive (WFD) in Ireland, the EPA routinely monitors a network of approximately 287 groundwater wells to assess water quality (Daly, 2009) (Fig. 3.1a). The EPA groundwater data used in this study (1993 – 2012) is from a spatially distributed monitoring network that was established to account for the different groundwater usage patterns and hydrogeological settings (Toner et al., 2005). Generally these monitoring points are contained within productive aquifers, which are regionally or locally important aquifers as sources of groundwater for public and private supply schemes (DELG/EPA/GSI, 1999)). However, to assess water quality in poorly productive aquifers (PPAs), which underlie approximately 70% of Ireland, this network was expanded in 2007 (Fig. 3.1b) to assess water quality in poorly productive aquifers. These PPAs are considered unproductive (i.e. low well yields) and not regarded as important sources of water for public water supplies, although sometimes high-yielding wells can be drilled in fault-zones (Moe et al., 2010). The expansion included 65 multilevel piezometers in seven hydrogeologically different catchments (Daly, 2009; Moe et al., 2010). Groundwater samples were taken from taps (pre-treatment) for pumping boreholes, from the upwelling for spring sources and generally using a low-flow sampling protocol for non-pumped boreholes by EPA personal (Anthony Mannix, personal communication, March 21, 2016). These samples were filtered (0.45 μm) prior to analysis using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). Within the database there are 8270 analyses for arsenic and of these 1005 analyses (~12%) are from the PPA sites. Detection limits for arsenic analyses improved throughout this study with the PPA sites having the most sensitive DLs.

3.1.2) Statistical analysis

The EPA database was used as a tool to monitor the distribution of arsenic at a national level and two datasets were analysed; the first dataset included all locations (8270 measurements) (hereafter referred as EPA-Total) and the second dataset included all sites remaining after the PPA project data were removed (7334 measurements) (hereafter referred as EPA-NPPA). This comprised 287 and 222 unique monitoring locations for the EPA-Total and EPA-NPPA data respectively. The PPA data were analysed separately because these monitoring locations are likely to be representative of small private supplies in poorly fractured, low yield aquifers with localised groundwater flow systems. In contrast, the larger public supplies that draw groundwater from more productive aquifers with more extensive groundwater flow paths. They are not pumped other than for sampling purposes. Spatial mapping of arsenic was presented as

containing five intervals, namely ((0,1], (1,7.5], (7.5,10], (10,100] and (100, 234]) where (1,7.5] means $\geq 1 \mu\text{g L}^{-1}$, but $< 7.5 \mu\text{g L}^{-1}$.

Between 1 and 41 arsenic measurements were determined at each monitoring locations from 1993 to 2012. However, approximately 70% of the data were below a reportable detection limit (DL) for the analytical technique; this DL changed over the study period and approximately 50% of sites had between 80 and 100% of measured values below a DL. Therefore, to reduce the complexity of each database, only the maximum arsenic concentration at each site was included in the analysis, which provides a “worst-case scenario” description of the data. However, to account for possible bias the analysis was repeated using the median arsenic level at each site with very small changes in the results for the EPA-Total database and moderate changes in the results for the EPA-NPPA database.

In order to determine potential controlling factors on arsenic concentrations GSI databases were examined including the ‘National Generalised Bedrock Map (Rock Unit Group)’, ‘Bedrock Aquifer,’ and ‘Groundwater Vulnerability’ maps (www.gsi.ie). The Rock unit groups (RUGs) were reduced from 27 to 11 classifications so that a smaller number of divisions could be achieved to allow an appreciable sample number per class similar to Zhang et al. (2008a). Tables 3.1 and 3.2 show the aquifer and groundwater vulnerability classification descriptions (maps monitoring points over rock type, aquifer and vulnerability classifications are seen in Fig. 3.2a-c). There are five groundwater vulnerability categories defined by the GSI that characterise the risk of contamination of groundwater by polluting activities. The categories are based on: (i) the permeability and thickness of the subsoils that overlie the groundwater; (ii) the type of recharge – whether point or diffuse; and (iii) the thickness of the unsaturated zone through which the contaminant moves. Further information in relation to these databases is given elsewhere (Daly and Warren, 1998; DELG/EPA/GSI, 1999; Misstear and Daly, 2000).

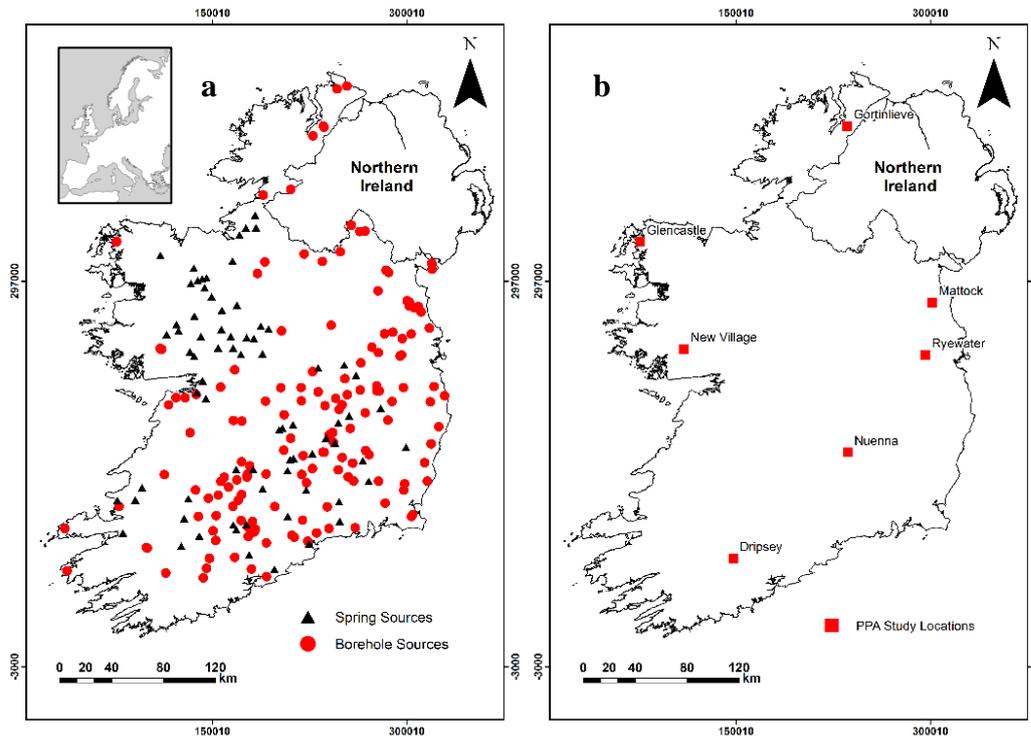


Fig. 3.1. Geographic distribution of the Irish EPA (a) 287 mixed groundwater monitoring locations and (b) seven clustered PPA study sites.

Table 3.1. Data description from ‘Groundwater Aquifers’ dataset (in order of decreasing groundwater resource value)

Group	ID	Description
Karstic aquifers	Rk	Regionally Important Aquifer – Karstified
	Rkd	Regionally Important Aquifer - Karstified (diffuse)
	Rkc	Regionally Important Aquifer - Karstified (conduit)
Productive fractured aquifers	Lk	Locally Important Aquifer – Karstified
	Rf	Regionally Important Aquifer - Fissured bedrock
Poorly productive aquifers	Lm	Locally Important Aquifer - Bedrock which is Generally Moderately Productive
	LI	Locally Important Aquifer - Bedrock which is Moderately Productive only in Local Zones
	Pu	Poor Aquifer – Bedrock Aquifer which are Generally Unproductive
	PI	Poor Aquifer - Bedrock which is Generally Unproductive except for Local Zones

Table 3.2. Data description from ‘Groundwater Vulnerability’ dataset (in order of decreasing groundwater vulnerability)

ID	Description
X	Rock at or near surface or karst
E	Extreme
H	High
M	Moderate
L	Low
W	Water

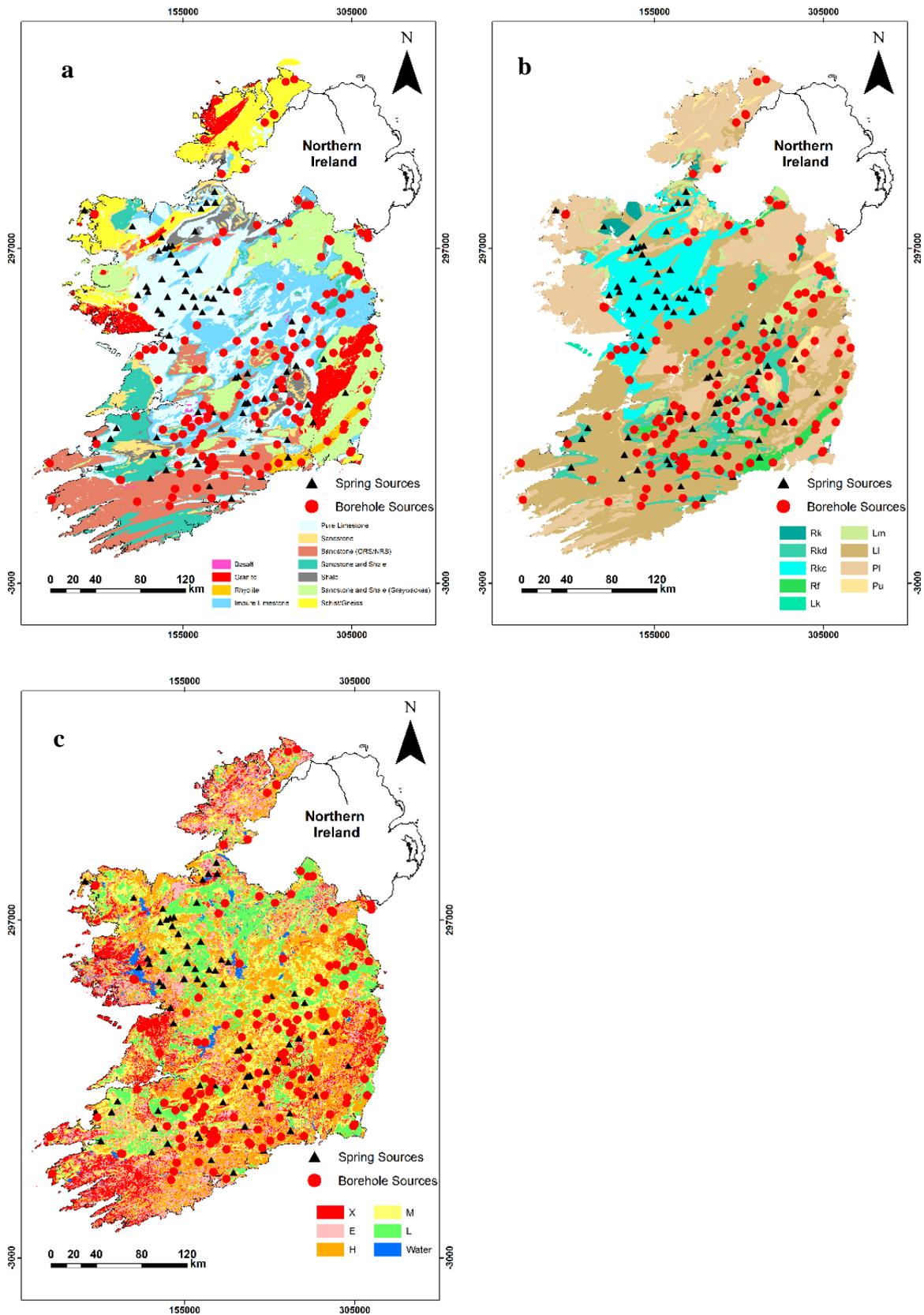


Fig. 3.2. Spatial distribution of the (a) 11 rock types, (b) 9 aquifer types and (c) 6 groundwater vulnerability categories in relation to the Irish EPA groundwater monitoring network with borehole and spring monitoring locations.

3.1.2.1) Rationale for the reclassification of 27 'groundwater rock units' into 11 rock types

For parsimony of analysis and to make the analysis more meaningful, the National Draft Generalised Bedrock Map (NDGBM) was reclassified from 27 ('Groundwater rock units' into a smaller set of 11 rock types (Table 3.3; Fig. 3.2a). NDGBM rock units DPUL, DPBL, DDL, and PM were grouped together into the 'Pure Limestone' rock type. NDGBM rock units DUIL, DMSSL and DLIL rock units were grouped together into the 'Impure Limestone' rock type. The Old Red Sandstone rock unit (ORS) and the New Red Sandstone rock unit (PTS) were grouped together as rock type 'Sandstone (ORS/NRS)' both because of similar content of Fe and Mn mineralogy and because of their similar depositional environment. Mudstones are also found in the 'Sandstone (ORS/NRS)' rock type. The general 'Sandstone' rock type included NDGBM rock units DS, DKS, NSA and WSA. Consideration was given to place DS and DKS in a separate unit because they are more calcareous than NSA and WSA, which contain small amount of reduced iron and small amounts of shale. However, a separate unit was not created for DS and DKS because the number of samples within these units is very small, and because DKS contains a similar small amount of shale as found in NSA and WSA. The quartzites in rock unit PQGS are similar to sandstone but PQGS was assigned to its own rock type 'Schist/Gneiss', because it contains aluminosilicates. Sandstone and shale rock units were separated into two rock types. Rock units CM, OM, and SMV were grouped together as rock types 'Sandstone and Shale (Greywackes)' because of their marine origin. Rock units DESSL, NU, DMSC, and PTMG were grouped together as rock type 'Sandstone and Shale'. This decision was based on the presence of shales even though some of these materials contain sulphate, calcareous material and gypsum. Rock units NSH, DSL, and WSH were grouped together as the 'Shale' rock type, even though DSL has calcareous material present. Rock unit BV was classified as rock type 'Basalt' while II was classified as 'Granite'. Rock unit OV was classified as 'Rhyolite'.

Table 3.3. Grouping of data from ‘National Draft Generalised Bedrock Map (Groundwater rockunits)’ dataset (from 27 original classifications [‘Rockunit’] to 11 new reclassifications [‘Rocktype’])

Original data	Original data	Post-processing reclassification
Description	Rockunit	Rock type
Dinantian Pure Unbedded Limestones	DPUL	Pure Limestone
Dinantian Pure Bedded Limestones	DPBL	Pure Limestone
Dinantian Dolomitised Limestones	DDL	Pure Limestone
Precambrian Marbles	PM	Pure Limestone
Dinantian Upper Impure Limestones	DUIL	Impure Limestone
Dinantian Mixed Sandstones, Shales and Limestones	DMSSL	Impure Limestone
Dinantian Lower Impure Limestones	DLIL	Impure Limestone
Devonian Old Red Sandstones	DORS	Sandstone (ORS/NRS)
Permo-Triassic Sandstones	PTS	Sandstone (ORS/NRS)
Dinantian Sandstones	DS	Sandstone
Devonian Kiltorcan-type Sandstones	DKS	Sandstone
Namurian Sandstones	NSA	Sandstone
Westphalian Sandstones	WSA	Sandstone
Precambrian Quartzites, Gneisses & Schists	PQGS	Schist/Gneiss
Cambrian Metasediments	CM	Sandstone and Shale (Greywackes)
Ordovician Metasediments	OM	Sandstone and Shale (Greywackes)
Silurian Metasediments and Volcanics	SMV	Sandstone and Shale (Greywackes)
Dinantian (early) Sandstones, Shales and Limestones	DESSL	Sandstone and Shale
Namurian Undifferentiated	NU	Sandstone and Shale
Dinantian Mudstones and Sandstones (Cork Group)	DMSC	Sandstone and Shale
Permo-Triassic Mudstones and Gypsum	PTMG	Sandstone and Shale
Namurian Shales	NSH	Shale
Dinantian Shales and Limestones	DSL	Shale
Westphalian Shales	WSH	Shale
Basalts and other Volcanic rocks	BV	Basalt
Granites & other Igneous Intrusive rocks	GII	Granite
Ordovician Volcanics	OV	Rhyolite

3.1.2.2) Handling of non-detect data

In some instances, analytical results may be reported as non-detects (or left censored data), which indicates results are below the reportable detection limit (DL) for the analytical technique. This is usually expressed as $< x \mu\text{g L}^{-1}$ (where x is a numerical value). Typically, a single DL will exist within a database for an analyte. Since these data were measured over a period of 20 years, the sensitivity of the analytical techniques for arsenic improved and thus multiple DLs were present in the dataset. Since the primary aim of this investigation was to explore existing data to discover if there were statistically significant differences between the arsenic levels in groundwater across various geological and hydrogeological classifications, appropriate handling of non-detect data was essential to avoid biased results. The most commonly used methods to utilise non-detect data (e.g. substituting a fraction of the DL for each non-detect, logistic regression, non-parametric tests) suffer from drawbacks such as loss of information, loss of power, and inability to handle multiple detection limits (see Helsel, 2012 for a full discussion). As a result, score tests were used to compare the groups. The distribution function of a group is illustrated by its empirical cumulative distribution function (ECDF) and, according to Helsel (2012), facilitates a more precise depiction of the observations in a data set. In contrast to other approaches, ECDF plots and score tests use all information in the data and can handle multiple DLs.

The EDF was calculated for each category in the rock type, aquifer and groundwater vulnerability groupings. To determine if statistically significant differences exist between the distribution functions of arsenic in the different geological and hydrogeological groupings, a score test was performed using the NADA package (Lee, 2013) in the open source statistical program R (R Development Core Team, 2017). R outputs (i.e. ECDF plots) were processed in Adobe™ Illustrator®. To account for differences between the arsenic distribution functions across different groups pairwise comparisons were performed using a Bonferroni correction (to account for multiple testing) was implemented. A more detailed overview of the rationale for the statistical approach used in this study is present within the discussion.

3.1.2.3 Inverse distance weighting (IDW) interpolation

In recent years geographic information systems (GIS) have increased in use to interpret groundwater databases. Within a GIS, spatial interpolation techniques, such as inverse-distance (ID) methods, can be applied to the data to provide estimates of values at unsampled locations. Inverse distance methods attribute a weight to each sample which is inversely proportional to the distance that is between the sample and the location of the estimate (Srivastava, 2013). The resulting interpolated surface is influenced by adjacent points, and less influenced by points further away (Lu and Wong, 2008). The IDW map was generated in ArcGIS® 10.2 (ESRI®, Colorado) with the following parameters: power, 2; output cell size, 5000; search neighbourhood, standard circular; major semiaxis maximum neighbours, 15; minor semiaxis minimum neighbours, 10; sector type, 1 sector; radius, 10,000 m; coincident points, maximum (rationale for IDW parameters found discussion) The nearest neighbours' method of IDW was used instead of the search radius method with this database because of the number of blind spots present in the dataset, i.e. areas where no values fell into the search radius as described by Gong et al. (2014). Maps are displayed using seven quartile ranges.

The Kerry area in the south west of Ireland has a high density of monitoring locations. For this reason, the Kerry data were used to establish a value to input for the IDW interpolation of the national data from the generation of a semivariogram. One borehole in the north of this region had a borehole with the maximum value of 21020 $\mu\text{g L}^{-1}$ with subsequent measurements below 1000 $\mu\text{g L}^{-1}$. This borehole was removed from the analysis. Of the 471 sites, 133 sites (28.23%) had a maximum value below a DL (these were <1, <0.5, <0.12, <0.3, <1.8, <0.1, <0.4, <0.7, <1.58, <1.64, <1.7, <1.88 and <1.9 $\mu\text{g L}^{-1}$). The proportion of sites within intervals were; (0,1], 314; (1,7.5], 134; (7.5,10], 6 and (10,100], 17. No site had a value above 100 $\mu\text{g L}^{-1}$. The maximum distance between two locations was 107.63 km and the minimum distance

between two locations was 0 km. The semivariance (squared difference between the arsenic values at two sites) and corresponding distance were calculated for all possible pairs of sites and plotted as a variogram cloud. Four of the semivariance values were very large, and further investigation revealed that these related to four sites with the largest maximum arsenic values (maximum arsenic values at four sites: 66.3, 41.7, 29 and 26.9 $\mu\text{g L}^{-1}$). Because outliers can distort the fitted variogram, these sites were removed from the analysis and a new variogram cloud was produced (Fig. 3.3a). Several of the standard variogram models were fitted (spherical, exponential, Gaussian, linear). The spherical model fit well and also provided an estimate of the range (as required for IDW). Several bin sizes were used (from the default of 2.8km, up to 4km) and the impact on the estimate of the range was assessed. The model-fitting process was repeated using Cressie's variogram estimate, which is robust to any remaining outliers. An example of a fitted variogram is given (Fig. 3.3b), all other variograms were similar to this example shown. The estimated range varied from approximately 5.3 km to 9.3 km across the different models fitted. When examining the full EPA dataset however, only 1% of pairwise distances were $\leq 9.2\text{km}$ and 95% of pairwise distances were $\geq 31\text{km}$. Therefore, applying the results of the variogram fitting may prove difficult for IDW in the larger dataset as specifying a search radius of 9-10 km (say) could produce 'duck-egg' patterns where some areas cannot be predicted due to sparsity of the data in those locations. The radius of 10 km was used for the IDW interpolation.

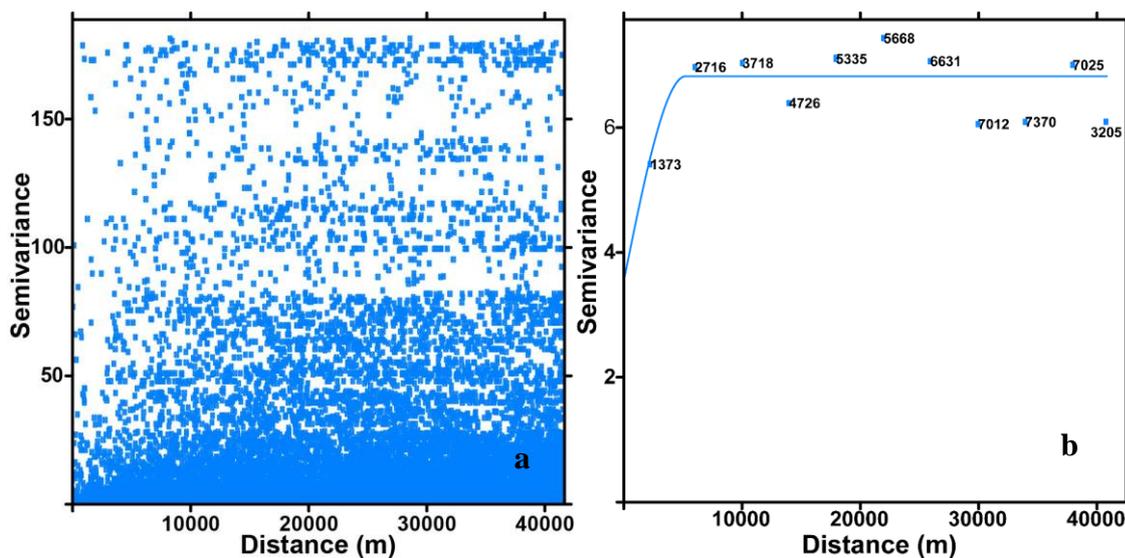


Fig. 3.3. Kerry data: (a) Variogram cloud after the removal of the four most elevated sites, and (b) example of fitted semi-variogram

3.1.2.4) Local indicator of spatial association (LISA)

In addition to IDW, Local Indicator of Spatial Association (LISA) or Local Moran's I statistic, a class of local statistics, was also performed. LISA can be used to address outliers, locate spatial associations and identify local clusters (i.e. high value clusters) (Anselin, 1995; Anselin, 1996). A 1-sample Kolmogorov-Smirnov (K-S) non-parametric test for normality was performed in addition to a normal score transformation using was applied to both datasets. Following this, a Local Moran's I cluster map was created in GeoDa™ 1.4.6 using a threshold distance of 75 km and $p = 0.05$ (Anselin et al., 2006).

3.1.2.5) PPA subsoil monitoring points

Within each of the seven PPA clusters (Fig. 3.1b) there are bedrock, shallow bedrock, transition zone and subsoil boreholes in addition to surface water monitoring points. Subsoil boreholes represent lithologies like glacial till and sediments along stream courses above the transition zone boreholes (Moe et al., 2010). Statistical analyses were performed with and without the subsoil monitoring locations. Subsoil boreholes can be a non-negligible source of arsenic in groundwater because rainwater percolating through subsoils can ultimately reach fractured bedrock and may introduce dissolved arsenic into the groundwater system. The results are therefore presented with these sites included.

3.1.2) HSE and local government

Additional groundwater arsenic data were acquired through the HSE in three regions (Mayo, Leitrim and Sligo for the period 2001 – 2007). For the remaining regions (Donegal, Cork, Galway, Kilkenny, Longford, Louth, Meath, Monaghan, Waterford and Wicklow) data analysed from 2001 – 2011 were provided by local government. An extensive database was collected from one region in southwest Ireland (Kerry) with 1494 arsenic measurements. Regional monitoring locations are illustrated in Fig. 3.4. In any instance where elevated levels were observed, the Environmental Health Service (EHS) would have investigated potential human risk and advised on remediation. It must be noted that drinking water sourced from private wells, i.e. wells abstraction of $< 10 \text{ m}^3 \text{ day}^{-1}$ or serving fewer than 50 people (Brady and Gray, 2010), are not included in the legal framework and thus the responsibility of testing groundwater is with the homeowner.

In general, arsenic concentrations in groundwater samples (generally domestic taps) collected by local government and the HSE were determined using ICP-MS. Although a substantial amount of data were generated from these investigations, only limited statistical

analysis could be performed due to the lower density coverage across Ireland. All maps are presented in Irish National Grid (1965 Datum).

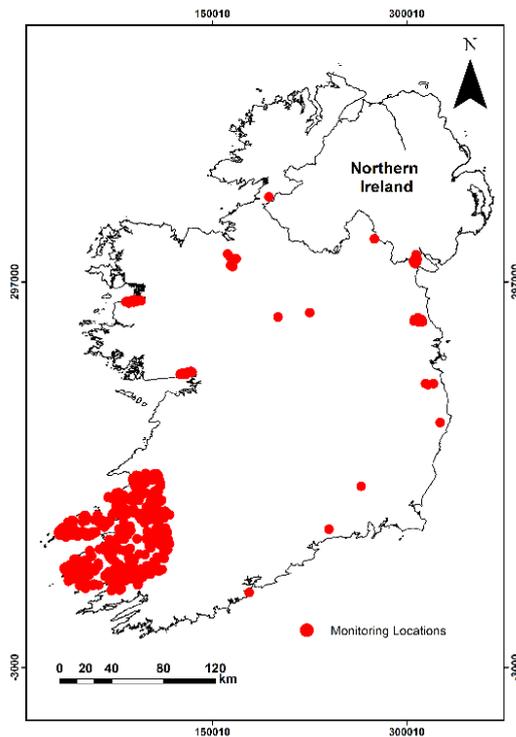


Fig. 3.4. Spatial distribution of the monitoring locations of the HSE and local government.

3.2) Results and Discussion

3.2.1) EPA database

Interval maps for both EPA-Total and EPA-NPPA data are presented in Figs. 3.4a and 3.4b. The proportion of sites in each interval classification is given in Table 3.4, with descriptive statistics presented in Table 3.5. The majority of values fall into the first two intervals of (0,1] and (1,7.5] (Figs. 3.5a and 3.5b, Table 3.4) demonstrating that the vast majority of locations fall under the GTV value of $7.5 \mu\text{g L}^{-1}$. For the EPA-Total and EPA-NPPA databases there are 25 and 9 sites with a maximum arsenic value of $\geq 7.5 \mu\text{g L}^{-1}$, respectively (PPA database contains 17 of these sites). The removal of the PPA database (Fig. 3.5b) reduces the number of locations within the interval (100,234] (i.e. reduction in the number of sites that are considered elevated). Some locations scattered around Ireland (Figs. 3.4a and b) were above the GTV value (Table 3.5) of $7.5 \mu\text{g L}^{-1}$ (25 locations) and the WHO value of $10 \mu\text{g L}^{-1}$ (9 locations) and are considered to represent elevated arsenic groundwater conditions.

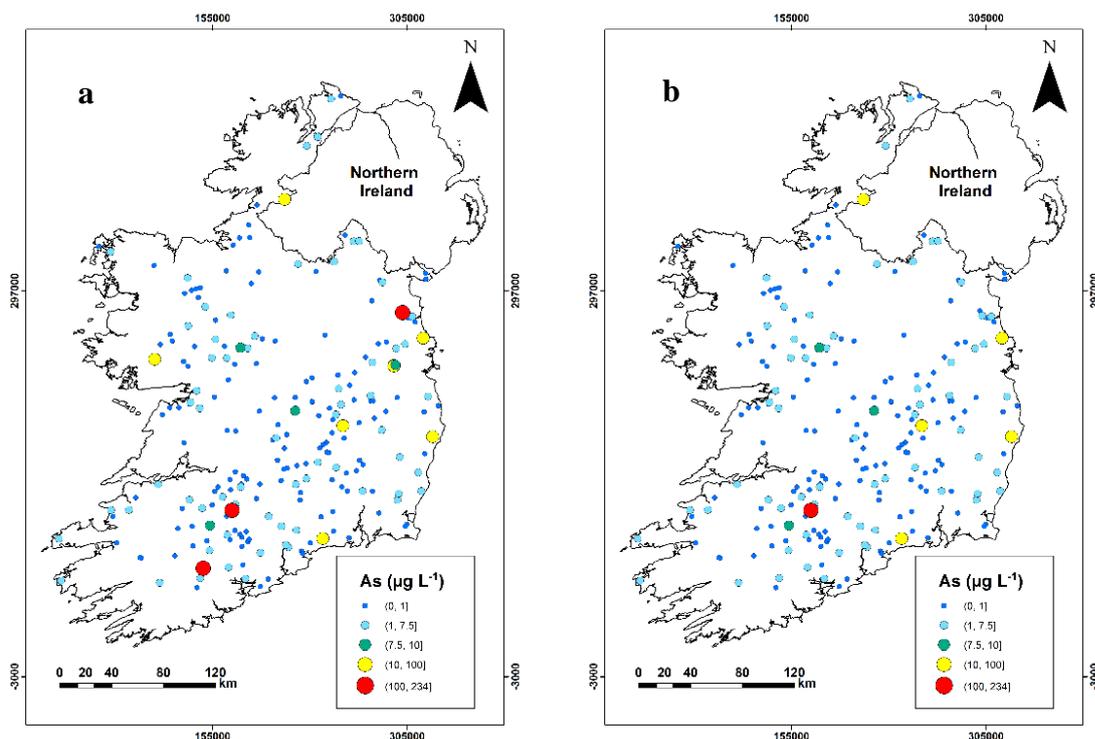


Fig. 3.5. Spatial distribution of the Irish EPA arsenic data with five geochemical classifications of (a) EPA-Total data and (b) EPA-NPPA data. Geochemical classifications are based on the following arsenic concentration ranges ($\mu\text{g L}^{-1}$); (0, 1] (blue), (1, 7.5] (teal), (7.5, 10] (green), (10, 100] (yellow) and (100, 234] (red).

Table 3.4. Interval classification of sites with arsenic values for EPA-Total and EPA-NPPA databases

Interval ($\mu\text{g L}^{-1}$)	Number of sites	
	EPA-Total	EPA-NPPA
(0,1]	169	150
(1,7.5]	93	63
(7.5,10]	4	3
(10,100]	18	5
(100, 234]	3	1

Table 3.5. Summary statistics of EPA-Total and EPA-NPPA databases.

	EPA-Total	EPA-NPPA
Number of monitoring points	287	222
Number of analyses	8270	7334
Number of values below DL	4903 (59.28%)	4575 (62.38%)
Number of sites where max value < DL	158 (55%)	144 (64.86%)
Number of values $\geq 7.5 \mu\text{g L}^{-1}$ (%)*	167 (2.01%)	117 (1.6%)
Number of values $\geq 10 \mu\text{g L}^{-1}$ (**)	143 (1.73%)	103 (1.4%)
Number of sites with $\geq 7.5 \mu\text{g L}^{-1}$ (%)	25 (8.71%)	9 (4.05%)
Number of sites with $\geq 10 \mu\text{g L}^{-1}$ (%)	22 (7.48%)	7 (3.15%)

* Irish GTV value

** WHO/USEPA/EU maximum allowable concentration (MAC)

3.2.1.1) Geological and hydrogeological constraints on aqueous arsenic concentrations

ECDF plots for rock type, aquifer and vulnerability data for both EPA-Total and EPA-NPPA are shown in Figs. 3.6a – 3f. Data were tabulated for each group (rock type, aquifer and vulnerability) and classification (EPA-Total and EPA-NPPA) in Tables 3.6-3.11. These plots are essentially survival curves and can be read by looking for a desired concentration on the x-axis and reading where it intersects on a curve for an exploratory grouping. For example, approximately 80% of all sites are $< 7.5 \mu\text{g L}^{-1}$ for the aquifer classification of L1 (Fig. 3.6c)

3.2.1.1.1) Removal of sites for statistical analysis

Because only two sites were present in EPA-Total/EPA-NPPA in the ‘Basalt’ rock type, it was removed from the analysis. The removal of the PPA dataset from the EPA-NPPA dataset also lowered the number of sites in which granite intersects (from New Village PPA study site – Fig. 3.1a and 3.1b) from 12 to two sites, and for this reason this rock type was removed from the EPA-NPPA analysis. The rock type ‘Shale’ only had four sites for EPA-Total/EPA-NPPA so its power to find statistically significant differences between the rock types has been reduced, however it remains in the analysis. Similarly, the removal of the PPA study sites lowered the number of sites within the rock type ‘Schist/Shale’ from 26 to 5, consequently its statistical power has been reduced. Table 3.6 and 3.7 show that the rock types with the most sites are ‘Pure Limestones’ and ‘Impure Limestone’ with a combined site number of 160 and 145 for EPA-Total and EPA-NPPA (55.7% and 65.3% respectively) which is consistent with the geology of Ireland. Because only one site was present in the aquifer Lk group in the EPA-Total & EPA-NPPA dataset, it was removed (Table 3.8 and 3.9). In addition to this, Pu only had 3 sites within the EPA-NPPA dataset, so it was also removed. Aquifer type Rk only had 4 sites and could have been removed but was included in the analysis. The major type of groundwater aquifer associated with elevated arsenic is the locally important aquifer that is moderately productive in local zone (L1) followed by poor aquifer (P1) and karstified regionally important aquifer (Rkd). Between both extreme and high vulnerability, it accounts for 58.5% and 54.05% & of sites for EPA-Total and EPA-NPPA datasets (Table 3.10 and 3.11). For the vulnerability dataset no groups were removed.

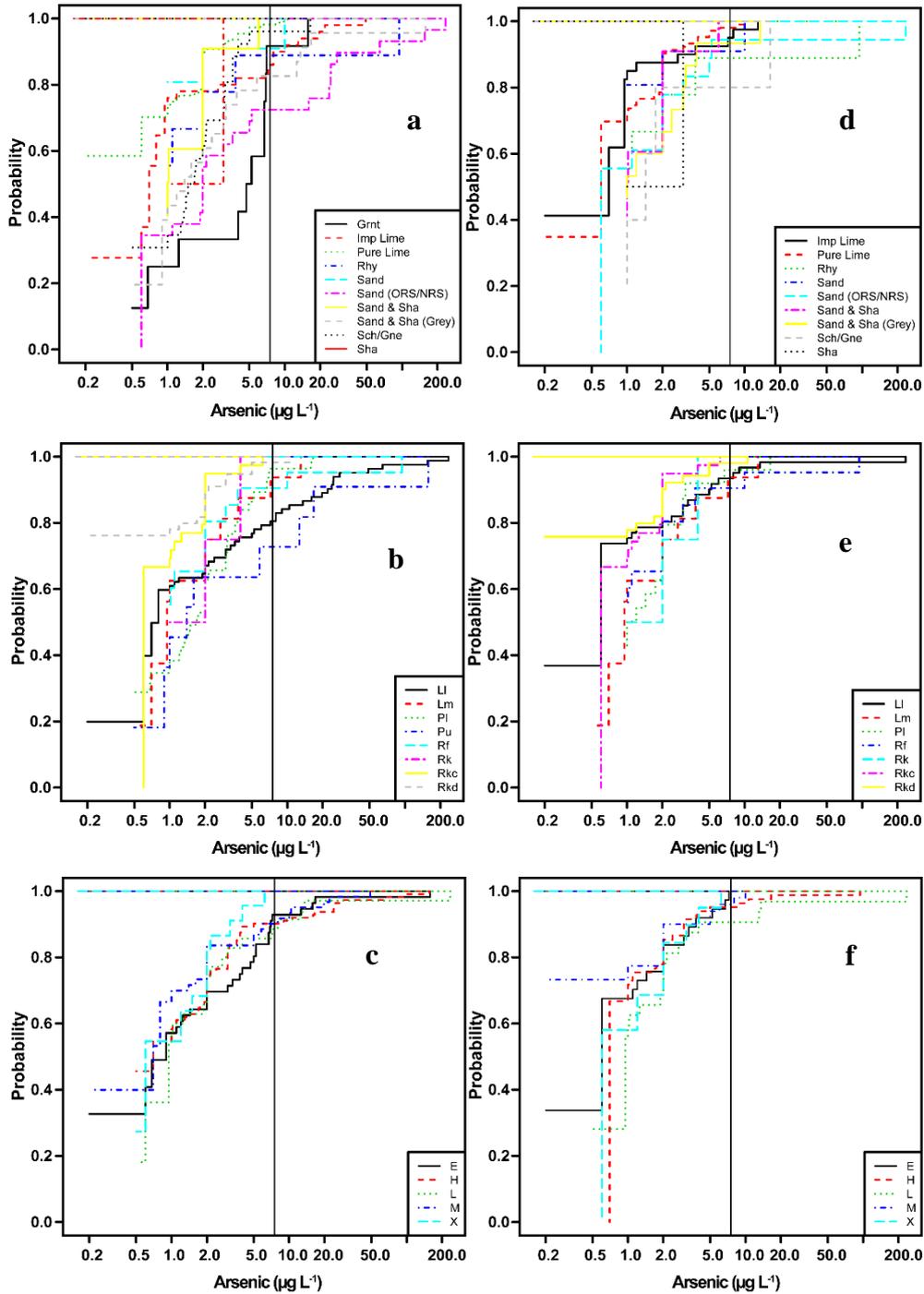


Fig. 3.6. Empirical cumulative distribution function (ECDF) plots of (a) EPA-Total Rock type, (b) EPA-NPPA Rock type, (c) EPA-Total aquifer, (d) EPA-NPPA aquifer, (e) EPA-Total vulnerability, and (f) EPA-NPPA vulnerability. The arsenic GTV value of $7.5 \mu\text{g L}^{-1}$ is represented as a black vertical line.

Table 3.6. Comparison of maximum arsenic values within rock type categories (EPA-Total)

Rock type	Number of sites	Number of values < DL	Percentage of values < DL
Basalt	2	1 (1 site <1)	50
Granite	12	2 (1 site <0.5, 1 site <1)	17
Impure Limestone	50	32 (1 site <0.2, 2 sites <0.5, 29 sites <1)	64
Pure Limestone	110	77 (1 site <0.2, 4 sites <0.5, 69 sites <1, 3 sites <5)	70
Rhyolite	9	5 (5 sites <1)	56
Sandstone	11	9 (8 sites <1, 1 site <5)	82
Sandstone (ORS/NRS)	29	9 (9 sites <1)	31
Sandstone & Shale	11	5 (4 sites <1, 1 site <5)	45
Sandstone & Shale (Greywackes)	23	8 (1 site <0.5, 7 sites <1)	35
Schist/Gneiss	26	8 (4 sites <0.5, 4 sites <1)	31
Shale	4	2 (2 sites <1)	50

Table 3.7. Comparison of maximum arsenic values within rock type categories (EPA-NPPA)

Rock type	Number of sites	Number of values < DL	Percentage of values < DL
Basalt	2	1 (1 site <1)	50
Granite	2	1 (1 site <1)	50
Impure Limestone	40	31 (1 site <0.2, 1 site <0.5, 29 sites <1)	78
Pure Limestone	105	73 (1 site <0.2, 69 sites <1, 3 sites <5)	70
Rhyolite	9	5 (5 sites <1)	56
Sandstone	11	9 (8 sites <1, 1 site <5)	82
Sandstone (ORS/NRS)	18	9 (9 sites <1)	50
Sandstone & Shale	11	5 (4 sites <1, 1 site <5)	45
Sandstone & Shale (Greywackes)	15	7 (7 sites <1)	47
Schist/Gneiss	5	1 (1 site <1)	20
Shale	4	2 (2 sites <1)	50

Table 3.8. Comparison of maximum arsenic values within aquifer categories (EPA-Total)

Aquifer	Number of sites	Number of values < DL	Percentage of values < DL
Lk	1	1 (1 site <1)	100
Ll	82	45 (1 site <0.2, 1 site <0.5, 43 sites <1)	55
Lm	16	7 (1 site <0.5, 6 sites <1)	44
Pl	56	19 (5 sites <0.5, 13 sites <1, 1 site <5)	34
Pu	11	3 (1 site <0.5, 2 sites <1)	27
Rf	21	12 (11 sites <1, 1 site <5)	57
Rk	4	2 (2 sites <1)	50
Rkc	39	25 (25 sites <1)	64
Rkd	57	44 (1 site <0.2, 4 sites <0.5, 36 sites <1, 3 sites <5)	77

Table 3.9. Comparison of maximum arsenic values within aquifer categories (EPA-NPPA)

Aquifer	Number of sites	Number of values < DL	Percentage of values < DL
Lk	1	1 (1 site <1)	100
Ll	61	44 (1 site <0.2, 43 sites <1)	72
Lm	16	7 (1 site <0.5, 6 sites <1)	44
Pl	25	11 (10 sites <1, 1 site <5)	44
Pu	3	2 (2 sites <1)	67
Rf	21	12 (11 sites <1, 1 site <5)	57
Rk	4	2 (2 sites <1)	50
Rkc	39	25 (25 sites <1)	64
Rkd	52	40 (1 site <0.2, 36 sites <1, 3 sites <5)	77

Table 3.10. Comparison of maximum arsenic values as a function of groundwater vulnerability (EPA-Total)

Aquifer	Number of sites	Number of values < DL	Percentage of values < DL
E	56	29 (1 site <0.2, 3 sites <0.5, 25 sites <1)	52
H	112	61 (5 sites <0.5, 54 sites <1, 2 sites <5)	54
L	35	17 (1 site <0.5, 16 sites <1)	49
M	61	39 (1 site <0.2, 2 sites <0.5, 34 sites <1, 2 sites <5)	64
X	23	12 (1 site <0.5, 10 sites <1, 1 site <5)	52

Table 3.11. Comparison of maximum arsenic values as a function of groundwater vulnerability (EPA-NPPA)

Aquifer	Number of sites	Number of values < DL	Percentage of values < DL
E	37	24 (1 site <0.2, 23 sites <1)	65
H	83	55 (53 sites <1, 2 sites <5)	66
L	32	17 (1 site <0.5, 16 sites <1)	53
M	50	37 (1 site <0.2, 34 sites <1, 2 sites <5)	74
X	20	11 (10 sites <1, 1 site <5)	55

3.2.1.1.2) EPA-Total database

The distribution of arsenic concentrations differs across rock types (Fig. 3.6a). Groundwater from Sandstone aquifers in particular exhibited higher arsenic concentrations and between 3 and 10% of sites with Rhyolite, Sandstone and Shale (ORS/NRS), and Impure Limestone also exhibited elevated groundwater arsenic concentrations. Among the sedimentary rocks globally, sandstones usually have the lowest concentrations of arsenic (Garelick et al., 2009). Statistically significant differences in arsenic distribution functions across different rock types existed (p -value < 0.001) and pairwise comparisons identified statistically significant differences between the arsenic distribution functions of Granite and Pure Limestone (p -value < 0.001), Pure Limestone and Sandstone (ORS/NRS) (p -value < 0.001), Pure Limestone and Sandstone and Shale (Greywackes) (p -value < 0.001), and Pure Limestone and Schist/Gneiss (p -value < 0.001) differed significantly. Typically, these trends were mostly apparent when a variant of a sandstone-derived rock type was compared to a limestone-derived rock type. The

arsenic distribution functions differed significantly (p value = 0.002) between aquifer classifications (Fig. 3.6b). All groundwater monitoring locations within the aquifer classifications Rkc and Rk (Table 3.8) exhibited arsenic concentrations below $7.5 \mu\text{g L}^{-1}$, but it is important to note that these monitoring locations are associated with low storage, high transmissivity zones in these systems. Over 95% of sites with aquifer types Rkd, Pl, and Lm had arsenic concentrations below $7.5 \mu\text{g L}^{-1}$, while between 5 and 10% of sites with aquifer types Pu, Ll and Rf had elevated arsenic values. Pairwise comparisons indicated that the arsenic distribution functions of Pl and Rkd (p -value < 0.001), Pl and Rkc (p -value = 0.001), Pu and Rkd (p -value = 0.001) differed significantly. A greater number of regionally important aquifers (e.g. Rk and Rkc) contained arsenic concentrations below the arsenic GTV, and locally important or poor aquifer classifications (e.g. Pl and Lm) were predominantly above this. Arsenic distribution functions (Fig. 3.6c) across the vulnerability categories were not significantly different (p -value = 0.745), although groundwater vulnerability categories H, L and E (Table 3.2) contained a larger proportion of monitoring locations with elevated arsenic concentrations (Table 3.10). This may suggest that some contamination within these locations may be anthropogenic in origin due to surface vulnerability and/or weathering from the subsoil region.

3.2.1.1.3) EPA-NPPA database

Significant differences for arsenic distribution functions across rock types (p -value = 0.034) (Fig. 3.6d). Pairwise comparisons indicated that there was some evidence of a difference between Impure Limestone and Schist/Gneiss (p -value = 0.001). While there was some evidence of a difference between the arsenic distribution functions for aquifer classifications, this was not statistically significant (p -value = 0.07) (Fig. 3.6e). There was no evidence of a significant difference between the arsenic distribution functions across the different vulnerability categories (p -value = 0.49). Minor differences between the different vulnerability categories were identified (Fig. 3.6f) however vulnerabilities in categories H and L represented a slightly larger proportion of sites with elevated arsenic concentrations in comparison to other vulnerability categories. In contrast to the EPA-Total database, this affected the vulnerability categories H, L and E (Table 3.2).

3.2.1.2 Interpolation and hot-spot analysis

Surface interpolation and cluster analysis were performed to determine potential local arsenic hot-spots with IDW and LISA (Fig. 3.7a-d). For both LISA and IDW the maximum value in

each monitoring location was used for analysis. However, in locations where the maximum value was below a DL, a substitution of one-half the DL was used (EPA-Total and EPA-NPPA datasets contained 55% and 64.86% respectively of sites with a maximum value below a DL – Table 3.5). In the EPA-Total database, 158 sites (55%) had a maximum arsenic value below a detection limit, two sites had maximum values $<0.2 \mu\text{g L}^{-1}$, 12 sites had a maximum value $<0.5 \mu\text{g L}^{-1}$, 139 sites had maximum values $<1 \mu\text{g L}^{-1}$ and five sites had maximum values $<5 \mu\text{g L}^{-1}$. Similarly for the EPA-NPPA database, 144 sites (64.86%) had a maximum arsenic value below a detection limit, two sites had maximum values $<0.2 \mu\text{g L}^{-1}$, one site had maximum values $<0.5 \mu\text{g L}^{-1}$, 136 sites had maximum values $<1 \mu\text{g L}^{-1}$ and five sites had maximum values $<5 \mu\text{g L}^{-1}$.

This is the most common method for utilizing left-centered data (Helsel, 2005; Gong et al., 2014). While the use of this substitution methodology may have resulted in limitations in the IDW and LISA analyses, it was employed to give a general overview of the contaminative potential of arsenic within groundwater. Indeed, both IDW and LISA analyses revealed similar trends based on the analyses of these discrete groundwater data, and do not take into account any three or four dimensional data.

3.2.1.2.1) Local indicator of spatial autocorrelation (LISA) hot-spot analysis

Using spatial analysis, environmental contamination can be described as existing in either coldspots or hotspots (Zhang et al., 2008b). When the Moran's I local spatial autocorrelation had a positive value, localities under investigation have similarly high or low values as its neighbours and are thus considered spatial clusters (Anselin, 2005; Zhang et al., 2008b). Spatial clusters can be categorised as high-high (high values in a high value neighbourhood) and low-low (low values in a low value neighborhood) (Zhang et al., 2008b). When a negative local spatial autocorrelation value is present, then the locality under investigation is a spatial outlier and is generally a single locality (Anselin, 2005; Zhang et al., 2008b). Spatial outliers are categorised as high-low (a high value in a low value neighbourhood) and low-high (a low value in a high value neighbourhood) (Zhang et al., 2008b). The presence of various spatial clusters and outliers in the database (not significant, 63.8%; high-high, 5.2%; low-low, 19.1%; low-high, 6.3% and high-low, 5.6%) were identified for EPA-Total data (Fig. 3.6a). In the south, southwest and northeast of Ireland there were a number of high-high clusters some of which correspond to the PPA study sites (Fig. 3.1b). These sites generally exhibited elevated arsenic concentrations above the GTV; however, some of the locations in the southwest do not belong to the PPA database (one site had a maximum arsenic concentration of $234 \mu\text{g L}^{-1}$).

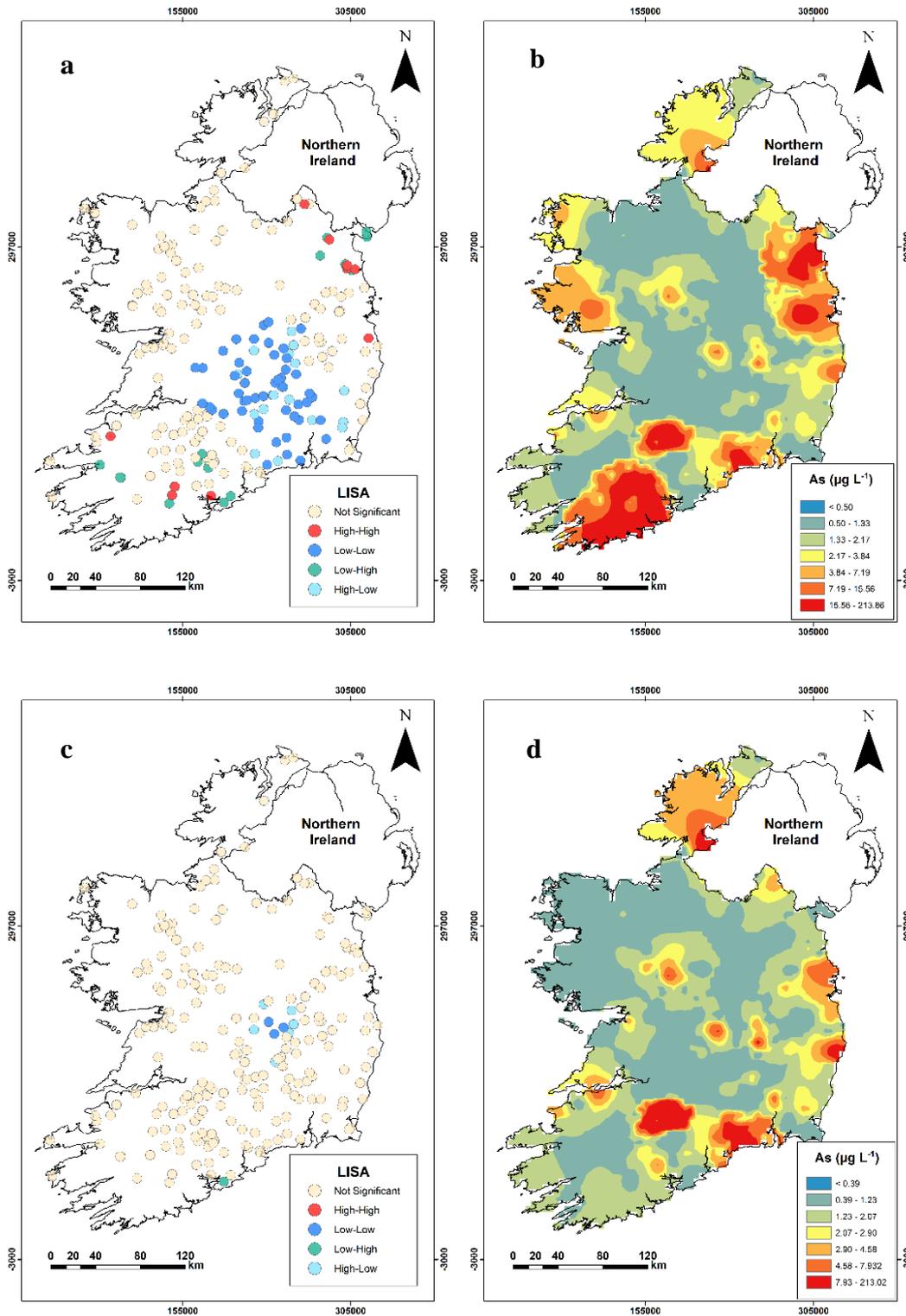


Fig. 3.7. Geostatistical analysis of arsenic data using (a) LISA hot-spot analysis (EPA-Total), (b) IDW interpolation (EPA-Total), (c) LISA hot-spot analysis (EPA-NPPA), and (d) IDW interpolation (EPA-NPPA). The range used for the LISA maps are not significant (pale cream), high (red), low-low (blue), low-high (green) and high-low (light blue).

The presence of a dense number of low-low spatial clusters from the midlands to the south of Ireland was identified. High-low outliers within these cool spots (southeast of Ireland) can be

described as isolated, individual hotspots. A spatial outlier group of low-high is evident in the south west of the country, while the west and northwest region had a greater density of not-significant groups (Fig. 3.7c), which corresponds to a lower density of the EPA monitoring grid which may have contributed to potential hotspots not being identified. This trend is similarly evident after the removal of the PPA data (Fig. 3.6c; not significant, 93.7%; high-high, 0%; low-low, 2.7%; low-high, 0.45% and high-low, 3.2%). However, there was a removal of high-high clusters and a small percentage of low-low clusters within the northeast representing PPA monitoring locations. A small number of low-high and high-low spatial outliers occurred in the northeast and midlands, respectively. Furthermore, some low-low and high-low groups still remained following the removal of the PPA database (Fig. 3.6c). An important component revealed by the LISA analysis indicated that the majority of the monitoring points are not-significant groups; however, there are possible localised hot-spots (high-high) and indeed isolated cool spots (high-low) around Ireland. This interpretation is reflected within the IDW analysis where contaminative potential was highest near PPA study sites.

3.2.1.2.2) Inverse distance weighting (IDW) interpolation

IDW maps indicate a greater level of potential contamination in the north east and south west of Ireland (Figs. 3.7b). This becomes less apparent with the removal of the PPA database (Fig. 3.7d) which is especially evident in the west of Ireland. By contrast, the removal of the PPA database increased the apparent intensity of arsenic contamination in the northwest. The removal of the PPA database did not affect the interpolated contamination concentrations within the midlands, as no PPA study sites are located here (Fig. 3.1b). Generally, when compared with the entire country, the midlands display low levels of potential contamination.

A recent report of the PPA study sites noted that arsenic values were persistently elevated within the New Village, Mattock and Ryewater study sites, but arsenic was grossly elevated at Dripsey (Fig. 3.1b) (Moe et al., 2010). These poorly productive aquifer boreholes are not pumped as regularly as they are not monitoring boreholes. The majority of these elevated values were recorded in either deep or transition zone boreholes, which could suggest that arsenic mobilization may be occurring in deeper groundwater. To examine the role of depth the method of co-kriging (that incorporates well depth and/or elevation as co-variates) could have been adopted (Gong et al., 2014), but because the current database contains multiple DLs this analysis could not be performed.

Both LISA analyses and IDW interpolation indicate that groundwater in the west of Ireland contains lower levels of arsenic contamination, and that the majority of potentially contaminated locations in the west are springs (Fig. 3.1a). The south and east of Ireland showed higher overall levels of arsenic contamination, and the majority of these locations are boreholes (Figs. 3.7a-d). This interpretation and assessment of the contaminative potential based on IDW and LISA analyses of arsenic contamination agree with European-wide and national soil assessments (Salminen et al., 2005; Fay et al., 2007) that identified higher concentrations of arsenic in the east and south of Ireland with lower concentrations in the west.

3.2.1.3) Statistical differences in the removal and retention of subsoil monitoring locations

Within the PPA project, each study site has bedrock, shallow bedrock, transition zone, and subsoil boreholes, in addition to surface water monitoring points. Surface water monitoring points were removed from analysis. Parallel statistical analyses were done both in including and excluding the subsoil monitoring locations. These represent lithologies like glacial till and sediments along stream courses above the transition zone boreholes (Moe et al., 2010). After comparing the results, the subsoil monitoring boreholes were included in the reported analyses. Differences were slight: for the EPA-Total rock type, analyses with the subsoils included showed stronger evidence of a difference between the Pure Limestone and Sandstone and Shale (Greywackes) rock types and between the Pure Limestone and Schist/Gneiss rock types.

Only a slight change in p-values for difference between the distribution functions of LI vs Rkd and PI vs RKC was evident for the EPA-Total aquifer results. Results of analysis including the subsoil monitoring boreholes show a significant difference between the arsenic distribution functions of Pu and Rkd (possibly due to the additional sites with Pu aquifer type and reduction in percentage values below detection limit as these sites had measured arsenic levels rather than arsenic value < DL). No differences were observed with the subsoil locations removed from the groundwater vulnerability analysis of the EPA-Total dataset.

For the interval data, with the subsoil monitoring boreholes included there were 169 sites within the interval (0,1], 93 for (1,7.5], four for (7.5,10], 18 for (10,100] and three for (100,234] (287 sites in total). In comparison, with subsoil locations removed there was 167 sites within the interval (0,1], 87 for (1,7.5], four for (7.5,10], 16 for (10,100] and three for (100,234] (277 sites in total). For the LISA figures including the subsoil data there were 183 sites within the not-significant classification, 15 in the high-high classification, 55 in the low-low classification, 18 in the low-high classification and 16 in the high-low classification. With the subsoil monitoring boreholes removed from the analysis this changed to 191 sites within

the not-significant classification, 9 in the high-high classification, 47 in the low-low classification, 16 in the low-high classification and 14 in the high-low classification. This deletion of the subsoil locations showed that the number of isolated spatial outliers was decreased with a broadly similar low or high hot-spot. After the removal of the subsoil monitoring locations from the IDW a potential area of contamination was highlighted within the west of Ireland along the coast at the Glencastle PPA study site (data not shown). It is worth noting that all three subsoil boreholes had low concentrations of arsenic (below arsenic GTV). No other differences were observed as a result of the removal of subsoil data.

3.2.2) Regional studies

In Ireland, a number of smaller regional sampling campaigns have been conducted (e.g. for public health and new boreholes drilled) that represents more clustered regional monitoring localities (i.e. private wells) that are not associated with the WFD monitoring network (Fig. 3.1a). In some instances, these regional sampling campaigns identified groundwater sources with elevated arsenic concentrations that contained no EPA monitoring network locations nearby. However, the presence of sampling artefacts based on analyses notes (i.e., limited filtration of samples and sampling methodologies) and different scales make it difficult to compare regional studies to those within the EPA monitoring network. No statistical analysis was performed (as in the case with the national databases in Section 3.1.1.1) due to the patchy spatial resolution. Regional study boreholes are illustrated in Fig. 3.3 and those with an arsenic concentration $> 7.5 \mu\text{g L}^{-1}$ on at least one monitoring occasion are shown in Fig. 3.8a. Geological data (using the same classification from Section 3.1.1.1) for the regional study localities are presented in Table 3.12. A spatially dense monitoring network in the south west of Ireland (Fig. 3.8b) contained a borehole with the highest recorded concentration of arsenic during the 1993-2012 period (concentrations ranged from <1 -21,020 $\mu\text{g L}^{-1}$). This locality was not included in the interval mapping in Fig. 3.8b (Section 3.2.1). However, similar to the national data, the majority of sites are below the GTV of arsenic with the presence of isolated clusters (Fig. 3.8a and b).

In this region, local government have made water monitoring a priority and have a dedicated ICP-MS laboratory for water-quality screening. By comparison with the rest of Ireland, this region has greater intensity of testing (491 monitoring locations represented by 1494 arsenic analyses), rather than a lot of cases of arsenic contamination, a sampling artefact that has been observed in other parts of Europe by Ravenscroft et al. (2009). Bedrock strata in this region include Namurian-age black shales (Sevastopulo, 2009). Black shales have been

recently been classified as a potential geohazard in relation to arsenic (Paikaray, 2012) due to the presence of pyrite, which may contain 10-77,000 mg kg⁻¹ of arsenic (Smedley and Kinniburgh, 2002; Garelick et al., 2009). The presence of black shales has been demonstrated to give rise to elevated arsenic in groundwater elsewhere (Ryan et al., 2015b). Similar to the national data, the majority of sites are below the GTV of arsenic with the presence of isolated clusters (Fig. 3.8b).

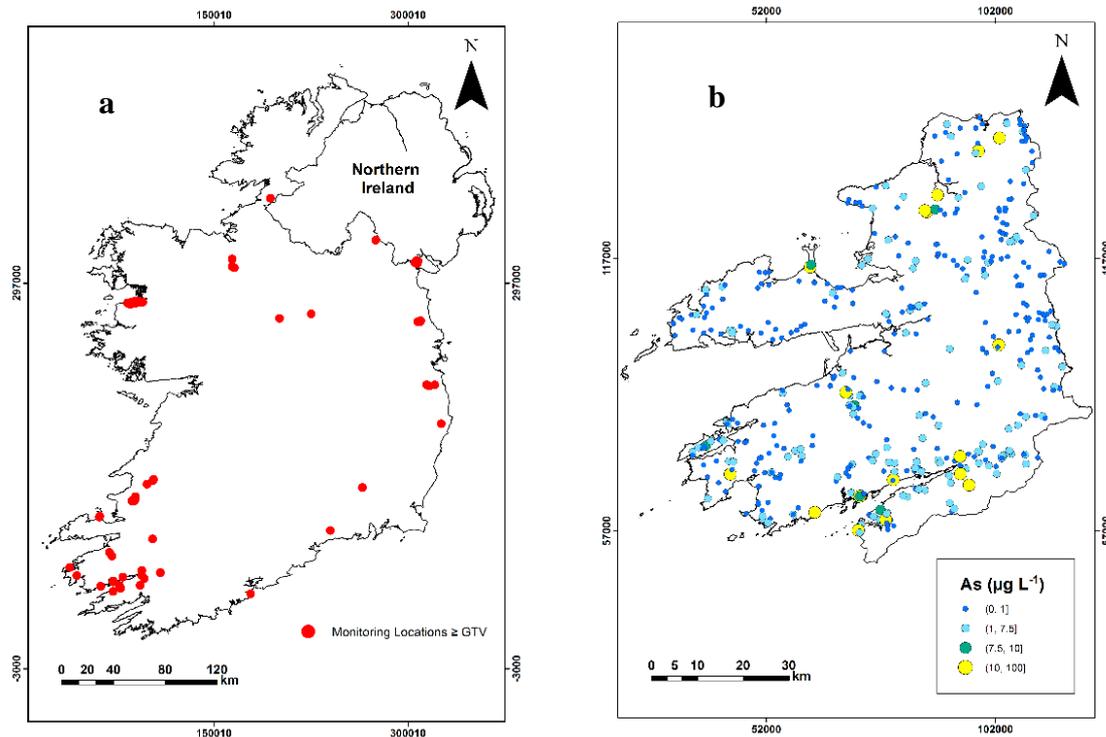


Fig. 3.8. Regional data showing (a) spatial distribution monitoring locations by the HSE and local government locations $\geq 7.5 \mu\text{g L}^{-1}$, and (b) Spatial distribution of the Kerry arsenic data with four geochemical classifications. Geochemical classifications are based on the following arsenic concentration ranges ($\mu\text{g L}^{-1}$); (0, 1] (blue), (1, 7.5] (teal), (7.5, 10] (green), and (10, 100] (yellow).

Table 3.12. Information on regional studies on arsenic in groundwater within Ireland

Monitoring region	Arsenic range ($\mu\text{g L}^{-1}$)	Rock type	Comment
NW	9.5-18.9	Schist/Gneiss	NA
NW	<4-471	Pure limestone/Shale	NA
W	<5-193	Sandstone and Shale (Greywackes)/Pure Limestone	Area of gold mineralisation
SE	0.1-21020	Sandstone and Shale/ Pure Limestone/Impure Limestone/Sandstone (ORS/NRS)/Sandstone/Sandstone and Shale (Greywackes)	Entire county monitored
S	<0.2-30.3	Sandstone and Shale	NA
SE	44-94.3 (source)	Rhyolite	As treatment
SE	<0.5-197	Sandstone and Shale (Greywackes)	NA
SE	13.4-14.5	Pure Limestone/Impure Limestone	NA
E	<0.37-32	Sandstone and Shale (Greywackes)/Rhyolite/Granite	NA
E	<0.37-242	Sandstone and Shale (Greywackes)/Rhyolite/Granite	NA
M	<0.37-29	Pure Limestone	NA
M	21	Impure Limestone	NA

Table 3.12. (continued).

Monitoring region	Arsenic range ($\mu\text{g L}^{-1}$)	Rock type	Comment
NE	9.70-17.76	Sandstone and Shale (Greywackes)	Proximity to Sb source
NE	<0.37-40	Sandstone and Shale (Greywackes)/Impure Limestone/Granite	Groundwater monitored during road construction project
NE	0.37-139	Sandstone and Shale (Greywackes)/Impure Limestone/Granite	NA

*NW, Northwest Ireland ; SW, Southwest Ireland; SE; Southeast Ireland; W, West Ireland; E, East Ireland; S, South Ireland; NE, Northeast Ireland

The EPA database also shows that the north eastern region of Ireland (Co Meath) as an area with elevated arsenic in groundwater (Figs. 3.3 and 3.8a). Both regional and national data also highlight arsenic contamination is present in the north east of Ireland along the border with Northern Ireland (NE Ireland). The area contains a dense cluster of monitored private groundwater sources in Silurian metasedimentary rock (Clontail Formation) (Table 3.12). A recent survey of Dublin soil found that median arsenic values for Silurian metasedimentary rocks were elevated at 24.7 mg kg^{-1} due to arsenopyrite mineralisation and historic mine workings (Glennon et al., 2014). Studies in the US have also identified metasedimentary bedrock aquifers as sources of elevated arsenic in groundwater (Ayotte et al., 2003 and 2006; Ryan et al., 2013 and 2015b; O’Shea et al., 2015). Wilkinson and Hitzman (2015) note that the Lower Carboniferous carbonates of the Irish Midlands host significant accumulations of base metals. These deposits are structurally controlled by deep seated faults that penetrate to the Silurian metasedimentary rocks or to the underlying Precambrian basement (Blake et al., 2016). Arsenopyrite is one of the common sulphides or ore minerals associated with these deposits (Banks et al., 2002).

In contrast, there are examples where the EPA monitoring network does not identify arsenic contamination in regions with known issues such as the Clew Bay region of western Ireland (Fig. 3.3 and Fig. 3.5a). Although no EPA monitoring points are present within this locality, regional data from private sources have recorded arsenic concentrations from $<5\text{-}193 \mu\text{g L}^{-1}$ (Table 3.12 and Fig. 3.8a). In this area gold mineralisation hosted in mesothermal quartz shear-veins occurs in a sequence of Silurian and Ordovician metasedimentary rocks (Aherne et al., 1992). Gilligan et al. (2015) measured arsenic in groundwater sources in this area and associated with the weathering of minerals within the gold-bearing quartz veins. In addition, elevated concentrations of arsenic were noted in streams discharging to Clew Bay in the vicinity of the elevated groundwater arsenic concentrations locations (Morrison and Petrunic, 2012). A similar site in north east Ireland (Clontibret, Monaghan) has arsenic of geogenic nature, which may be released as a result of anthropogenic activities such as mining (Table

3.12). Within this locality there is a borehole south-west of a gold-antimony vein-hosted deposit within Ordovician felsic greywackes where antimony – gold mineralisation occurs (Morris et al., 1986; Steed & Morris, 1986; Geraghty, 1997) that contained elevated levels of arsenic. This borehole was subsequently decommissioned.

3.2.3) Global comparisons of arsenic contamination in groundwater

The groundwater spatial distribution maps for arsenic using intervals ((0, 1], (1, 7.5], (7.5, 10], (10, 100], and (100, 234]; Figs. 3.5a and b) within Ireland were compared and contrasted with similar studies conducted elsewhere. The spatial assessment of arsenic in groundwater across the USA by the United States Geological Survey (USGS) (Focazio et al., 2000; Welch et al., 2000; Ryker, 2001; Gronberg, 2011) showed that 10% of values were $>10 \mu\text{g L}^{-1}$ (the USEPA maximum allowable concentration, MAC). This compares to 1.73% and 1.4% for the EPA-Total and EPA-NPPA data using the $10 \mu\text{g L}^{-1}$ Irish drinking water limit and 2.01% and 1.6% using the Irish GTV value for arsenic of $7.5 \mu\text{g L}^{-1}$ (Table 3.5).

Regional European studies have recorded a range of arsenic concentrations in groundwater that encompasses different hydrological, geological and environmental settings with different geogenic sources (Table 3.13). In a survey of 25 European groundwaters, the range of arsenic concentrations was $<0.02\text{-}79 \mu\text{g L}^{-1}$ (Shand and Edmunds, 2008). However, within the present study it was found that the ranges of arsenic concentrations for the Irish national database were $<0.2\text{-}234 \mu\text{g L}^{-1}$, and higher values were found in regional studies (Table 3.12). A national study focusing on arsenic in groundwater within Europe has been conducted in Greece (Dokou et al., 2015); however geological and hydrogeological data were not incorporated into the statistical analysis of that study.

Table 3.13. Regional European studies

Country	Region	Arsenic range ($\mu\text{g L}^{-1}$)	Reference
Greece	Eastern Thessaly	1-125	Kelepertsis et al., 2006
	Northern Greece	10-70	Katsoyiannis et al., 2007
	Chalkidiki	1-1,840	Kouras et al., 2007
Italy	Northern Italy	$<0.4\text{-}431$	Carraro et al., 2013
Denmark		10-30	Jessen et al., 2005
Northern Ireland		14-36	Doe and McConvey, 2006
Croatia	Eastern Croatia	0.14-611.89	Ćaver et al., 2005
	Eastern Croatia	$<1\text{-}490.8$	Bošnjak et al., 2012
Hungary		7.2-201.3	Sugař et al. 2012
	Pannonian Basin	$<0.5\text{-}240$	Rowland et al., 2011
Norway		19 (no min)	Frengstad et al., 2000
Ireland	Whole country	$<0.2\text{-}234$	This study

3.2.4) Rationale for statistical approach in this study

The primary aim of this investigation was to explore existing data to discover if there are statistically significant differences between the arsenic concentrations in groundwater across various geological and hydrogeological classifications. To compare groups, appropriate handling of non-detect data was essential to avoid biased results. The most commonly used method to utilise non-detect data is to substitute a fraction of the DL for each non-detect and use standard parametric techniques such as t-tests or ANOVA to compare groups. However, this can produce inaccurate and non-reproducible results (Helsel, 1990, 2005, 2006 and 2010). An alternative approach utilised by Ayotte et al. (2006) focused on logistic regression modelling in order to analyse censored data, but this becomes problematic when DLs are present. The simplest approach is to use the binary method, which compares the percentage of uncensored observations (values above a single specified DL, across groups). This is a simple test, but it results in loss of information. An alternative is to use a non-parametric method such as the Kruskal-Wallis test or Mann-Whitney test, which does not require that the data follow a specific distribution such as the normal or log-normal distribution. However, these tests require censoring of all the data below the highest DL and can thus lose power when there are multiple DLs within a database. The maximum likelihood estimation (MLE) method performs standard tests for differences between groups by fitting a censored regression model that appropriately accounts for values below the DLs. This approach is more useful than the non-parametric methods, since multiple DLs can be handled. However, MLE is based on the assumption that the data follow a specified distribution which can prove to be restrictive for a small sample. As a result, score tests were used to compare the groups. They test whether the distribution functions differ among groups of censored data and can handle data censored at multiple DLs. The score tests are based on standard survival analysis methods and are non-parametric. The distribution function of a group is illustrated by its empirical distribution function (EDF), which shows the sample percentiles of each observation in the database. According to Helsel (2012), an ECDF plot facilitates a more precise depiction of the observations in a data set. All information in the data is used, including information about the proportion of values below each DL and information contained in data between DLs.

Spatial interpolation was also undertaken. IDW maps are used to identify areas with potential contamination (Zhang, 2006; Zhang et al., 2008a; Gross and Low, 2013). The heterogeneity of Ireland's geology (O'Brien et al., 2013) limits the scope of IDW interpolation in predicting arsenic values at unmeasured locations, but it is a useful tool for examining trends and variations at a national level. This method has been used with success to estimate

groundwater depth (Adhikary and Dash, 2014) and groundwater quality parameters (Arslan and Turan 2015; Gnanachandrasamy et al., 2015). Further work has demonstrated that IDW outperformed various kriging methodologies (Guassian, kriging, spherical-model kriging, and co-kriging) (Gong et al., 2014). It should be noted that IDW maps do not represent actual arsenic contamination, but illustrate areas with the likelihood of potential contamination, show overall patterns and trends (i.e., contamination potential) (Zhang, 2006 and 2008a; Gross and Low, 2013), and can be useful in guiding more detailed local studies.

3.2.5) Limitations, recommendations and future work

In Ireland, demand for groundwater resources is increasing with certain regions using groundwater for 100% of their drinking water needs. This study has demonstrated that while there is a good spatial distribution in the EPA monitoring network, it was unable to fully delineate areas of potential contamination that have been noted as part of regional studies. Broadly similar conclusions have been reached in the US (Focazio, 2001) in that regional data revealed additional insight in contrast to the available national datasets. In Ireland, upgrading of the EPA network to include more rock types and lower yielding wells (e.g. private sources) could help reconcile the differences between regional and national data in order to generate more insight into elevated arsenic concentrations in groundwater. This may be hard to achieve because of the technical difficulty in sampling poorly productive aquifers and capturing heterogeneity in rock types at a national level (Daly, 2009). Better harmonization of data sharing and the creation of a central digital data repository would help to build the database on arsenic concentration in groundwater over time for identifying impacted areas. This would help to define groundwater management strategies, at the local and national-scales to protect and promote public health.

Recent work has elucidated that long-term, low-dose arsenic exposure can induce varying chronic health effects (Moon et al., 2012; Bräuner et al., 2014; Stea et al., 2014; Tsuji et al., 2014). While no epidemiology data exists within Ireland (or the EU) for arsenic, the current IDW maps show that the east and southwest of Ireland may be potentially affected areas (Fig. 3.7b and 5d), with lower levels of potential arsenic risk in the west. No single map can attempt to fully summarise an entire database at a national level (Ryker, 2001). Similarly, in this study no map could fully illustrate arsenic contamination within groundwater. However, the production of these maps provides an initial framework which can be used as an initial estimate of risk in unmonitored locations and to guide future studies and sampling. Under current regulations in Ireland and elsewhere in the EU, local government is under no legal

obligation to test private wells. This is the norm for most of the world, where public water supplies may be routinely monitored, but private sources are usually untested (Naujokas et al., 2013). Additionally, these maps may be used to guide targeted monitoring, which could be applied to reduce the economic cost of environmental monitoring and assessment for drinking water resources (these costs have been highlighted by Sanders et al. (2012)).

The PPA study sites indicate that borehole depth may play a role in arsenic concentrations, however determining this was beyond the scope of this current study. Future work on the PPA study sites may assist in determining if depth is an important factor in the mobilisation of arsenic in poorly productive aquifers.

3.3) Conclusions

For the majority of sampled locations in this study, the concentration of arsenic in groundwater is below both the Irish GTV value of $7.5 \mu\text{g L}^{-1}$ and the WHO and USEPA value of $10 \mu\text{g L}^{-1}$, while a small number of locations exhibit elevated arsenic concentrations. Regional studies have shown that in several areas elevated arsenic concentrations in groundwater are associated with Silurian and Ordovician metasedimentary formations (Table 7), while the national study indicate that the Sandstone and Shale (Greywackes) rock unit group as primarily associated with elevated arsenic in groundwater [the metasedimentary formations are in the Sandstone and Shale (Greywackes) group]. This study provides the preliminary steps towards the creation of a national database on arsenic in groundwater within Ireland. Arsenic is not persistently elevated in groundwater throughout Ireland, but the presence of regional hotspots of contamination warrant further detailed investigations. Statistical analysis using EDFs and score tests to appropriately handle non-detect data with multiple detection limits, has suggested certain rock types present a greater risk of elevated concentrations of arsenic in groundwater. The identification of potentially at-risk regions is beneficial prior to the commencement of groundwater source development programmes. If there is a potential high concentration of arsenic, then arsenic removal technologies could be used as remediation. Due to a relatively small network of sampling locations, the full extent of the potential for elevated arsenic in groundwater sources within Ireland is unknown. This study indicates that Sandstone and Shale and metasedimentary bedrock present a greater risk of arsenic contamination in groundwater. To identify the geochemical conditions that are conducive to arsenic mobilisation in groundwater within these rock types, further detailed regional geochemical studies need to be established. While there are studies focusing on arsenic within the EU, this study presents a statistical approach in determining the spatial distribution of arsenic at a national-scale. This

methodology may be applied in other countries to help understand arsenic contamination of groundwater.

3.4) Summary

The approach of this chapter was to use existing groundwater data to undertake statistical analysis to identify potential controls of arsenic using explanatory variables. This was achieved using censored data analysis to avoid bias. While most locations were below $10 \mu\text{g L}^{-1}$, there are isolated hotspots where elevated arsenic is occurring in groundwater sources.

Chapter 4

Arsenic in groundwater in south west Ireland: occurrence, controls and hydrochemistry

The work outlined in this chapter was published in:

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Abstract

Globally numerous regions have been identified with elevated arsenic within groundwater which can result in potential adverse health risks. In Ireland, a previous national-scale research assessment of groundwater identified isolated clusters of elevated arsenic and indicated that lithology was a major controlling factor on arsenic in groundwater. Complementary comparisons of national-scale and regional-scale groundwater assessments of arsenic are lacking in Europe when compared to other global regions. The aims of this study were to demonstrate the value of a regional-scale groundwater hydrochemistry dataset with an existing national-scale approach, describe anomalies that can become the focus of attention for public health and economic reasons, and to provide a wider context for arsenic in groundwater within Ireland and Europe. Regional-scale data using 470 locations comprising 1493 analyses using several hydrochemical parameters (arsenic, pH, conductivity, iron, manganese, sodium, potassium, calcium, magnesium, and total hardness) in south west Ireland were integrated with geological, hydrogeological, and land use datasets. Statistical analysis was performed using a combination of methods including score tests of geological groups using an empirical cumulative distribution function plot in addition to spatial analysis. Results revealed that hydrochemical parameters exhibited different spatial clusters, which was generally associated with lithology. Arsenic was elevated in sandstone derived bedrock. Weak correlation of arsenic with other hydrochemical parameters were observed and redox-sensitive elements like manganese and iron showed a greater diversity in spatial occurrence. This study has shown that the variation of hydrochemical parameters are controlled by regional geology. Finally, the paper focuses on anomalies identified by concentrations of individual ions or statistical associations in the context of, for example, historical mineral exploration and mining in the area and also discusses whether groundwater chemistry sampling on this scale can assist in future mineral exploration, as well as guiding the future development of high quality public and private water supplies.

Keywords: arsenic, geology, spatial analysis, groundwater, iron, manganese

4.0) Introduction

Arsenic contamination of groundwater via geogenic processes occurs in various locations globally with the most affected area being documented within the Quaternary deltas of south east Asia (Smedley and Kinniburgh, 2013). The health effects of arsenic exposure are well known and include skin, lung, and bladder cancer (Kapaj et al., 2006; Baris et al., 2016).

National-scale studies in the US by the US Geological Survey (USGS) (Focazio et al., 2000; Welch et al., 2000 and 2001; Ryker, 2001 and 2003; Lee and Helsel, 2005; Gronberg, 2011) and others (Frederick et al., 2016; Lockwood et al., 2004) have led to the generation of spatial distribution maps of arsenic in groundwater. To fill the voids as a result of a national-scale assessment approach, regional groundwater studies (especially for areas with insufficient data, e.g. Mid-Atlantic states), have been used to demonstrate arsenic contamination on greater spatial scales (Sanders et al., 2012). These regional studies incorporated in part or full, secondary data (or historical, and/or ancillary data) including from areas of New England (Ayotte et al., 2003, 2006 and 2015; Ayotte, 2017), New Hampshire (Ayotte et al., 2016; Andy et al., 2017), Maine (Yang et al., 2009 and 2012), Minnesota (Erickson and Barnes, 2005a and 2006), Michigan (Meliker et al., 2008), North Carolina (Kim et al., 2011b; Sanders et al., 2012), California (Ayotte et al., 2016), Texas (Gong et al., 2014), New Mexico (Hoover et al., 2017), and Pennsylvania (Peters and Burkert, 2008; Gross and Low, 2013). Similar studies have been conducted in Canadian provinces, including Nova Scotia (Drummer et al., 2015; Kennedy and Drage, 2017), Saskatchewan (McLeod et al., 2017) and New Brunswick (Klassen et al., 2009). In Asia various prediction-based models have been used in numerous regions (Rodríguez-Lado et al., 2008 and 2013; Winkel et al., 2008a).

Conversely in Europe there have been two (Greece and Ireland) previous national-scale arsenic groundwater assessments (Dokou et al., 2015; Chapter 3) with no regional-scale assessments having occurred. Greater numbers of national-scale assessments would assist in providing information on the patterns and distribution of arsenic in groundwater resources. This is a key consideration as the distribution of arsenic in groundwater in Europe, with no characteristic pattern occurring, when compared with Asia and South America (Ravenscroft et al., 2009). In most European countries naturally occurring arsenic is generally lower than the World Health Organisation (WHO) standard of $10 \mu\text{g L}^{-1}$ (van Halem et al., 2009).

Regional-scale assessments can complement national-scale studies through assisting in the understanding of the potential controls of arsenic by determining the distribution at a greater scale. The presence of these regional datasets of arsenic within Europe is expected to be high due to the greater intensity of routine monitoring practices. These types of datasets have been

previously harnessed (e.g. in Ireland (Chapter 3), Greece (Dokou et al., 2015) and for manganese in Scotland (Homoncik et al., 2010)) for improved groundwater management. While the use of geostatistical modelling can be used with success for generating prediction maps, these techniques suffer from limitations including data availability, data quality, and local-scale arsenic mobilisation variations due to complex groundwater flow paths (Ayotte et al., 2011; Bretzler et al., 2017a). As outlined by Frederick et al. (2016), generally when exploring potential relationships between elevated arsenic and various explanatory variables two primary modelling strategies can be used: logistic regression (e.g. Ayotte et al., 2003; Gross and Low, 2012; Winkel et al., 2008a; Bretzler et al., 2017b), or decision tree analysis (Hossain and Piantanakulchai, 2013; Tesoriero et al., 2017). However in this present study, an alternative approach to these modelling techniques, previously applied successfully in the previous chapter which used similar predictor variables in addition to detailed aqueous geochemistry data that can potentially explain the spatial distribution of arsenic in relation to groundwater controls (e.g. bedrock geology) was utilised. A distinct advantage of this approach is that some datasets, as is the case here, do not include well-depth information and therefore can't be analysed using these other modelling approaches which can integrate depth as a co-variate in the model.

One potential drawback of utilising these extensive and valuable datasets is that they often encompass long term monitoring data (i.e. datasets often span years to decades) which can result in the presence of censored data, often with different limits of detection (DL) due to advancements and developments in instrumental and analytical technology over time. These censored data are reported as being below the (DL), i.e. data reported as $< x \mu\text{g L}^{-1}$ where x is a numerical value. Numerous approaches have been adopted to overcome these limitations, such as removal of censored data (with resulting loss of information), censored data analysis and/or substitution methods. These substitution methods (i.e. $\text{DL} * 1/2$) are the most commonly used for the assessment of groundwater quality parameters at various spatial scales (Meliker et al., 2008; Homoncik et al., 2010; Sanders et al., 2012; Gong et al., 2014; Frederick et al., 2016; McLeod et al., 2017).

Surface geochemistry has been traditionally adopted for geochemical exploration, but recently the use of groundwater geochemistry data has been used as an alternative approach as it is an important medium for exploration of many different styles of mineralisation including porphyry copper, volcanogenic massive sulphide (VWS), sandstone uranium and gold (Leybourne and Cameron, 2010). The advantage over these surface geochemical methods is that it provides 3-dimensional perspective of the area as groundwater recharges to depth, which

increases the likelihood of interaction with buried mineralisation (Leybourne and Cameron, 2010). Groundwater can be collected as a geochemical sampling medium and its chemistry can be used to fingerprint groundwater-mineralisation interactions with this approach leading to significant cost-savings for the mineral exploration industry using existing boreholes (de Caritat and Kirste, 2005). Incorporation of regional and local hydrology for the interpretation of groundwater geochemistry for geochemical exploration can assist in tracing an anomaly back to its source (Carey et al., 2003; Gilliss et al., 2004; Leybourne and Cameron, 2010). By evaluating existing groundwater geochemical datasets, anomalies can be detected and evaluated as an initial geochemical exploration tool.

Building upon previous work the objectives of this current study were to a) assess the spatial distribution of arsenic (and other hydrochemical parameters including iron, manganese, pH, etc.) within groundwater at a regional-scale in relation to different geological, hydrogeological, and land use categories, b) identify if any correlations exist between arsenic and other hydrochemical parameters (e.g. iron, manganese, pH, etc), c) elucidate potentially controlling factors of elevated arsenic in groundwater, and d) compare observations with a national-scale approach and past mining activities.

4.1) Methodology

4.1.1) Study area

County Kerry is located in the southwest region of Ireland and covers an area of 4,807 km² (Fig. 4.1) with a total population of 145,502 (CSO, 2011). The topography of Kerry includes mountains, lowlands and hills. The MacGillycuddy Reeks (mid Kerry) are a high-relief massif which consists of Devonian sandstones and shales (Anderson et al., 2000). Due to the prevailing south-westerly winds and the mountainous landscape, Kerry receives one of the highest amounts of rainfall in Ireland. The landscape occurred as a result of large-scale folding, faulting, and thrusting during the Variscan Orogeny (290 mya) with the subsequent erosion by water and ice (Pracht, 1997). Upper Carboniferous shales are located at the east and north, while Lower Carboniferous limestones dominate western Kerry. Silurian and Devonian sandstones are located within the south and west, with pockets of volcanic rocks scattered throughout Kerry.

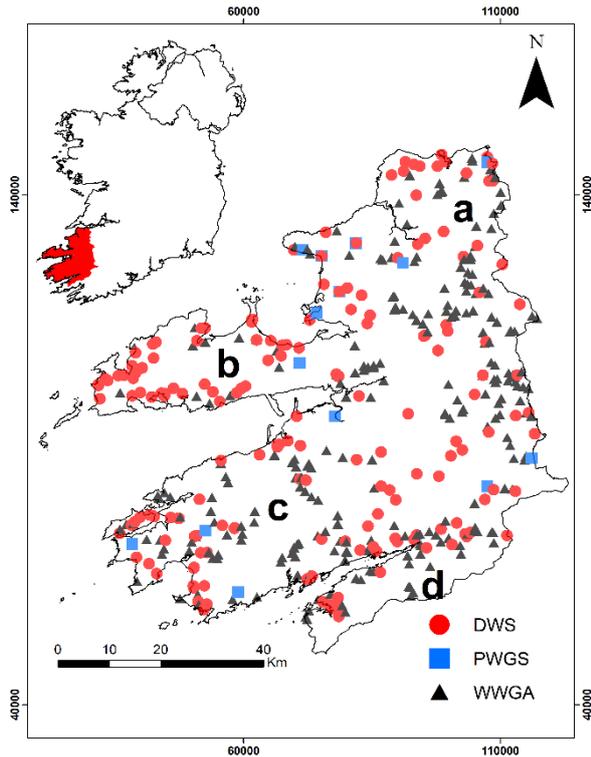


Fig. 4.1. Spatial distribution of monitoring locations in Kerry in relation to the three datasets used in this study (where DWS = drinking water supplies, WWGAs = well water grant applications, and PWGS = public water groundwater sources) and regions (where a = northern area of study site, b = Dingle Peninsula, c = Iveragh Peninsula, and d = Beara Peninsula).

4.1.1.1) Borehole design and construction

The bedrock below the Republic of Ireland is ancient. All the rocks are over 300 million years old and have undergone multiple phases of compression and deformation (EPA, 2013). The hard, unweathered bedrock does not contain open pore spaces through which groundwater can flow. As a result, groundwater flows through major and minor joints, fractures or gaps in the bedrock. The bedrock aquifers of Ireland are not aquifers in the classic sense. They are not homogeneous porous media, but rather they are heterogeneous, impermeable and non-porous (EPA, 2013).

In the past, boreholes which were designed and constructed in Ireland in order to maximise the flow of groundwater into the borehole. The design of these old-type boreholes resulted in a blend of both shallow and deep groundwater flowing into the borehole (Fig. 4.2a). This often leads to these groundwater supply sources being polluted by shallow groundwater. The inadequacy of the old type boreholes has been realised. A modern borehole design is being adopted that deliberately excludes the shallow, more easily contaminated groundwater and draws upon only the deeper, less easily polluted groundwater (Fig. 4.2b) (IGI, 2007; EPA, 2013). Unfortunately, in Kerry, most drinking water supply boreholes in the past have been

constructed according to Fig. 4.2a, and therefore for this study it is presumed that many water samples could be a blend of shallow and deeper groundwater. Water coming into a borehole at a shallow level will usually have had a shorter and more rapid travel path than water entering a borehole at greater depth. Therefore, deeper groundwater will have had a longer contact time with the rock and minerals exposed in the sides of the fractures or conduits through which the water has passed. The chemistry of groundwater changes with depth and length of travel path. It is not possible to determine the proportion of the water sample coming from different depths in each borehole, because the geological and construction records for the older type boreholes are either absent or less than adequate. It is possible to retro-actively determine the proportion of water entering boreholes at different depths if the producing section hole is not lined or screened. However, this determination involves different types of pumping tests, video camera surveys, geophysical logging and depth sampling. This work could take several days if not weeks for each borehole. This level of investigation for over 400 boreholes in Kerry was beyond the scope of either this study or the original local authority water quality monitoring programme.

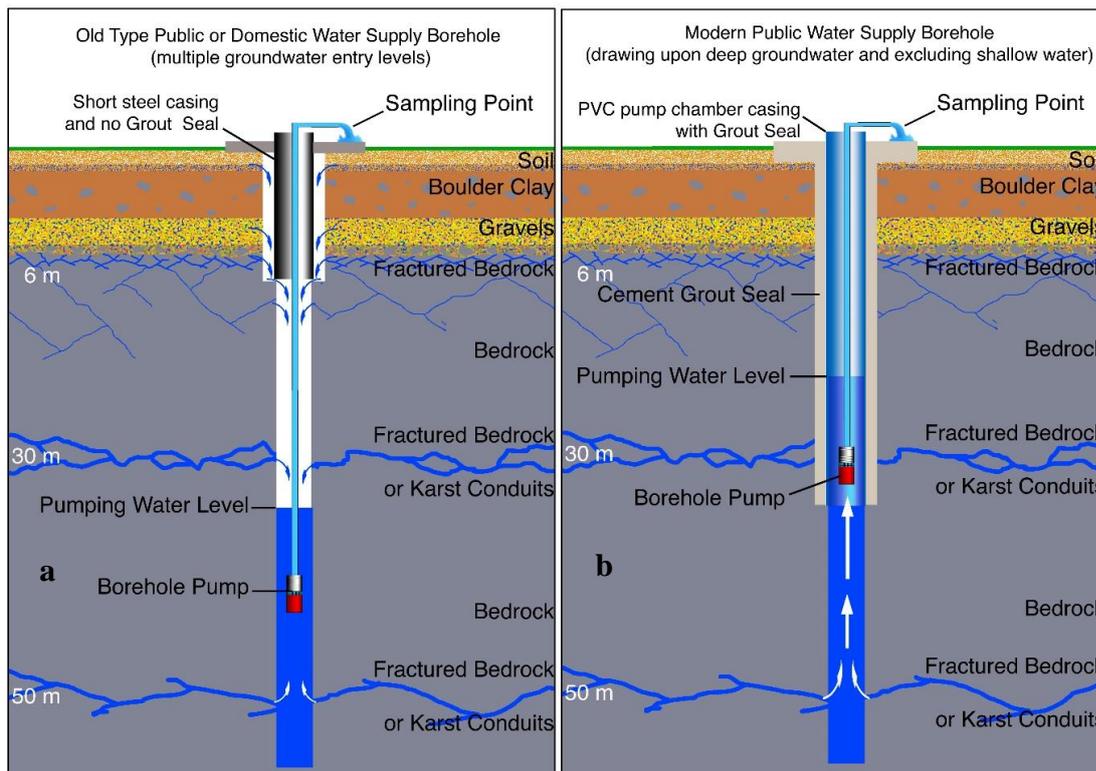


Fig. 4.2. Graphical representation of an (a) older and (b) more modern borehole construction. The pumps in older boreholes are often too powerful and set deep. These boreholes are usually pumped intensely for short periods. Groundwater cascades down the borehole from shallow levels to the pump. On the other hand, more modern boreholes have pumps set within the pump chamber casing. The pumps are usually operated gently and continuously. The deep groundwater flows to the pump (source: David Ball).

4.1.2) Data description

As part of a national-scale assessment of arsenic in groundwater in Ireland (Chapter 3), regional-scale datasets were also collected, including one from County Kerry. This dataset in Kerry was composed of laboratory analyses (As, Fe, Mn, pH, conductivity, Na, Ca, K, Mg and total hardness) of samples collected from routine monitoring of public and private water supplies by local authority officials, and also laboratory analyses submitted to Kerry County Council by private householders when they applied for a government grant after they had drilled and pumped a new water supply borehole. The Kerry dataset forms an amalgamation of three datasets; drinking water supplies (DWSs), well water grant applications (WWGAs), and public groundwater sources (PWGS), with the majority of samples coming from private sources (Fig. 4.1). Samples from WWGAs dataset are spread throughout county Kerry and are a good indicator of the extent of spatial variations in arsenic concentration. Hydrochemical parameters in the dataset include arsenic (As, $\mu\text{g L}^{-1}$), iron (Fe, $\mu\text{g L}^{-1}$), manganese (Mn, $\mu\text{g L}^{-1}$), hydrogen ion potential (pH, pH units), electrical conductivity (EC, $\mu\text{S cm}^{-1}$), sodium (Na, mg L^{-1}), potassium (K, mg L^{-1}), calcium (Ca, mg L^{-1}), magnesium (Mg, mg L^{-1}), and total hardness (TH as CaCO_3 , mg L^{-1}). Other parameters were sometimes measured (e.g. selenium, zinc, lead), but as these were not always analysed, they were not included in the overall analysis and assessment, except where appropriate in order to inform the interpretation and discussion of the results. Redox potential and major anions were not measured.

The three datasets (DWS, WWGA and PWGS) were amalgamated to create a central database. Table 4.1 shows the number of missing values for each of the parameters. For example, at two of the monitoring sites, there were three analyses for arsenic, which had no reportable DLs for arsenic, but had missing arsenic values. Both of these sites were removed in addition to another site from the statistical analysis leaving 467 sites and 1490 analyses. One locality from the DWS dataset was removed from any statistical analysis. In the northwest of Kerry, one borehole had a maximum arsenic value of $21,020 \mu\text{g L}^{-1}$ (in addition to iron, $52,340 \mu\text{g L}^{-1}$) in 2008 and it results from a potential sampling artefact from the presence of high amount of suspended solids). These suspended solids may have overestimated the arsenic concentration which as a result may not be reflective of arsenic concentrations within the groundwater within this locality. Leaching of arsenic from the sediment due to acid preserving may have elevated the arsenic in the sample which can give an unrealistic result. While subsequent measurements at this borehole contain lower levels of arsenic ($<1-958.4 \mu\text{g L}^{-1}$) no suspended solids were present. As a result of the possible sampling irregularities, this locality

was removed from any statistical analysis (total of eleven analyses) for all hydrochemical parameters.

The local authority did not have hydrogeologists, hydrochemists or geochemists on their staff, or engage outside expertise, to collect the groundwater samples, carry out analyses of unstable physicochemical parameters at the well head, and specify parameters to be analysed in the laboratory. As a result, this dataset is imperfect and less than ideal, but the fact that a local authority conducted this sampling and analysis was a major step forward, and the fact that this, albeit imperfect, groundwater arsenic dataset from the Atlantic coast exists is important for the scientific community interested in arsenic in groundwater. While the authors were not involved in the sampling design or analysis of this dataset, the paper is an attempt to show what can be done successfully with such an imperfect dataset, and also shows that with such a dataset some interpretation techniques are of limited value. The paper shows, in effect, the limitations that such a sampling methodology and suite of analysis parameters impose on the interpretation.

Table 4.1. Site numbers for each variable (total sites 470) (where Cond is conductivity and TH is total hardness)

Variable	As	pH	Cond	Fe	Mn	Na	K	Ca	Mg	TH
Number of sites	467	455	440	469	468	457	451	453	430	349
Sites with missing/removed values	3	15	30	1	2	13	19	17	40	121

4.1.3) Groundwater sampling and analysis

Groundwater samples were either collected from taps or in some instance's samples were taken from the borehole directly by members of Kerry County Council. Samples were filtered (0.45 µm) if they were highly turbid and were analysed using an Agilent 7500 series inductively coupled plasma – mass spectrometer (ICP-MS) (Agilent Technologies, Japan) using USEPA method 200.8 (1999). Data were collected from 2004-2012 (DWS, 2004-2012; WWGA, 2006-2012; PWGS, 2004-2011) and is a combination of individual 1493 analyses from 470 locations (DWS, 833; WWGA, 613; PWGS, 47) with the number of analyses at each site ranged from 1 to 39. Information relating to borehole design and construction was not investigated during the sampling programme.

4.1.4) Explanatory variables

Aqueous geochemical data were incorporated into a geographical information system (GIS), where geological data were integrated using a spatial join. Data included Geological Survey Ireland (GSI) databases: ‘National Generalised Bedrock Map (Rock Unit Group)’, ‘Bedrock Aquifer,’ ‘Groundwater Vulnerability’, ‘1:100000 Bedrock Geology’ and ‘Quaternary (Sediments)’ maps. The 27 rock unit groups (RUGs) of the ‘National Generalised Bedrock (Rock Unit Group)’ are classified based on differing water-flow characteristics (GSI, 2005; Bruen, 2009). Details on these databases used can be seen in Chapter 3. However only a subset of these classifications were used in this study due to the regional nature of the study site with additional datasets been used for this detailed study. For each site, land cover was derived in this study in the form of the updated CORINE (Co-Ordinated INformation on the Environment) land cover (CLC 2012) databases (Lydon and Smith, 2014). Inclusion of the 1:500,000 ‘Quaternary (Sediments)’ GIS layer was included to assist in linking Quaternary deposits to arsenic concentrations (Meehan, 2013; Meehan et al., 2014). Tables 4.2, 4.3 and 4.4 show details for bedrock geology, quaternary geology, and CORINE land use data. For the CORINE dataset there are three levels of classification with more detail present at each sequential level; Level 1, 2, and 3 were specified as CORINE (L1), CORINE (L2), and CORINE (L3) respectively. For example, the 3rd (L3) level classification of Peat Bogs (4.1.2) is present in the 2nd (L2) level classification of Inland Wetlands (4.1), which is subsequently found in the 1st (L1) classification of Wetlands (4).

Table 4.2. Data descriptions from ‘1:100,000 (Bedrock Geology)’ dataset

Abbreviation	Name	Geological description	Rock type
CL	Cloonagh Limestone Formation	Bedded bioclastic limestone	PL
CLcr	Cracoean Reef Member	Unbedded calcilutite limestone	PL
DIN	Dinantian Limestones (undifferentiated)	Limestone	PL
VIS	Visean Limestones (undifferentiated)	Undifferentiated limestone	PL
WA	Waulsortian Limestones	Massive unbedded lime-mudstone	PL
BA	Ballysteen Formation	Dark muddy limestone, shale	IL
DI	Dirtoge Limestone Formation	Bioclastic cherty grey limestone	IL
RF	Rockfield Limestone Formation	Well-bedded argillaceous limestone	IL
BD	Ballydavid Formation	Sandstone with conglomerate	SS(O/N)
BH	Bird Hill Formation	Purple siltstone & fine sandstone	SS(O/N)
BJ	Ballinskelligs Sandstone Formation	Purple sandstone & siltstone	SS(O/N)
BM	Ballymore Sandstone Formation	Rhythmically bedded sandstone	SS(O/N)
CA	Cappagh Sandstone Formation	Purple cross-bedded sandstone	SS(O/N)
CH	Caha Mountain Formation	Purple & green sandstone & siltstone	SS(O/N)
EK	Eask Sandstone Formation	Purple sandstone & siltstone	SS(O/N)
GB	Glashabeg Conglomerate Formation	Conglomerate & sandstone	SS(O/N)
GC	Glenflesk Chloritic Sandstone Formation	Green sandstone & purple siltstone	SS(O/N)
GCdl	Doo Lough Pebbly Sandstone Member	Pebbly sandstone & conglomerate	SS(O/N)
GH	Glandahalin Formation	Red cross bedded siltstone & sandstone	SS(O/N)
GP	Gun Point Formation	Green-grey sandstone & purple siltstone	SS(O/N)
IY	Inshaboy Formation	Sandstone, siltstone & mudstone	SS(O/N)
KM	Kilmore Formation	Yellow - olive mudstone to sandstone	SS(O/N)
LA	Lough Acoose Sandstone Formation	Well-bedded grey sandstone	SS(O/N)

Table 4.2. (continued).

Abbreviation	Name	Geological description	Rock type
LK	Lack Sandstone Formation	Micaceous sandstone and siltstone	SS(O/N)
SF	St. Finans Sandstone Formation	Green sandstone & siltstone	SS(O/N)
SH	Slea Head Formation	Pebbly sandstone & conglomerate	SS(O/N)
SL	Slaheny Sandstone Formation	Cross-bedded sandstone & siltstone	SS(O/N)
TH	Toe Head Formation	Cross-bedded sandstone & minor mudstone	SS(O/N)
VS	Valentia Slate Formation	Purple mudstone & siltstone	SS(O/N)
CF	Cloone Flagstone Formation	Greywacke, siltstone & silty shale	S
FS	Feale Sandstone Formation	Sandstone, siltstone & shale	S
BW	Ballynahown Sandstone Formation	Sandstone & shale	S
AL	Annascaul Formation	Mudstone, siltstone & breccia	SSh(G)
CM	Croaghmarhin Formation	Fossiliferous green to grey siltstone	SSh(G)
DP	Drom Point Formation	Grey siltstone with trace fossils	SSh(G)
CCG	Central Clare Group	Sandstone, siltstone & mudstone	SSh
KNrg	Reenagough Member	Massive & flaser-bedded sandstone	SSh
LLS	Lower Limestone Shale	Sandstone, mudstone & thin limestone	SSh
NAM	Namurian (undifferentiated)	Shale & sandstone	SSh
OH	Old Head Sandstone Formation	Flaser-bedded sandstone & minor mudstone	SSh
SHG	Shannon Group	Mudstone, siltstone & sandstone	SSh
GN	Glenoween Shale Formation	Grey silty mudstone	Sh
SFr	Lough Guitane rhyolites	Rhyolitic lavas	B
SFv	Lough Guitane Volcaniclastics	Massive & bedded volcaniclastic deposits	B

Table 4.3. Data descriptions from ‘Quaternary (Sediments)’ dataset

Abbreviation	Description
A	Alluvium
BktPt	Blanket Peat
Cut	Cut over raised peat
GDSs	Gravels derived from Devonian sandstones
KaRck	Kartsified bedrock outcrop or subcrop
Rck	Bedrock outcrop or subcrop
TDSs	Till derived from Devonian sandstones
TLPSsS	Till derived from Lower Palaeozoic sandstones and shales
TLs	Till derived from limestones
TNSSs	Till derived from Namurian sandstones and shales
Urban	Urban
Wsd	Windblown sands and dunes

Table 4.4. Data descriptions from ‘CORINE’ land use dataset

First level Code (L1)	First level name	Second level code (L2)	Second level name	Third level code (L3)	Third level name
1	Artificial Surfaces	11	Urban Fabric	112	Discontinuous urban Fabric
		14	Artificial, Non-Agricultural Vegetated Areas	142	Sport and Leisure Facilities
2	Agricultural Areas	23	Pastures	231	Pastures
		24	Heterogeneous Agricultural Areas	242	Complex Cultivation Patterns
				243	Land Principally Occupied by Agriculture
				243	Broad-Leaved Forest
3	Forest and Seminatural Areas	31	Forests	311	
				312	Coniferous Forest
				313	Mixed Forest
		32	Shrub and/or Herbaceous Vegetation Associations	322	Moors and Heathland
				324	Transitional Woodland Shrub
				331	Beaches, Dunes, and Sand Plains
4	Wetlands	41	Inland Wetlands	411	Island Marshes
				412	Peat Bogs

4.1.5) Statistical analysis

Due to the presence of multiple analyses at some locations, the maximum value recorded for each parameter was utilised (i.e. on a worst-case scenario basis) (Kim et al., 2011b). In order to determine the statistical relationship between hydrochemical and explanatory variables, the empirical cumulative distribution function (ECDF) was computed for censored data using the Kaplan-Meier method (Helsel, 2012). To determine if statistically significant differences existed between the distribution functions of the hydrochemical parameters in the different geological and hydrogeological groups, a score test was performed using the NADA package (Lee, 2013) in the statistical environment R (R Development Core Team, 2017). In order to account for the differences between the aqueous parameters across different groups, pairwise comparisons using a Bonferroni correction was performed. Groupings with <5 sites, e.g. Basalt ($n = 2$) for arsenic rock type, were removed prior to forming the descriptive ECDF plots and applying the score tests. Figures were plotted with regulatory values: groundwater threshold value for arsenic ($7.5 \mu\text{g L}^{-1}$) (EC, 2010), indicator parameters for pH, conductivity, sodium, manganese and iron (6.5-9.5 pH units, $2500 \mu\text{S cm}^{-1}$, 200 mg L^{-1} , $50 \mu\text{g L}^{-1}$ and $200 \mu\text{g L}^{-1}$ respectively) (EC, 2014), interim guideline values for potassium, magnesium, calcium, and total hardness (as CaCO_3) (5 mg L^{-1} , 50 mg L^{-1} , 200 mg L^{-1} , and 200 mg L^{-1} respectively) (EPA, 2003). While the GTV for arsenic is $7.5 \mu\text{g L}^{-1}$ its parametric value is $10 \mu\text{g L}^{-1}$ (EC, 2014).

A correlation analysis was performed to ascertain if any relationship of arsenic and other hydrochemical parameters were present. For censored correlation analysis either one value is censored (singly censored) or both values in the observation pair are censored (doubly censored) (Helsel, 2012), and a combination of both singly and doubly censored data were present within this dataset (except for conductivity and pH). Due to the presence of multiple DLs, the nonparametric correlation coefficient Kendall's tau (τ) was used to determine the strength of the monotonic relationship between two variables, x and y (Helsel and Hirsch, 2002; Helsel, 2012) using the *cenken* function in the NADA package (Lee, 2013). The highest value at each site was used for the correlation, however, when there was a tie for the highest value (i.e. 3 analyses within the same site had the same highest value for arsenic), with a differing y value (i.e. iron) then all of these tied values were included as repeated measures. In the instance where the maximum arsenic concentration had a missing value (NA) for the other variable (e.g. NA calcium value), then the next available pair was included for which arsenic value is maximised within those available pairs.

4.1.6 Interval mapping

Interval mapping of each hydrochemical parameter was generated using a system of five classes (the class division depended on the parameter being investigated) using ArcGIS® 10.2 (ESRI®, Colorado) in Irish National Grid (1965 Datum).

4.1.7 Hot-spot analysis

In order to identify spatial clusters and outliers, the hot-spot analysis technique of Local Indicator of Spatial Association (LISA) or Local Moran's I statistic, a class of local statistics, was performed. This technique can be used to address outliers, locate spatial associations and identify local clusters (i.e. high value clusters) (Anselin, 1995; Anselin, 1996). A 1-sample Kolmogorov-Smirnov (K-S) non-parametric test for normality was performed in addition to a normal score transformation to each parameter. Following this, a Local Moran's I cluster map was created in GeoDa™ 1.4.6 using a threshold distance of 10 km at a significance level of 0.05 (999 permutations) (Anselin et al., 2006) with the resulting shapefile being analysed in ArcGIS® 10.2 (ESRI®, Colorado) in Irish National Grid (1965 Datum). The threshold distance of 10 km was used based on a variogram computed as part of the national-scale assessment of arsenic in groundwater (Chapter 3). To briefly explain the designations of the hot-spot analysis, when a positive value results from an autocorrelation, then these locations have similarly high or low values as its neighbours which are termed spatial clusters then this site is defined as high-high (i.e. high values in a high value neighbourhood) or low-low (i.e., low values in a low value neighbourhood) (Zhang et al., 2008b). In comparison, a negative autocorrelation results in a spatial outlier which is categorised as either low-high (a low value in a high value neighbourhood) or high-low (a high value in a low value neighbourhood) (Zhang et al., 2008b).

4.2) Results

4.2.1 Interval mapping

Interval mapping of groundwater quality parameters are illustrated in Fig. 4.3a-j with the corresponding number of values per classification illustrated in Table 4.5. Most sites exhibited concentrations that are below the guideline values for most parameters. Manganese and iron were observed to be above the indicator values and showed a greater spatial distribution when compared to arsenic for a higher proportion of sites for a higher proportion of sites with both elements showing a greater spatial distribution when compared to arsenic which may result from greater variation in lithology. Widespread elevated concentration of manganese (> 50 µg

L^{-1}) and iron ($> 200 \mu g L^{-1}$) occur around Kerry with concentrations reaching a maximum of $9,987 \mu g L^{-1}$ and $24180 \mu g L^{-1}$ respectively. A distinct spatial cluster of elevated arsenic occurred in-between the Dingle Peninsula and Beara Peninsula (Fig. 4.3a). Within this location of elevated arsenic, the pH is at a neutral to alkaline range. To the north of the study area there are smaller clusters with elevated arsenic concentrations. Other parameters such as conductivity, sodium and magnesium exhibit similar spatial patterns to calcium and total hardness (i.e. similar low and elevated locations), while potassium exhibits a distinct spatial pattern.

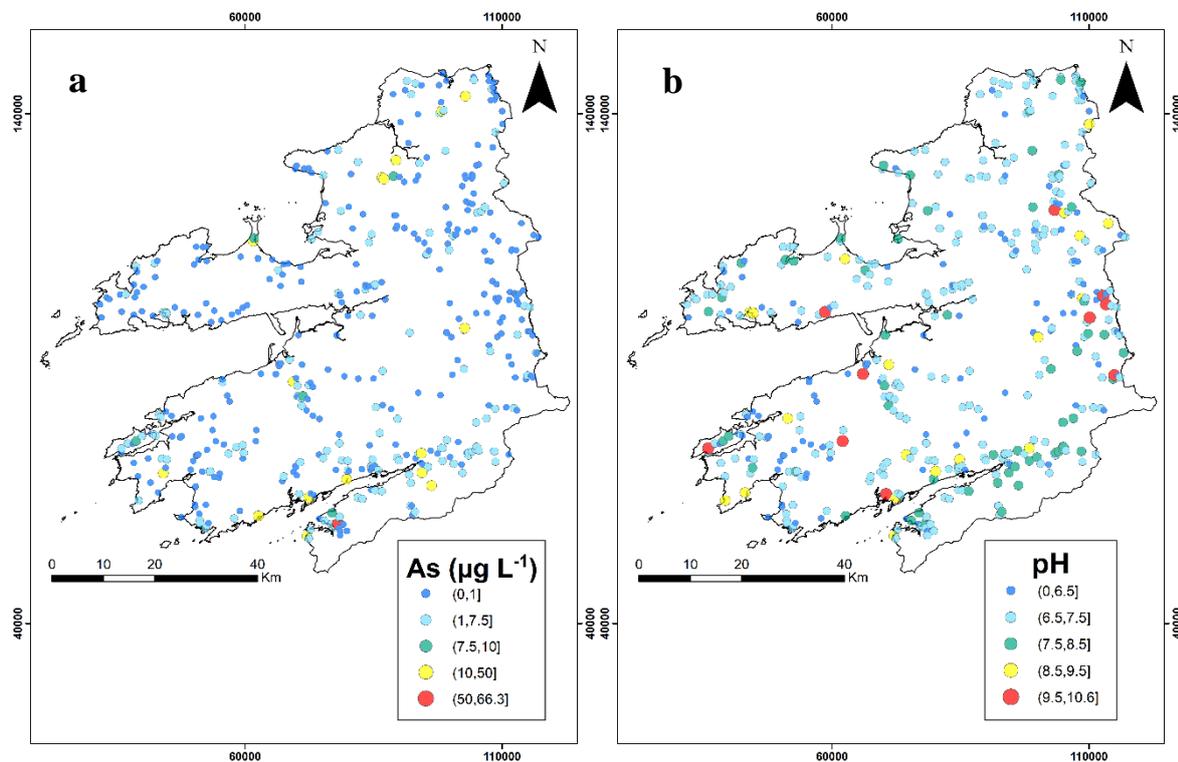


Fig. 4.3. Spatial distribution of groundwater quality parameters divided into five intervals: (a) arsenic (b) pH, (c) conductivity, (d) Fe, (e) Mn, (f) Na, (g) K, (h) Ca, (i) Mg, and (j) total hardness.

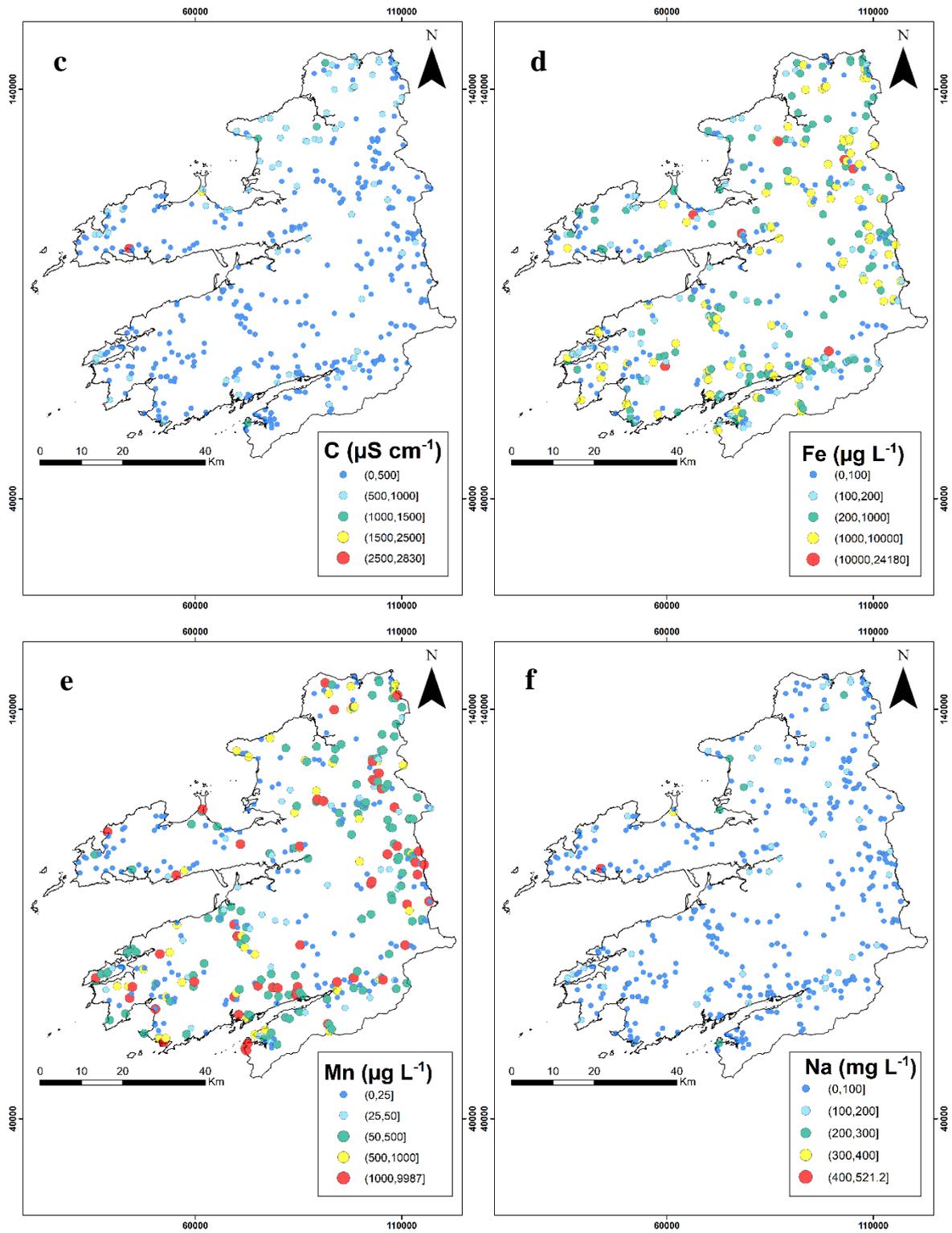


Fig. 4.3. (continued).

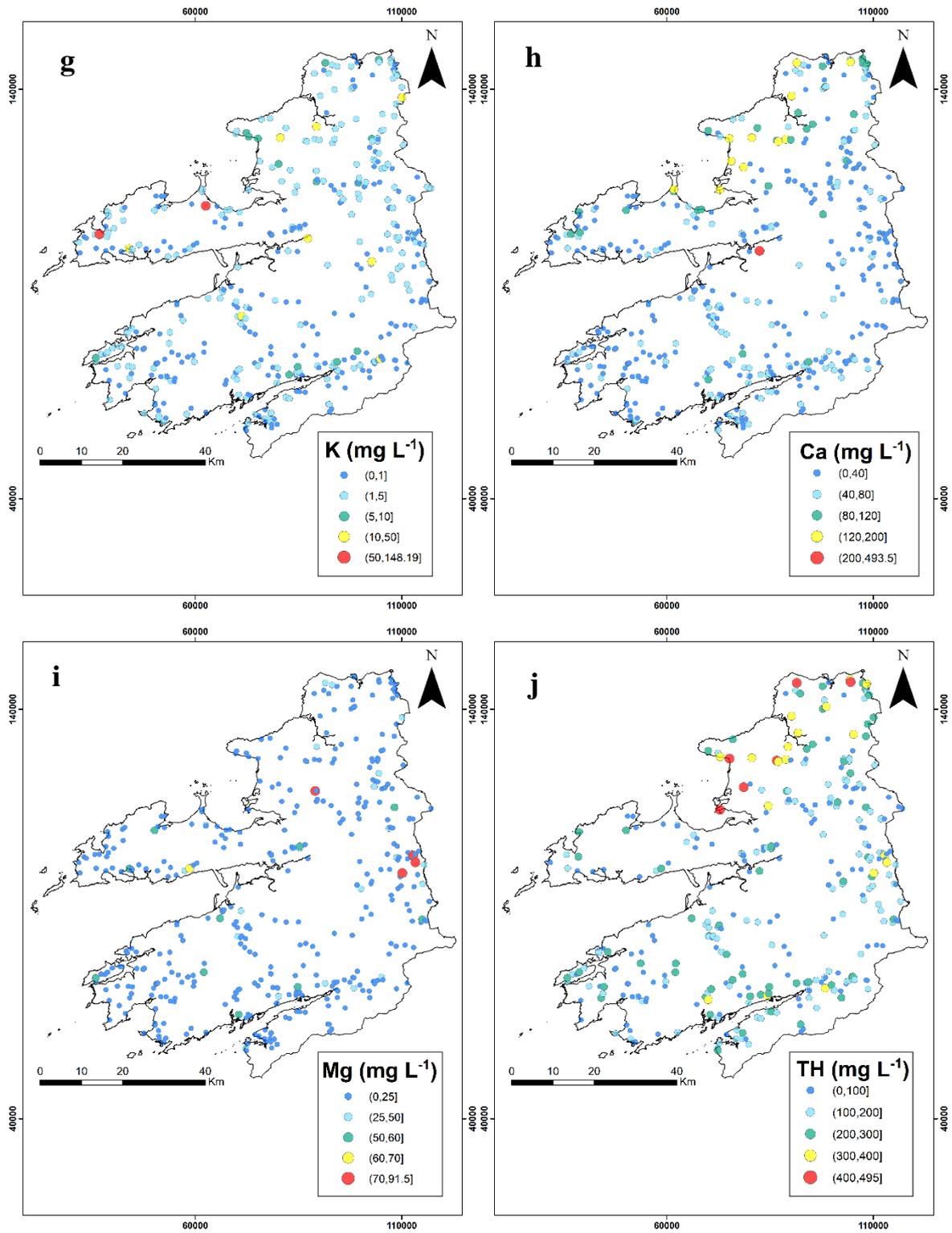


Fig. 4.3. (continued).

Table 4.5. Number of sites per interval classification (refer to Fig. 4.3 for classification).

Classification	As	pH	Cond	Fe	Mn	Na	K	Ca	Mg	TH
1	311	124	361	181	201	404	227	303	392	145
2	134	243	73	74	43	45	200	111	23	119
3	5	58	4	120	123	6	14	27	10	61
4	16	20	1	87	43	1	8	11	1	18
5	1	10	1	7	58	1	2	1	4	6

4.2.2) Hot-spot analysis

Hot-spot analysis of groundwater quality parameters are illustrated in Fig. 4.4a-j with Table 4.6 showing the corresponding number of values per classification. In this study, the hot-spot analysis revealed that most locations are defined as not-significant groups, i.e. these are spatial locations that do not contribute to either spatial outliers or clusters (i.e. not significant at the 5% significance level). Generally, in the study area, there is a greater presence of spatial clusters rather than spatial outliers, and in north Kerry a high-high spatial cluster occurred for conductivity, sodium, potassium, calcium, magnesium and total hardness. Another large spatial cluster is present within the Iveragh Peninsula as a low-low cluster for the previous parameters. However, this spatial cluster is less defined for calcium and total hardness.

Arsenic also presents the greater number of spatial outliers within the dataset as either low-high or high-low. Within the north of the study area high-low spatial outliers are present, while to the south (Beara Peninsula) there is a group of low-high spatial outliers within a group of high-high spatial clusters. The majority of the arsenic high-high groups are contained within this cluster. To the east there is also a group of high-high pH values and manganese values to the west. There are no iron spatial clusters within this high-high pH area, but present in the north of the study area. The low-low arsenic spatial cluster is contained within the east of Kerry, with this locality containing a high-high manganese cluster.

Table 4.6. Number of sites per hot-spot classification (where NS = not-significant, HH = high-high, LL = low-low, LH = low-high, and HL = high-low).

Classification	As	pH	Cond	Fe	Mn	Na	K	Ca	Mg	TH
NS	259	325	290	385	293	242	287	298	264	263
HH	64	42	52	21	66	80	47	42	67	36
LL	60	47	59	25	51	87	68	56	46	25
LH	41	19	10	20	42	11	18	21	33	11
HL	43	22	29	18	16	37	31	36	20	14

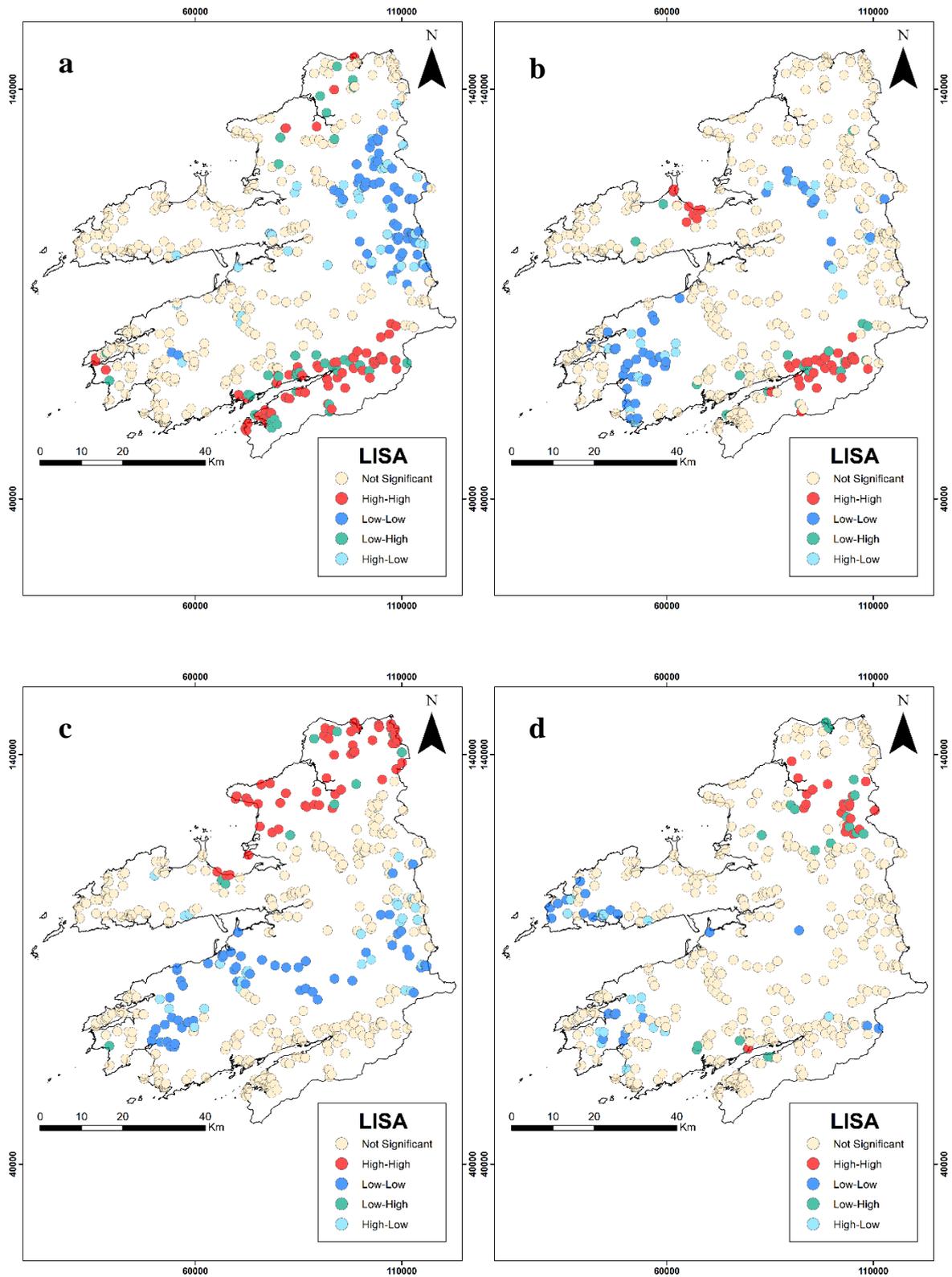


Fig. 4.4. Hot-spot distribution of groundwater quality parameters: (a) arsenic (b) pH, (c) conductivity, (d) Fe, (e) Mn, (f) Na, (g) K, (h) Ca, (i) Mg, and (j) total hardness.

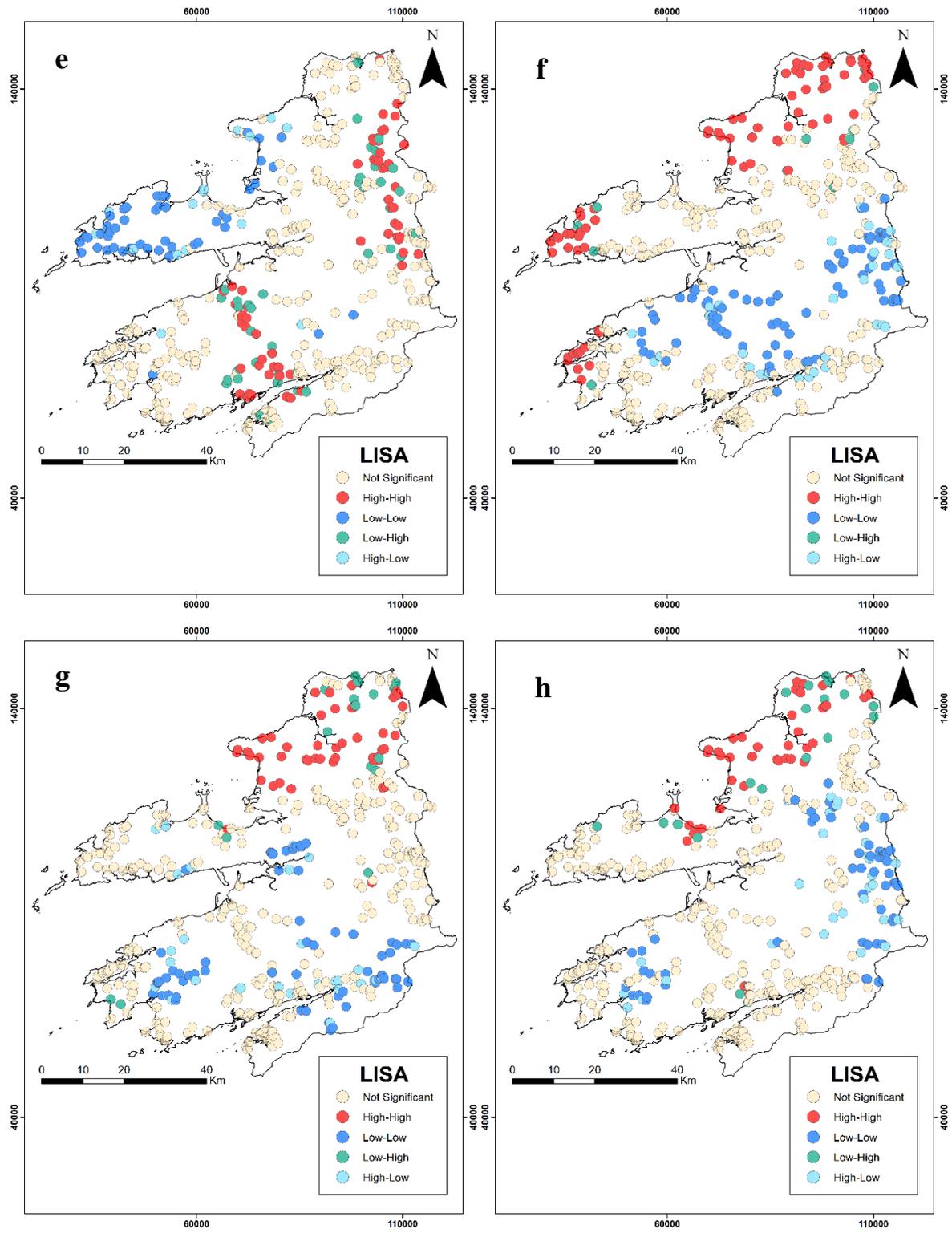


Fig. 4.4. (continued).

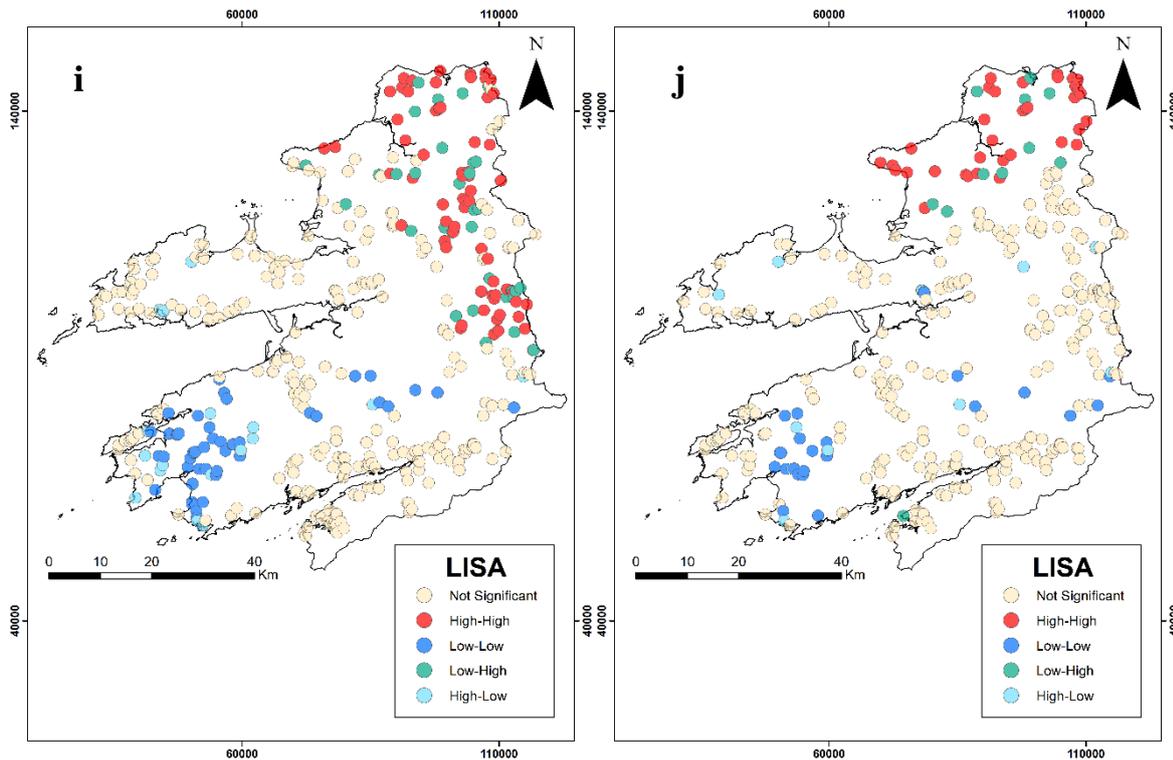


Fig. 4.4. (continued).

4.2.3) Geological constraints on groundwater parameters

4.2.3.1) Arsenic

Arsenic ECDF plots for rock type, aquifer, vulnerability, rock, quaternary, CORINE (L1), CORINE (L2), and CORINE (L3) are illustrated in Fig. 4.5a-j as an example of ECDFs for one water quality parameter. The observations give evidence to suggest distributions of arsenic concentration in groundwater differ across rock types ($p < 0.05$) with pairwise comparisons indicating statistically significant differences between Sandstone (ORS/NRS) and Sandstone ($p = 0.0403$) and between Sandstone (ORS/NRS) and Sandstone/Shale ($p = 0.0203$). While some differences were observed between Pure Limestone and the groups Sandstone/Shale, Sandstone, and Sandstone (ORS/NRS) these differences are not statistically significant. Figure 4.5d presents the ECDFs for the more detailed categorisation of rock, while Figs. 4.5e and f, provide additional ECDFs for the contrasts of rock types found statistically significant (i.e. between Sandstone (ORS/NRS) and Sandstone/Shale, and between Sandstone (ORS/NRS) and Sandstone). Pairwise comparisons show that differences exist between the groups NAM and CH ($p < 0.05$).

The distributions of arsenic concentration differ across the quaternary groupings ($p \approx 0.000$) with pairwise comparisons showing that differences exist between the groups of TNSSs

and Rck ($p = 0.002$), between TNSSs and TDSs ($p = 0.012$), between Urban and TLPSsS ($p = 0.003$) and between Urban and TNSSs ($p = 0.001$).

There is evidence the distributions of arsenic concentration differ across aquifer groupings ($p = 0.016$) with pairwise comparisons showing differences between the groups Pl and L1 ($p = 0.020$). Generally, more elevated concentrations of arsenic were observed in the group L1. For groundwater vulnerability groupings the distributions of arsenic concentration also differ ($p = 0.005$), with pairwise comparisons illustrating differences exist between the groups X and E ($p = 0.022$), between X and H ($p = 0.040$), and between X and M ($p = 0.007$).

For CORINE land cover, three levels of categorisation were investigated depending on their detail, CORINE (L1), CORINE (L2), and CORINE (L3) (refer to Section 4.1.4). The distributions of arsenic concentration differ across the CORINE (L1) groupings ($p = 0.004$) with pairwise comparisons showing differences between Agricultural Areas (1 on Fig. 4.5h) and Wetlands (4 on Fig. 4.5h) ($p = 0.036$). The further detailed categorisation of CORINE (L2) pairwise comparisons showed differences exist between the groups Urban Fabric (11 on Fig. 4.5i) and Pastures (23 on Fig. 4.5i) ($p = 0.038$), between Pastures (23 on Fig. 4.5i) and Heterogeneous Agricultural Areas (24 on Fig. 4.5i) ($p = 0.002$), and between Pastures (23 on Fig. 5i) and Inland Wetlands (41 on Fig. 4.5i) ($p = 0.005$). For CORINE (L3) groupings, pairwise comparisons showed differences between groups Pastures (231 on Fig. 4.5j) and Land Principally Occupied by Agricultures (243 on Fig. 4.5j) ($p = 0.006$), and between groups Pastures (231 on Fig. 4.5j) and Peat Bogs (412 on Fig. 4.5j) ($p = 0.004$).

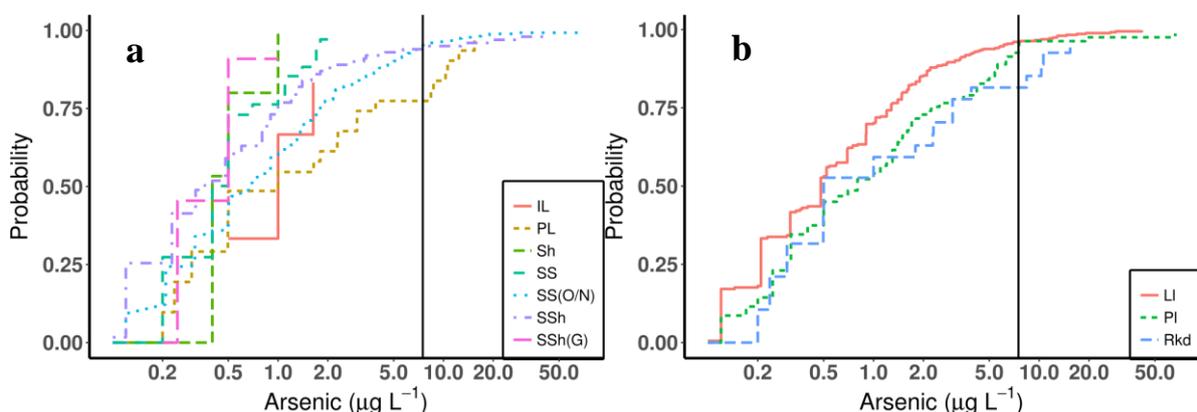


Fig. 4.5. ECDF plot displaying the empirical distribution function of arsenic in relation to (a) rock type, (b) aquifer, (c) groundwater vulnerability, (d) rock, (e) rock (SS(ON) and SSH), (f) rock (SS(ON) and SS), (g) quaternary, (h) CORINE(L1), (i) CORINE(L2), and (j) CORINE(L3). The arsenic GTV value of $7.5 \mu\text{g L}^{-1}$ is represented as a black vertical line.

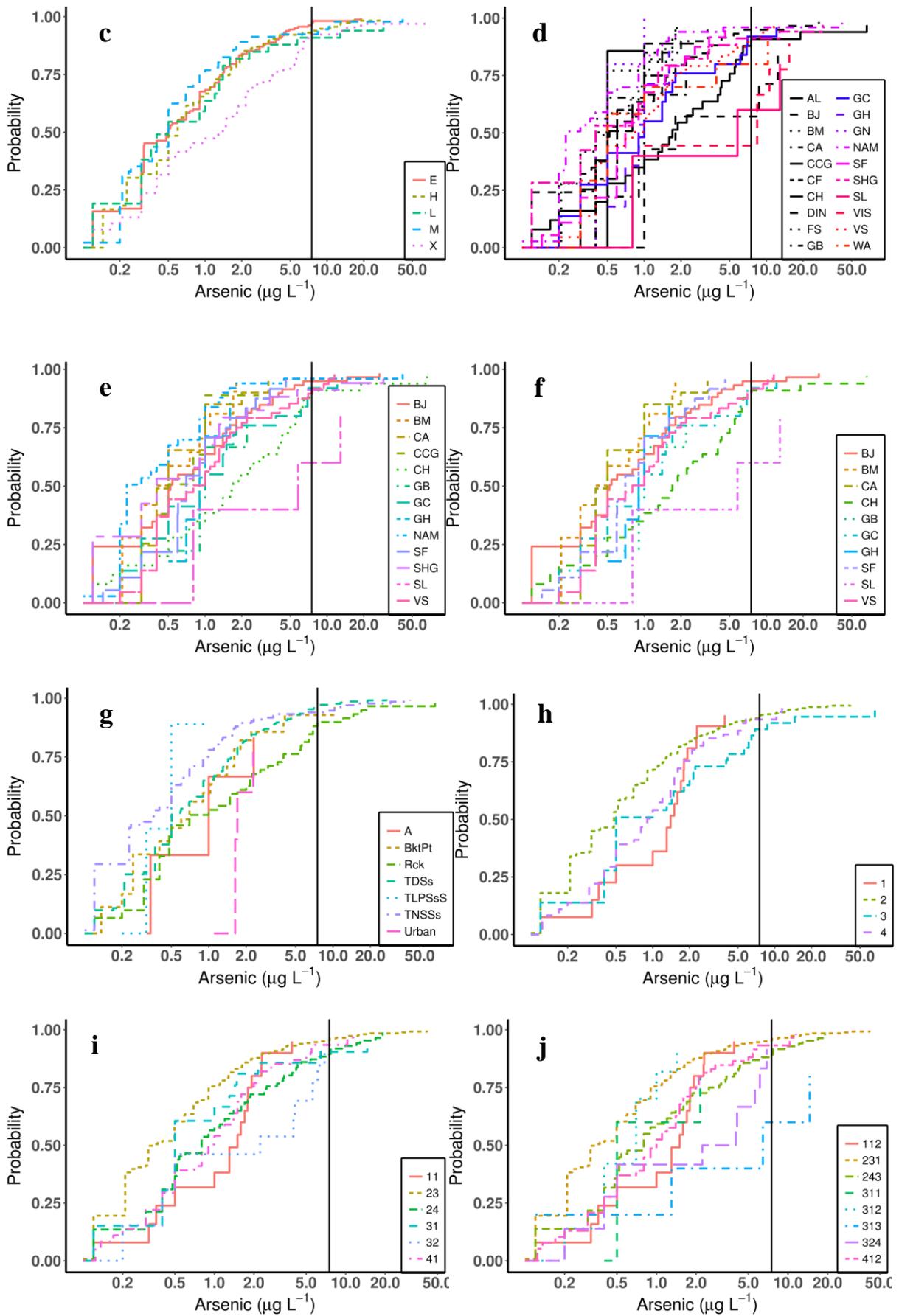


Fig. 4.5. (continued).

4.2.3.2) pH

The data gave no evidence to suggest the distribution of pH differ across rock types, or across aquifer groupings, or between groundwater vulnerability groupings. For rock groupings, the observations give no evidence to suggest the distributions of pH differ; however, pairwise comparisons highlighted a difference between the groups SF and CH ($p = 0.048$). The distributions of pH differ across the different quaternary groupings ($p = 0.014$), with pairwise comparisons showing that statistical differences exist between the groups Urban and TDSs ($p = 0.015$) and between Urban and TNSSs ($p = 0.006$). The distribution of pH did not differ across any of the CORINE groupings.

4.2.3.3) Electrical Conductivity

The distributions of electrical conductivity differ across rock type ($p < 0.05$) with pairwise comparisons indicating statistically significant differences between Pure Limestone and Sandstone ($p \approx 0.000$), between Pure Limestone and Sandstone (ORS/NRS) ($p < 0.05$), and between Pure Limestone and Sandstone/Shale ($p < 0.05$). The distribution of electrical conductivity differ across the different rock groupings ($p < 0.05$) with pairwise comparisons showing statistical differences between the groups of BJ and GH ($p < 0.05$), BJ and SHG ($p < 0.05$), BJ and VIS ($p < 0.05$), BJ and WA ($p < 0.05$), BM and GH ($p < 0.05$), BM and SHG ($p = 0.011$), BM and VIS ($p = 0.009$), BM and WA ($p = 0.043$), CA and GH ($p = 0.007$), CA and VIS ($p = 0.006$), CA and WA ($p = 0.016$), CF and GH ($p = 0.015$), CH and GH ($p < 0.05$), CH and SHG ($p = 0.001$), CH and VIS ($p < 0.05$), CH and WA ($p < 0.05$), FS and GH ($p < 0.05$), FS and SHG ($p = 0.011$), FS and VIS ($p < 0.05$), FS and WA ($p = 0.006$), GC and GH ($p < 0.05$), GC and SHG ($p = 0.003$), GC and VIS ($p < 0.05$), GC and WA ($p = 0.001$), GH and NAM ($p < 0.05$), GH and VS ($p < 0.05$), NAM and SHG ($p < 0.05$), NAM and VIS ($p < 0.05$), NAM and WA ($p < 0.05$), SF and VIS ($p = 0.020$), SF and WA ($p = 0.021$), SHG and VS ($p = 0.003$), VIS and VS ($p < 0.05$), and between VS and WA ($p < 0.05$). The distributions of electrical conductivity differ across the quaternary groupings ($p = 0.004$) with pairwise comparisons showing a difference between TNSSs and TDSs ($p = 0.025$).

For aquifer groupings the distributions of electrical conductivity differ ($p < 0.05$) with pairwise comparisons showing differences between Rkd and Ll ($p < 0.05$) and between Rkd and Pl ($p < 0.05$). Groundwater vulnerability groupings also show significant differences in electrical conductivity ($p < 0.05$) with pairwise comparisons showing differences between L and E ($p < 0.05$), and between L and X ($p = 0.025$). The observations give no evidence of any differences in conductivity across any of the three CORINE groupings.

4.2.3.4) Iron

The distributions of iron concentration do not differ across rock type groupings and across rock groupings, nor across aquifer groupings, groundwater vulnerability groupings, or any of the three CORINE groupings. While there was evidence to suggest the distribution of iron concentrations differ across the different quaternary groupings ($p = 0.026$), however in the global test, pairwise comparisons applying the correction for multiple testing showed no differences between pairs of groups.

4.2.3.5) Manganese

For rock types the distributions of manganese concentration differ ($p < 0.05$) with pairwise comparisons indicating differences between Sandstone/Shale and Sandstone (ORS/NRS) ($p = 0.001$). The distribution of manganese concentrations differ across rock groupings ($p = 0.001$) with pairwise comparisons mainly showing differences between BM and other categories of rock, i.e. between BM and BJ ($p = 0.029$), BM and CCG ($p < 0.05$), BM and CF ($p = 0.006$), BM and FS ($p = 0.003$), BM and GN ($p < 0.05$), BM and NAM ($p = 0.015$), BM and SF ($p = 0.037$), BM and SHG ($p < 0.05$), BM and SL ($p = 0.040$) and between BM and VS ($p = 0.010$). The distributions of manganese concentrations also differ across quaternary groupings ($p = 0.002$) with pairwise comparisons indicating differences between the TNSSs and TDSs ($p = 0.011$).

The observations give no evidence to suggest distributions of manganese concentrations differ across aquifer groupings and groundwater vulnerability groupings

For CORINE (L1) and CORINE (L2) groupings, there is no evidence of a difference in manganese concentration, however significant differences are found when looking at CORINE (L3) groupings ($p = 0.027$), in specifically between groups Pastures and Broad-Leaved Forest as shown from the pairwise comparisons ($p = 0.015$).

4.2.3.6) Major cations

To maintain brevity of this section, the statistical results of the pairwise comparisons of the major cations (sodium, potassium, calcium, magnesium, and total hardness) have been moved to the Appendix (A1).

4.2.4) Correlation of arsenic with other variables

Table 4.7 displays the correlation of arsenic with other hydrochemical variables with an example of the correlation plot of arsenic (with pH and manganese) provided in Fig. 4.6a-b

which highlights the presence of censoring. Arsenic displays a weak positive correlation with the other hydrochemical parameters at the 0.05 significance level, however, no correlation with potassium at the is observed at the 0.05 significance level. In addition, weak correlations are also observed between other the trace elements (i.e. iron and manganese) and the hydrochemical parameters. Interestingly, only a very weak correlation is observed between iron and pH (-0.02), manganese and pH (-0.05) while for iron and manganese evidence of a moderate correlation exists (0.30). In contract to the trace elements, a weak to moderate positive correlation exists between conductivity, calcium, sodium, and magnesium. Kendall's tau is generally 0.15 lower than Spearman's rho and Pearson's r given the same strength of correlation as it is measured on a different scale (Helsel and Hirsch, 2002). In this study, the degree 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).

Table 4.7. Correlation matrix of water quality parameters (all correlation coefficients denoted by * are not significant at the 5% significance level)

Variable	As	pH	Cond	Fe	Mn	Na	K	Ca	Mg
pH	0.16								
Cond	0.18	0.36							
Fe	0.13	-0.02*	0.03*						
Mn	0.12	-0.05	0.07	0.3					
Na	0.13	0.22	0.53	-0.02*	0.0*				
K	0.04*	0.04*	0.27	0.14	0.15	0.19			
Ca	0.15	0.25	0.25	0.17	0.17	0.19	0.37		
Mg	0.16	0.29	0.29	0.13	0.18	0.4	0.4	0.45	
TH	0.14	0.31	0.31	0.13	0.15	0.2	0.36	0.65	0.52

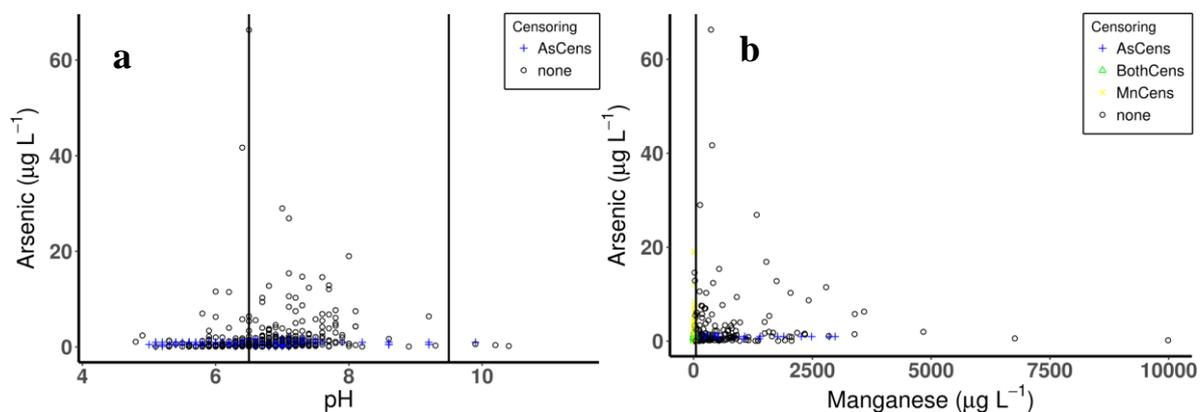


Fig. 4.6. Correlation plot of arsenic (a) and pH (6.5, 9.5) and (b) Mn (50 $\mu\text{g L}^{-1}$). Values in parenthesis are water quality standard values. Where AsCens is censored values for arsenic, BothCens are both values censored and none indicates no censoring.

4.3) Discussion

4.3.1) *Source of arsenic: geogenic or anthropogenic?*

4.3.1.1) *Lithology*

The primary rock type associated with elevated concentrations of arsenic in groundwater in this regional study were sandstone-derived rocks, which was also previously observed from a national-scale assessment of arsenic in groundwater in Ireland (Chapter 3). The national-scale assessment indicated that elevated concentrations of arsenic were primarily associated with the sandstone derived rock type of Sandstone/Shale (Greywacke) (Chapter 3), but in the present regional study this rock type was not statistically significant with regards to arsenic distribution in groundwater (however it is worth noting that it had a low sample number). Elsewhere, elevated arsenic concentrations have been recorded in fractured bedrock aquifers within calcareous metasedimentary bedrock (Ayotte et al., 2003 and 2006) similar to the sandstone derived rock type (Sandstone/Shale (Greywacke)). While a difference was observed in arsenic levels from wells in Pure Limestone and these sandstone rock types, it was not statistically significant at the 5% significance level and it is worth noting that a vast abundance of different sandstone-derived lithologies occur in this region of Ireland, i.e. Old Red Sandstones (Fay et al., 2007). Furthermore, lower concentrations of arsenic in sandstone rocks reflect the predominance of low-arsenic minerals (i.e. feldspar and quartz) in this rock type (Smedley and Kinniburgh, 2013).

The present study illustrates that favourable geochemical conditions for arsenic mobilisation may exist within the Devonian rock type Sandstone (ORS/NRS). Similarly, groundwater from the Devonian Old Red Sandstones of the Welsh borders (Shard et al., 2003), South Wales (Moreau et al., 2004) and the Moray Firth and Strathmore in Scotland (Ó Dochartaigh et al., 2006 and 2010) exhibited elevated arsenic concentrations. Frequently Old Red Sandstones often produce groundwater that contain high concentrations of iron and manganese in Ireland (Sleeman and Pracht, 1999).

Groundwater from the Caha Mountain Formation, which is derived from the Devonian Sandstones (TDSs, Quaternary) exhibited elevated arsenic concentrations. This high arsenic cluster is located on the northern margin of the south Munster Basin, a boundary extending from south Cork to Kenmare (north of Beara Peninsula). The Caha Mountain Formation lies south of the Beara Peninsula, where groundwater contains elevated arsenic which may also extend into other regions of the Peninsula, including County Cork. While a relationship exists

between arsenic in groundwater and the surrounding lithology, it shows a weak correlation amongst other hydrochemical parameters which has also been observed elsewhere (Ayotte et al., 2003; Liesch et al., 2015).

Similarly, groundwater of the poorly exposed Namurian (Undifferentiated) Formation, included within the Sandstone/Shale rock type, also contained elevated concentrations of arsenic. This Namurian Formation contains bedrock strata which include black shales (Sevastopulo, 2009) which have been demonstrated to give rise to elevated arsenic in groundwater (Peters and Burkert, 2008; Ryan et al., 2015b; Rddad, 2017) due to the presence of pyrite (Paikaray, 2012). Black shales can also be enriched in other redox-sensitive elements, e.g. selenium and uranium. To the north of this Namurian Formation (within the Sandstone/Shale rock type), concentrations of molybdenum and selenium (68-155 mg kg⁻¹ and 16-42 mg kg⁻¹ respectively) are elevated within the bedrock while arsenic concentrations (17-29 mg kg⁻¹) remain somewhat elevated (Parnell et al., 2016). The highest values of molybdenum and selenium in these shales in Kerry were recorded in Ballybunion (Parnell et al., 2016), but in the present study groundwater concentrations here were < 7.5 µg L⁻¹. Recent research has shown that these black shales in Kerry contain high than average concentrations of arsenic, selenium, uranium and molybdenum (Armstrong et al., 2019). Given that there are some localities within the Sandstone/Shale rock type that have elevated arsenic, manganese and to a lesser extent iron, further research is required to evaluate if other redox-sensitive elements (i.e. molybdenum, selenium, and uranium) are of concern in groundwaters.

Similar spatial patterns can be observed with rock types for arsenic and manganese (i.e. Sandstone (ORS/NRS) and Sandstone/Shale). Given that shale (i.e. Sandstone/Shale) contains elevated arsenic, the potential for arsenic mobilisation to groundwater through oxidation of sulphide minerals remains a possible mechanism (Ravenscroft et al., 2009).

While no differences were observed in groundwater iron across the different rock types, manganese concentrations were significantly different between Sandstone (ORS/NRS) and Sandstone/Shale, indicating the possible role of manganese oxyhydroxides in arsenic mobilisation. The overall correlation between these elements was weak, but some similar spatial clusters of arsenic, manganese and pH occurred in southern Kerry. While the spatial pattern of arsenic is clustered around small high-high clusters, both iron and manganese exhibited a greater spatial diversity. pH and redox potential (Eh) are dominant controls for the mobility of iron and manganese (in addition to arsenic) in groundwater, however Eh was not available in this present dataset. A potential explanation for the weak correlation of pH and

these trace elements is that several mobilisation mechanisms may be occurring in different areas of Kerry and thus the overall correlation is lower.

4.3.1.2) Aquifer and groundwater vulnerability classification

More elevated arsenic concentrations were observed within the aquifer classification L1 and the groundwater vulnerability classification E (extreme), H (high), and M (medium). It is possible that local contamination of anthropogenic origin may reflect the high concentrations in these groundwater vulnerability groups, however well depth data would help constrain this potential source. The L1 classification is a poorly productive aquifer (PPA) that is only moderately productive in local zones and is associated with the Sandstone (ORS/NRS) group, as well as igneous, metamorphic, carbonate and other clastic rock types across Ireland. This aquifer classification has also been found to contain elevated arsenic on a national-scale study in Ireland (Chapter 3). Some of these Devonian aquifers are fractured enough to have developed some permeability, however this is not to an extent to be classified as regionally important aquifers (Pracht, 1997). Recent research has demonstrated that fractured bedrock aquifers give rise to elevated concentrations of arsenic (Bondu et al., 2016) and other trace elements in groundwaters in the US, Canada, Africa, France, Italy, Greece and certain regions in Asia (Ayotte et al., 2003 and 2006; Smedley et al., 2007; Verplanck et al., 2008; Drummer et al., 2015; Ryan et al., 2011 and 2015b; Reyes et al., 2015; Zkeri et al., 2015; Andy et al., 2017). In Ireland, these hard rock aquifers, or poorly productive aquifers (PPA) underlie 60% of the country (Robins and Misstear, 2000) and provide an important water source for farms, houses, small housing estates, hotels and small businesses. Despite not being regarded as sources for large public water supplies, they are important for small public and public group supply schemes, and in terms of delivering water (and associated pollutants) via shallow groundwater pathways.

On a national-scale in Ireland, arsenic was not related to groundwater vulnerability (Chapter 3), but the present regional-scale study observed that differences occurred (X and E, X and H, and X and M). Areas of high or extreme groundwater vulnerability could be susceptible to surface contamination (i.e. historical pesticide application) with contaminant properties, travel time, groundwater depth and subsoil permeability being key characteristics that affect groundwater vulnerability within a location. Taking this and land cover into account, it could be possible that some arsenic sources are anthropogenic derived, however arsenic is more likely to be controlled by the lithology. Given that a higher proportion of groundwater

within agricultural land use areas contained elevated arsenic, some point source may exist which may also be the case for cations.

4.3.1.3) Land use categories

In New England variations in arsenic concentrations in groundwater occur across the different land use categories with the most variation being found in agriculture which was attributed to the use of arsenical-based pesticides (Ayotte et al., 1999). Historically in Ireland, arsenic based compounds have been used as wood preservatives, herbicides, and biocides (insecticides and rodenticides) with arsenic enriched soils in old orchards (FSAI, 2016). In the present study, while the agricultural (pastures and arable land) groups display significantly different levels of arsenic in their associated groundwater, it is not anticipated that anthropogenic activities such as the application of pesticides, resulted in the arsenic variation by land use (despite being an agricultural intensive area), but rather a function of the underlying lithology, i.e the parent material. However, this potential source of anthropogenic arsenic in the environment cannot be ruled out as specific locations of old orchards are not known. Spatial patterns of rock type and quaternary groups occur within the same areas of statistically significant land use categories. For example, the Agriculture Areas group (including Pastures) towards the north of the study area coincides with Sandstone/Shale rock types, quaternary groupings and TNSSs. To the south and west the land use category Wetlands (including Inland Wetlands and Peat Bogs) is overlies Sandstone (ORS/NRS) and quaternary grouping Rck and TDSs. It is therefore plausible that the weathered parent material is responsible for controlling arsenic in groundwater which is evident from the pairwise comparisons. The Namurian derived tills (TNSSs), Sandstone/Shale, and Pastures to the north and the TDSs and Rck, Sandstone (ORS/NRS) and Wetlands to the south and west had elevated concentrations of arsenic.

Another possible explanation could be the triggering of a release of geogenic arsenic via agricultural practices (i.e. nutrients) specifically the potentially critical risk factor being the presence of Peat Bogs which coincides with Sandstone (ORS/NRS). Reductive dissolution of iron oxyhydroxides influenced by a strong redox driver, i.e. organic matter, can release arsenic upon reduction of the ferrous state (Ravenscroft et al., 2009). The presence of peaty layers is a suitable risk factor for arsenic mobilisation (Ravenscroft, 2007). These peaty layers around Kerry coincide with arsenic concentrations in soil at $<6 \text{ mg kg}^{-1}$ (Fay et al., 2007). Although these peaty layers could provide organic matter to drive reductive dissolution of iron oxyhydroxides within this locality, further investigations are required in order to corroborate these preliminary observations. Other redox sensitive elements like manganese are also

generally present alongside arsenic in groundwater in this area, while groundwater pH generally shows an alkaline relationship, but little overlap was observed in relation to iron. In addition to arsenic, the hydrochemical parameters manganese, sodium, and potassium (and to a lesser degree total hardness) showed differences in land use categories.

The weaker relationship between arsenic in groundwater and land use categories in comparison to lithology may be as a result of comparing historic land use data and current water quality data, as groundwater may have travelled a distance from the land use category that initially affected the water quality (Ayotte et al., 1999). As a result locations with elevated arsenic concentrations in groundwater originating from a specific land use category could now occur and be sampled in a different land use category elsewhere (Ayotte et al., 1999; Liesch et al., 2015). This weaker relationship between arsenic and land use may be a result of the use of agriculturally based compounds, due to bias in areas requiring pesticide application. Manganese, sodium and potassium also showed a relationship with land use cover with differing groups observed. Potassium can be found in some macronutrient fertilizers such as N-P-K (nitrogen, phosphorous and potassium). Groundwater characterisation in Germany found that arsenic also showed a statistically significant difference with land-use classification and hydrogeological units (Liesch et al., 2015) but like the present study no statistical difference in regards to land-use for iron, manganese (for some categories) and pH occurred, while a statistical difference existed for calcium and magnesium (Liesch et al., 2015). In non-carbonate areas, such as the ORS/NRS areas in Kerry agricultural land can be limed, i.e. with calcium and magnesium.

4.3.2) Linking arsenic concentrations with historic mining activities

While the presence of arsenic within groundwaters around the study area are mainly geogenic in origin, some of the concentrations may have resulted from past mining activities. In the south of the study area (between the Iveragh and Beara Peninsula), a cluster of elevated groundwater arsenic occurs near metallic mineral locations such as malachite, copper, chalcopyrite, lead, zinc, silver and pyrite. Many metallic deposits were worked in this region such as silver, manganese, iron, and gold, but it was the copper deposits that generated economic interest (Pracht and Sleeman, 2002). Copper mineralisation in this area is hosted in Upper Devonian rocks that underwent low grade metamorphism during the Variscan Orogeny (Pracht and Sleeman, 2002). These copper ores are associated with three distinct styles of mineralisation: i) low grade stratiform deposits of disseminated copper-iron and copper sulphides, ii) poorly mineralised, quartz-calcite veinlets carrying the same ore minerals as the disseminated

stratiform deposits, and iii) thick quartz veinlets containing a more varied mineralogy including lead, bismuth, molybdenum, arsenic, antimony, and minor gold phases (Ni Wen et al, 1999; Pracht and Sleeman, 2002). In the West Carbery District, the majority of veins are hosted within the Toe Head and Old Head Sandstone Formations. One groundwater monitoring location in the Old Head Sandstone Formation had elevated arsenic in addition to copper, iron and manganese at Rosdohan (Table 4.8). Other monitoring locations from this area had low concentrations of copper (either not-detected or $<50 \mu\text{g L}^{-1}$), except for one location to the east. While low concentrations of arsenic were observed, copper concentrations approached $2827 \mu\text{g L}^{-1}$ (Table 4.9) and from this area of Slaheny, copper was extracted from the Lower Limestone Shales as chalcopyrite and tetrahedrite (Pracht, 1997). However, the highest concentrations of copper observed in the study area are present at north of the Iveragh Peninsula in low-arsenic acidic groundwaters in Killorglin with a maximum concentration of copper of $15580 \mu\text{g L}^{-1}$ in addition to zinc concentrations measured at a maximum of $1990 \mu\text{g L}^{-1}$ (Table 4.10). Historically, the Old Red Sandstones have been known to contain copper mineralisation. However, no known occurrence of historic mining or copper mineralisation is present within this location which may warrant further investigation for geochemical exploration. While no surrounding locations had elevated copper, a location east of the area had copper concentrations at $218 \mu\text{g L}^{-1}$ (Table 4.11). The lead concentrations are low in these locations because generally lead is insoluble in groundwater.

In relation to the scattered cluster of elevated arsenic in groundwater in northern Kerry, there is no evidence of elevated levels of copper detected. However, Cole (1922) recorded that the GSI in 1859 reported a former mine at Ballinglanna (2km north of the village of Causeway in north Kerry) (Sleeman, and Pracht, 1999). They reported evidence of lumps of galena in a stream running through the townland providing historic evidence of metal mineralisation in this area of elevated arsenic concentrations in groundwater.

Table 4.8. Site (KY_410; Rosdohan, south Kerry) with elevated copper (E:72385.8; N:64639.7).

Date	As $\mu\text{g L}^{-1}$	pH pH units	Cond $\mu\text{S cm}^{-1}$	Fe $\mu\text{g L}^{-1}$	Mn $\mu\text{g L}^{-1}$	Na $\mu\text{g L}^{-1}$	K mg L^{-1}	Ca mg L^{-1}	Mg mg L^{-1}	TH mg L^{-1}	Cu $\mu\text{g L}^{-1}$	Zn $\mu\text{g L}^{-1}$
01/11/2006	2.8	8.6	418	< 10	< 5	ND	3.16	25.5	ND	ND	136	ND
03/04/2008	9.47	ND	ND	166	< 20	21.2	0.71	43.2	10.57	ND	<25	< 20
28/05/2008	12.9	7.7	405	112	< 10	22.5	0.64	41.6	10.88	173	143	32
16/07/2008	9.8	ND	ND	65	20	22.3	1.42	41.6	10.34	ND	<25	106
16/07/2008	10.7	ND	ND	94	< 10	21.9	0.63	44	10.32	ND	1904	44
16/07/2008	19.1	ND	ND	132	< 10	19.8	0.55	40	9.39	ND	57	18
16/07/2008	12.3	ND	ND	24	40	21.4	0.61	43.1	10.22	ND	<25	23
16/07/2008	14.5	ND	ND	27	26	20.8	0.59	43.4	9.89	ND	<25	26
16/07/2008	11.2	ND	ND	89	< 10	21	0.64	45.9	9.87	ND	<25	< 15
16/07/2008	10.8	ND	ND	82	< 10	21.7	0.61	44.1	10.34	ND	25	< 15
21/04/2009	2.3	7.4	383	258	203	22.2	0.72	44.6	12.53	165	<25	38

Table 4.8. (continued).

Date	As µg L ⁻¹	pH pH units	Cond µS cm ⁻¹	Fe µg L ⁻¹	Mn µg L ⁻¹	Na µg L ⁻¹	K mg L ⁻¹	Ca mg L ⁻¹	Mg mg L ⁻¹	TH mg L ⁻¹	Cu µg L ⁻¹	Zn µg L ⁻¹
08/05/2009	1.6	ND	359	225	15	22.7	0.83	44.2	13.02	ND	<25	44
08/05/2009	< 1	ND	354	194	< 10	21.8	0.74	42.1	12.26	ND	<25	55
14/10/2009	6.62	7	415	254	516	17.8	0.79	43.8	15.04	176	<25	< 20
21/10/2009	5.23	7.2	345	392	142	17.5	0.76	43	13.74	187	<25	< 20
26/01/2010	14.7	7.3	376	< 20	10	22	ND	47.5	13.92	158	<25	< 15
10/05/2010	3.044	7.3	355	91	< 10	23.7	0.86	47.1	12.92	ND	33	16
21/02/2012	1.19	7.4	338	< 20	< 20	23.3	0.82	44.5	11.09	ND	<25	< 20

* ND = not determined

Table 4.9. Site (KY_434; Slaheny, east Kerry) with elevated copper (E: 100598.9; N: 71364.4).

Date	As µg L ⁻¹	pH pH units	Cond µS cm ⁻¹	Fe µg L ⁻¹	Mn µg L ⁻¹	Na µg L ⁻¹	K mg L ⁻¹	Ca mg L ⁻¹	Mg mg L ⁻¹	TH mg L ⁻¹	Cu µg L ⁻¹	Zn µg L ⁻¹
18/12/2008	5.8	7.5	378	124	180	5.4	0.82	14.4	18.39	183	2827	1810
22/02/2012	<1	7.4	369	< 40	< 20	16.7	0.62	46	17.47	185	<25	< 20

Table 4.10. Site (KY_410; Killorglin 048A, west Kerry) with elevated copper (E: 70355.5; N: 96568.6).

Date	As µg L ⁻¹	pH pH units	Cond µS cm ⁻¹	Fe µg L ⁻¹	Mn µg L ⁻¹	Na µg L ⁻¹	K mg L ⁻¹	Ca mg L ⁻¹	Mg mg L ⁻¹	TH mg L ⁻¹	Cu µg L ⁻¹	Zn µg L ⁻¹
14-Sep-04	< 0.3	6.3	216	< 20	27	18.3	ND	ND	ND	ND	90	ND
05-Jul-05	0.23	6.2	210	71	16	17	ND	ND	ND	ND	63	ND
29-Nov-05	0.48	6.4	ND	< 20	31	15.3	ND	ND	ND	ND	36	ND
20-Mar-06	< 0.3	6	219	< 20	25	16.5	ND	ND	ND	ND	<25	ND
09-Oct-06	0.13	5.9	155	< 20	11	12.7	ND	11.8	ND	ND	155	ND
14-Dec-06	< 0.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
29-Jan-07	< 1	6.1	159	56	< 20	12	1.4	10.4	2.87	ND	31	21
29-Jan-07	< 1	ND	ND	44	< 20	4.2	< 0.5	3.4	0.95	ND	2421	138
17-Apr-07	< 1	5.8	228	155	18	15	1.7	17.7	4.34	ND	6104	1990
17-Apr-07	< 1	6.2	232	129	50	14.7	4.02	18.2	4.36	ND	5466	110
17-Apr-07	< 1	5.9	208	69	< 10	14	1.45	16.4	4.06	ND	72	24
17-Apr-07	< 1	5.9	247	74	< 10	14.9	2.96	17.4	4.37	ND	15580	212
30-Apr-07	0.688	ND	213	69	< 10	15.1	1.48	19.3	ND	ND	1393	1615
23-Jul-07	< 1	7.1	54	< 40	< 20	6.9	< 0.5	1.7	1.32	ND	<12	< 20
17-Sep-07	< 0.5	6.8	46	39	5.92	5.7	0.52	1.3	1.05	ND	24	9.26
25-Oct-07	< 0.5	6.2	121	38	12	16	ND	7.8	3.91	34	21	< 15
03-Dec-07	< 0.12	6.4	66	32	< 10	6.4	< 0.5	3.3	1.41	ND	<25	< 15
26-May-08	0.121	7.8	66	< 20	< 10	6.5	< 0.5	2.6	1.16	ND	<25	< 15
10-Jun-08	< 1	6.5	86	55	< 20	8.1	1.02	6.5	1.6	ND	<12	< 20
18-Aug-08	< 1	6.3	197	130	< 20	15.2	1.41	17.2	4.06	ND	277	20
02-Dec-08	< 0.12	7	54	< 20	< 10	6.4	< 0.5	2.7	1.13	ND	<25	< 15

* ND = not determined

Table 4.11. Site (KY_273; Inchicorrigan West, east Kerry) with elevated copper (E: 102760.9; N: 97937.8).

Date	As µg L ⁻¹	pH pH units	Cond µS cm ⁻¹	Fe µg L ⁻¹	Mn µg L ⁻¹	Na µg L ⁻¹	K mg L ⁻¹	Ca mg L ⁻¹	Mg mg L ⁻¹	TH mg L ⁻¹	Cu µg L ⁻¹	Zn µg L ⁻¹
10-May-07	7.5	6.5	364	1013	1439	12.1	1.23	32.1	15.85	185	<25	< 20
14-Apr-08	14.7	6.6	387	1738	1684	14.5	1.21	36.1	17.66	208	142	21
13-May-08	5.3	6.6	383	666	1585	14.7	1.27	36.6	18.6	8	218	27
21-Oct-08	41.7	6.4	403	473	388	12.6	1.14	38.6	15.27	263	<25	23
07-Apr-09	2.4	6.4	426	200	< 20	18.2	10.71	41.9	18.79	171	<25	< 20

4.3.3) Relationship of other hydrochemical parameters

While arsenic demonstrates weak correlations with other hydrochemical variables in groundwater across the study area, moderate correlations are apparent between conductivity, sodium, calcium, magnesium and total hardness (and to a lesser extent potassium). A group of high-high spatial clusters for conductivity, sodium, calcium, potassium magnesium and total hardness are evident towards the north of Kerry with low-low spatial clusters observed around the Iveragh Peninsula. The high-high spatial clusters extend to a lesser extent for both sodium and magnesium. Interestingly, within the high-high arsenic spatial cluster the other hydrochemical parameters are observed as either low-low spatial clusters or not-significant groups. These hydrochemical parameters (conductivity, sodium, potassium, and calcium) also show the same pattern within rock types, i.e. between Pure Limestone and Sandstone, Pure Limestone and Sandstone (ORS/NRS), and Pure Limestone and Sandstone/Shale. For potassium in groundwater, additional differences were apparent within both rock types Sandstone/Shale and Sandstone (ORS/NRS) which were also observed for conductivity, potassium and calcium. As a result, fewer statistical differences between rock groupings are contained within total hardness and magnesium when compared to the larger diversity within conductivity, sodium, potassium, and calcium. Greatest variations occurred within the rock groups GC, SHG, VIS and WA.

4.3.4) Comparison with other regions

The national-scale assessment of arsenic in groundwater in Ireland reported concentrations ranging from <0.2 - $234 \mu\text{g L}^{-1}$ (Chapter 3). Concentrations of arsenic measured within this study are not grossly elevated as seen elsewhere globally, especially in south east Asia, but represent a level of low-to-moderate arsenic exposure. Similarly, low concentrations of arsenic have been observed in European groundwater (using bottled water as a proxy) (Table 4.12), but at concentrations higher than what was previously observed for Ireland. While the arsenic concentrations in this work are low-to-moderate, they represent the potential for long-term low-dose arsenic exposure, which can induce chronic health effects (Moon et al., 2012; Bräuner et al., 2014; Stea et al., 2014; Tsuji et al., 2014). Generally higher concentrations of cations have been observed elsewhere in Europe, whereas the concentrations of iron and manganese found within Kerry represents elevated concentrations when compared to other regions within Europe (Table 4.12). Lower concentrations of manganese were found in Scottish groundwater which ranged from <3 - $1900 \mu\text{g L}^{-1}$ (Homoncik et al., 2010).

Table 4.12. Comparison of arsenic within European regions

Parameter	<i>This study</i>		<i>Europe (mineral water)</i>		<i>Europe (bottled water)</i>		<i>Europe (bottled water) – Ireland</i>	
	Min	Max	Min	Max	Min	Max	Min	Max
As ($\mu\text{g L}^{-1}$)	0.1	66.3	0.012	21.6	<0.03	89.3	0.29	3.52
pH	5.1	10.6	-	-	3.95	9.9	5.5	7.55
EC ($\mu\text{S cm}^{-1}$)	9	2830	-	-	18	26500	384	730
Fe ($\mu\text{g L}^{-1}$)	<10	24,180	<1	403	<0.5	13500	0.25	8.75
Mn ($\mu\text{g L}^{-1}$)	<1	9987	<1	200	<0.11	1870	0.05	4.52
Na (mg L^{-1})	0.8	521.2	1.26	1723	0.4	8160	11.7	94.2
K (mg L^{-1})	0.5	148.19	0.254	30.25	<0.1	588	1.4	18.8
Ca (mg L^{-1})	0.2	493.5	2.61	488	0.43	611	38.1	108
Mg (mg L^{-1})	0.55	91.5	0.157	215	<0.01	4010	6.9	22.4
TH (mg L^{-1})	1	495	-	-	-	-	-	-
Reference	<i>This study</i>		<i>Misund et al., 1999</i>		<i>Reimann and Birke, 2010</i>			

4.4) Conclusions

Within this regional-scale study area, there is a relationship between arsenic and lithology (i.e. Sandstone/Shale (ORS/NRS) and Sandstone/Shale) which may indicate that the underlying rock is a strong predictor of arsenic in groundwater. However, more targeted studies are required to confirm this and further understand local-scale variations. Whilst the variation of trace elements like arsenic, manganese, and to some extent, iron are constrained within a small number of lithology groupings, the distribution of the major cations (sodium, potassium, calcium, magnesium, and total hardness) in addition to electrical conductivity exhibit a greater variation. This study has used an approach which integrated geological and hydrogeological data in order to reveal potential lithological controls of arsenic and other parameters in groundwater which will be of interest to researchers in other regions. With the growing body of secondary groundwater datasets being generated in Europe and elsewhere, the methods presented here will be of interest on how to utilise an imperfect dataset. This study demonstrates that groundwater geochemistry at the regional-scale can identify metal ion anomalies which can be used to assist in future mineral exploration, as well as guiding future development and sustainability of good quality water resources.

4.5) Summary

This chapter aimed to build upon the statistical methodology of the previous chapter, but at a regional scale to understand controls of arsenic in groundwater. In addition, other hydrochemistry parameters and datasets were incorporated into the analysis. As a result, a more detailed understanding of groundwater processes leading to elevated arsenic was achieved.

Chapter 5

**Assessment of groundwater processes using
censored data analysis incorporating non-detect
chemical, physical, and biological data**

Abstract

In Europe most environmental based water quality research has focused on both nutrient and microbial contamination which can arise from agricultural processes and inadequate wastewater treatment. Recent work in Ireland has linked the presence of arsenic in groundwater at elevated concentrations at national and subnational-scales with bedrock lithology serving as a strong predictor variable. Groundwater data were collected as part of an environmental impact assessment for a road construction project and this resulting groundwater geochemistry dataset was used in this present study to assess the geochemical controls of arsenic in natural waters in addition to biological and nutrient contamination. Physiochemical parameters, trace elements, nutrients, organics, and microbiological parameters were collected for every quarter for four years (2004-2008) in 67 wells. Due to differing sampling procedures and limitations in the data, only one quarter (November 2005) was used to understand groundwater geochemistry in greater detail. Multivariate statistical techniques were used to overcome the presence of non-detect data. This is an important consideration as while methods exist for chemical data, methods incorporating biological data are limited. Elevated levels of nitrate in groundwater may arise from the runoff of septic tanks and/or agricultural practices in the area. Both pesticides and polycyclic aromatic hydrocarbons were not detected in any wells signifying no anthropogenic contamination. However, fuel products such as methyl tert-butyl ether were detected and potentially illustrate point source contamination, these were detected in only one well. Geochemical data indicate that elevated arsenic concentrations are present within alkali-oxic groundwaters through the desorption from Fe and Mn oxyhydroxides, i.e. alkali desorption. This study examines of the geochemistry of arsenic in groundwater in Ireland at a local-scale. In addition, the multivariate methods used in this study were able to fully integrate both chemical and biological censored data, which may be applied in other regions with similar data.

Key words: arsenic, environmental monitoring, microbial contamination, trace elements, non-detects,

5.0) Introduction

Groundwater represents a source of drinking water for many regions in the world though abstraction in public and private sources. Historically, most research on groundwater contamination has focused primarily on nutrients, such as nitrate from agricultural practices (Fenton et al., 2009; Hansen et al., 2012 and 2017; Wick et al., 2012), microbial contamination arising from domestic wastewater treatment systems (DWWTS) (Gill et al., 2018; Balderacchi et al., 2013; Hynds et al., 2014; Keegan et al., 2014; Llopis-González et al., 2014), hydrocarbons from poor storage practices (Philips et al., 2007) and major ion chemistry from the dissolution of primary mineral phases in the bedrock (Reimann and Birke, 2010; Petrunic et al., 2012; Caulfield et al., 2014). Due to advances in analytical instrument (such as multielement determination and improved detection limits), there has been an increase in the detection of trace elements with elevated concentrations of arsenic observed in Europe (Katsoyiannis et al., 2014; Morrison et al., 2016; Medunić et al., 2020). Elevated concentrations of arsenic in groundwater can cause adverse health effects in humans (Bondu et al., 2017a; Katsoyiannis et al., 2014; Medunić et al., 2020). While public sources of groundwater (from boreholes, dugwells, etc) are regulated in Ireland, private sources of groundwater (located mainly in rural Ireland) remain largely unregulated, un-monitored and poorly maintained (Hynds et al., 2014). In Ireland, the onus remains on the homeowner to test the water quality of their private groundwater well. When these private groundwater wells are sampled, often there are frequent exceedances of trace elements (i.e. iron and manganese, and less frequently, arsenic) above the corresponding public water quality standards (Ayotte et al., 2003; Bondu et al., 2017a).

Localised studies, like the present study, can offer greater insights for understanding arsenic geochemistry in groundwater when compared to earlier larger scale studies (Chapter 3 and 4). This is an important consideration as there can be a large spatial variation in arsenic concentrations in groundwater over small spatial scales (Ravenscroft et al., 2009). Elevated arsenic concentrations observed from this present study location are most likely as a result of geogenic sources associated with bedrock lithology (Chapter 3). This is in line with a similar trend observed for other areas in Europe (Smedley and Kinniburgh, 2013; Medunić et al., 2020).

In environmental analysis, non-detect or censored data (i.e. data reported below the detection limit (DL)) are often encountered with either removal (i.e. deleting non-detect value) or substitution (i.e. replacing non-detect value with a numerical value such as 0) as common practices to handle these data (Farnham et al., 2002; Grunsky, 2010; Helsel, 2005, 2010 and

2012). These traditional approaches of controlling non-detects in datasets has led to over-estimation and under-estimation during interpretation of parameters in environmental studies. Due to the over or under-estimation during interpretation, these are not appropriate methods, which is evident by lack of harmonisation and consistent methodology between several regulatory and state agencies. For example, the substitution method of one-half of the detection limit has been historically advocated as the method of choice by the USEPA which is also adopted in Europe based on the EU Groundwater Directive (Annex IV) (USEPA, 2000; EC, 2006; Gibbons et al., 2009). However, it must be noted that in the EU (based on the EU Groundwater Directive), the method of using one-half of the detection limit, is not recommended for handling non-detect pesticide data (EC, 2006). In comparison, the USGS recommends that these substitution methods are not used (Helsel and Hirsch, 2002). While previous work has shown that censored-data analysis can be adopted for censored chemical data (i.e. arsenic in groundwater), these approaches are rarely encountered for biological data (i.e. microbiological parameters) in the literature. Microbiological data (such as number of colony forming units of a bacteria in a sample) may be represented mathematically as discrete data, (i.e. as a whole number), while the concentration of arsenic and other water quality parameters are often represented as continuous data (these data often contain decimal points). As a result, these substitution methods are not considered appropriate for successfully handling microbiological data (Canales et al., 2018). While there is a limited application of censored-data analysis for microbiological data in the literature, recent work has shown the applicability of interpreting both censored microbiological and chemical data using multivariate analysis as an effective methodology to overcome these limitations (Wangkahad et al., 2017).

The application of multivariate statistical analysis (MSA) can be conducted in order to understand the associations and relationships in a system with a large number of parameters (including chemical, microbiological and physical). While traditional MSA techniques fail to account for censored data (Farnham et al., 2002; Grunsky, 2010), several procedures can be applied prior to implementing MSA including binary methods (presence/absence), ordinal methods (ranks of data), and Wilcoxon-type methods (u-scores, Wilcoxon rank sum test) (Helsel, 2012). While binary procedures can result in a loss of information in the data, ordinal methods are suitable where one DL is present, while methods based on u-scores can handle multiple DLs present in the data (Helsel, 2012). Applications of ordinal-based approaches with MSA for water quality and microbiological parameters have been previously used elsewhere (Wangkahad et al., 2017). However, there has been a limited response to incorporate these censored-data MSA approaches in studies with censored microbiological data, especially

containing trace elements such as arsenic. One of the issues of these MSA methods for censored data is how to successfully incorporate both chemical and biological data together using a censored-data approach.

The purpose of this study is to illustrate how a MSA approach can be implemented to incorporate both censored chemical and biological data in order to understand the origin of constituents in groundwater using an existing dataset. This is an important consideration as currently there are a limited number of works showing how censored biological data are treated separately, with few studies showing how both can be incorporated and used for interpretation of groundwater processes (Helsel, 2012; Wangkahad et al., 2017; Canales et al., 2018). The trace element arsenic will be the focus of this study as historically, the north east of Ireland is known to contain elevated arsenic within groundwater (Chapter 3). In addition, there is limited understanding of the geochemical conditions giving rise to elevated arsenic in groundwater in local settings within Ireland. The objectives of this study are to implement censored data analysis in order to: a) investigate potential associations amongst the trace elements and with other variables such as microbiological, field parameters, nutrients, and depth to understand groundwater processes, b) determine if there are any spatial associations between water quality variables, c) assess the source of excessive nutrient contamination, d) illustrate how a censored-data MSA approach can successfully be used to incorporate both chemical and biological data and the interpretations thereof, and e) explore the level of detected organic geochemical parameters.

5.1) Materials and Methods

5.1.1) Study Site and initial desk study

The National Roads Authority (NRA) in Ireland supports research to determine if road construction may have an impact on local water quality (Bruen, 2009). As part of an Environmental Impact Statement (EIS) for the development of the cross-border (Ireland and Northern Ireland) 14km A1/N1 Newry-Dundalk Link Road (dual carriageway) (Mouchel Parkman, 2002), groundwater sources were monitored in an rural agricultural area in north east Ireland (Fig. 5.1a-b). Surface water were plotted on maps for context, but no surface waters were sampled for parameters in this study area. Sixty-seven wells were monitored quarterly for both physical and chemical parameters from November 2004-January 2008 within a 200 m buffer zone of the new road. A DWWTS or septic tank was present at each site. While the specific location of the septic tank was not recorded, field notes indicate that the majority were

within the vicinity of the groundwater well. The construction of this road was 30 months which started on February 2005 to July/August 2007, with the road opening on 2nd August 2007 (Troll et al., 2008). During road construction, cuttings were completed in Lower Palaeozoic age sediments and Carboniferous limestones (depth of cut, 5 m) with a majority arising from the granites (depth of cut, 10 m) of the Slieve Gullion Complex (Bazley, 2010). Separately, the dumping of oil has led to land contamination in some areas (Smith, 2012).

The main pressure from land use arises from mainly agriculture-based land (i.e. pastures = 321), with some forestry (mixed forest = 313 and 324 = transitional woodland-scrub) based on the CORINE land use datasets (Fig. 5.1c).

5.1.1.1) Geological, Hydrogeological and environmental setting

The geology of the area is mostly composed of Lower Palaeozoic (Silurian and Ordovician) turbidites and Carboniferous limestones (Buckley and Sweetman, 1991). Underlying these greywackes of the Central Belt are graptolitic shales (Chew & Stillman, 2009). To the north of the study area the local geology was deformed during the Caledonian intrusion and mountain building episodes, which resulted in faulting and low-grade metamorphism. The igneous complexes of Slieve Gullion were formed in the early Tertiary. Most sites intersect the Clontail Formation (Fig. 5.1b) with the remaining sites intersecting the Dinantian Limestones (Undifferentiated) formation. The quaternary geology of the area mainly consists of till derived from Lower Palaeozoic sandstones and shales, and till derived from granites with smaller amounts of alluvium, bedrock outcrop or subcrop, cut over raised peat lacustrine sediments, Estuarine silts and clays and drumlins within the locality of the study site.

The aquifers in the study area are classified as PI (Poor Aquifer - Bedrock which is Generally Unproductive except for Local Zones), Lm (Locally Important Aquifer - Bedrock which is Generally Moderately Productive), and LI (Locally Important Aquifer - Bedrock which is Moderately Productive only in Local Zones) (aquifer classification according to GSI methodology (Fig. 5.1d)) which limits the yield of some of these private groundwater sources. Indeed, the Lower Palaeozoic greywackes, which contains the greatest proportion of groundwater sources in this present study, are classed as Poor Aquifers, which have a low permeability with groundwater restricted to weathered zones or along fault or fissure zones (McConnell et al., 2001).

This area has high groundwater vulnerability (according to GSI methodology) with patches of extreme vulnerability with the main aquifer being PI (Fig. 5.1e). There are five groundwater vulnerability categories defined by the GSI that characterise the risk of

contamination of groundwater by polluting activities. The categories are based on: (i) the permeability and thickness of the subsoils that overlie the groundwater; (ii) the type of recharge – whether point or diffuse; and (iii) the thickness of the unsaturated zone through which the contaminant moves. The topography of the study area is hilly with higher elevation on the eastern side (182-272) which decreases on approach to the western side (91-182m) (Buckley and Sweetman, 1991) causing groundwater to flow from a north-eastern to south-western direction (Fig. 5.1f).

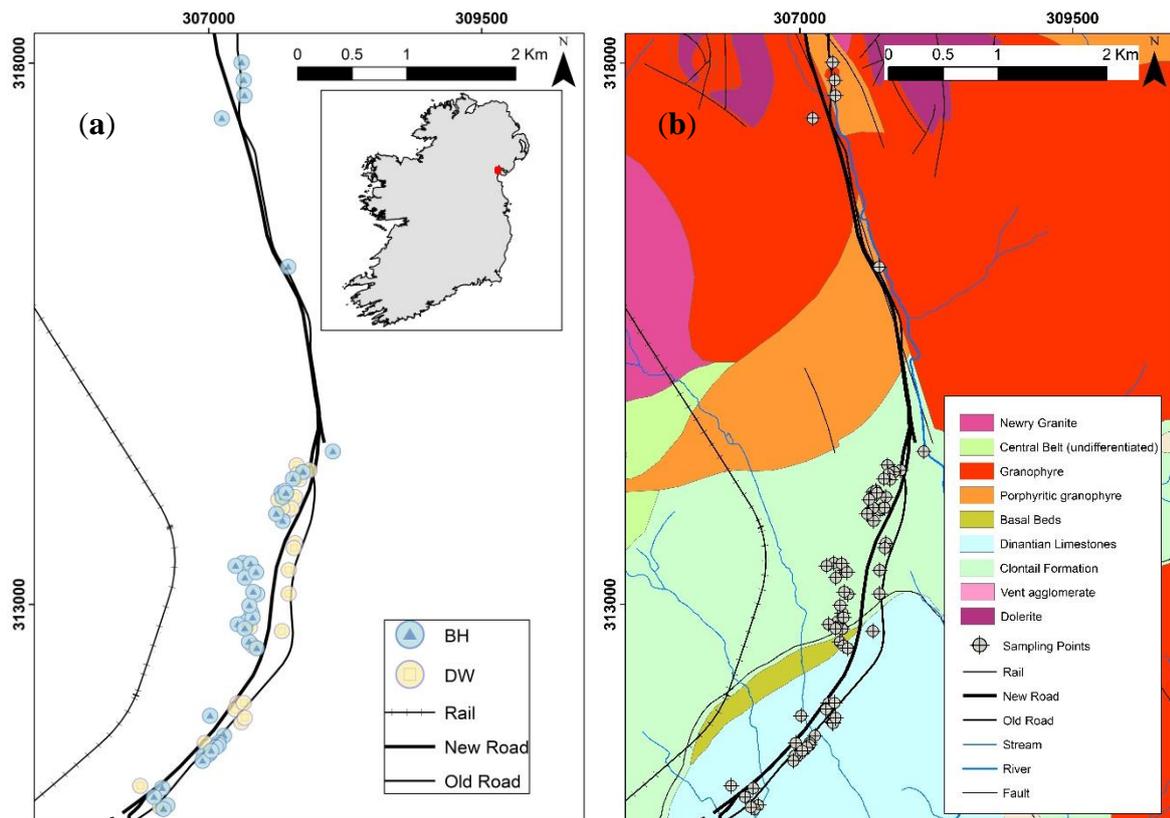


Fig. 5.1. Sampling points showing the (a) rail and road network (where DW is dug well and BH is borehole), (b) with bedrock geology (1:100K), (c) CORINE land use (where 112 = discontinuous urban fabric; 231 = pastures; 242 = complex cultivation patterns; 243 = land principally occupied by agriculture with areas of natural vegetation; 312 = coniferous forest; 313 = mixed forest; 321 = natural grassland; 322 = moors and heaths; 324 = transitional woodland scrub and 412 = peat bogs), (d) aquifer classification (where Pl = poor aquifer - bedrock which is generally unproductive except for local zones; Lm = locally important aquifer - bedrock which is generally moderately productive and Ll = locally important aquifer - bedrock which is moderately productive only in local zones), (e) groundwater vulnerability (where E = extreme; H = high; M = Moderate; L = low; W = water and X = rock at or near surface), and (f) elevation (meters; where contours were created from NASA's Shuttle Radar Topography Mission (SRTM) digital elevated model). The new dual carriageway is designated as 'New Road' while the old primary road is designated as 'Old Road'.

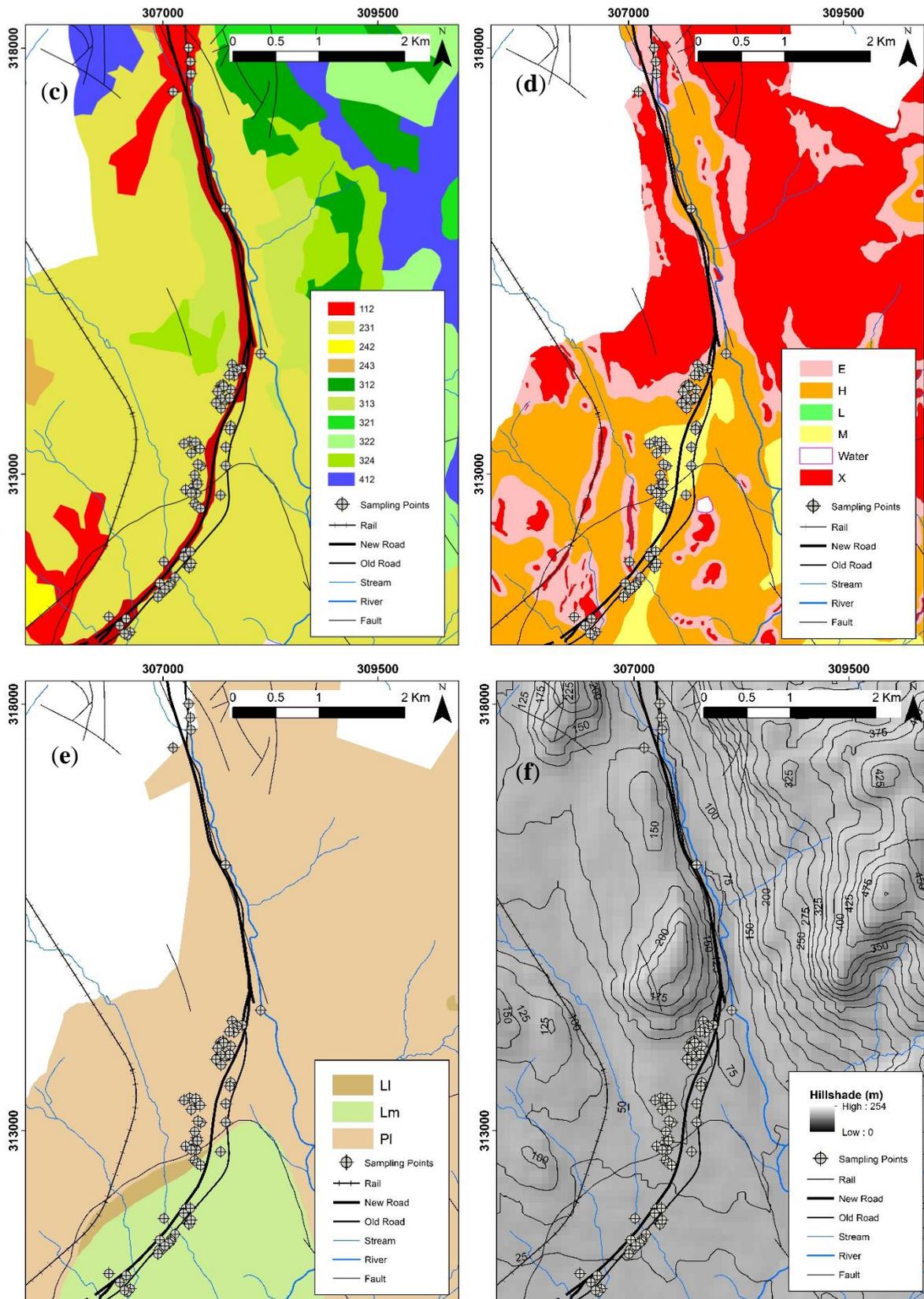


Fig. 5.1. (continued).

5.1.2) Groundwater sampling

Sampling of both shallow (≤ 6 m) and deep (> 6 m) groundwater wells was done quarterly by representatives of Mouchel Parkman on behalf of Louth County Council between 2004-2008 for 13 quarters. Sampling of private wells for 13 seasons monitored quarterly (2004-2008). Private groundwater wells were purged (3 well volumes) prior to sampling to remove stagnant water. However, due to the low permeability of the strata and groundwater ingress to the well was slow and thus full well volume was not recovered after each purge. This meant that the full 3 well volumes could not be accomplished at all sites. In these cases, one borehole volume was purged and was let recover where this process was repeated and then a groundwater sample was taken. Where it was impractical to purge (i.e. large diameter wells), a lower amount was completed, or a tap sample taken. At each sampling location water level measurements were taken using a dipmeter. For shorthand Well IDs are denoted numerically, i.e. W-22. Further information on the sampling of each well is seen in Table A1.1 (Appendix 1).

At each location, a dedicated bailer was used to recover a groundwater sample in order to prevent cross contamination and after each use, the bailer was cleaned and sealed in plastic sleeve. Field pH, conductivity and temperature was recorded at each site using a portable meter. These parameters were also recorded in the laboratory; however, field values are reported in the results. In some cases, it was not possible to monitor directly from the well, i.e. no access to the well, and samples were subsequently taken from the tap were after leaving it to run for 5-10 minutes.

Samples for dissolved trace elements (B, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Hg and Pb), anions (chloride (Cl^-), bromate (BrO_3^-), sodium (Na^+) fluoride (F^-), nitrate (NO_3^-), nitrite (NO_2^-), sulphate (SO_4^{2-})), turbidity, total organic carbon (TOC), and colour were collected in a plastic bottles (1000 cm^3). Samples for ammoniacal nitrogen ($\text{NH}_3\text{-N}$) were collected in plastic bottles with H_2SO_4 as a preservative. Microbiological samples (*Clostridium perfringens*, faecal Coliforms, faecal Streptococci and total Coliforms) were collected in four 250 cm^3 sterile bottles and were given to a courier for delivery to the laboratory for analysis (within a 6-hour limit). Pesticides and polycyclic aromatic hydrocarbons (PAHs) were collected in the field using 1000 cm^3 glass bottles. Volatile organic compounds (VOCs) were collected in 60 cm^3 vials at each sampling site.

5.1.3) Chemical analysis

Analysis of groundwater samples for a suite of microbiological, nutrient, organic and trace elements was completed by an ISO 17025 and UKAS accredited testing laboratory. Each

section below gives a more detailed overview on the analysis for each suite of parameters. Blank samples were analysed during the analytical run.

Specific details on the analysis of field parameters, microbiological parameters, nutrients, trace elements, and organic geochemistry (including polycyclic aromatic hydrocarbons, volatile organic compounds, and pesticides are presented in Appendix 2).

5.1.4) Data analysis

5.1.4.1) Rationale for statistical testing of one monitoring season

The 13 quarters of chemical data were collected from 2004-2008, however, the data from quarter five (November 2005) was used for analysis and interpretation due a high presence of censored data in the other quarters. Justification for choice of this quarter included; i) high DLs were observed from some parameters due to upgrading in analytical instrumentation during monitoring (2004-2008) by the testing laboratory, ii) greatest proportion of trace elements above the DL were present in November 2005, iii) quarter 5 shows low organic PAH contamination compared to other seasons, iv) several measurement anomalies (i.e. pH and temperature) occurred for physical parameters in later quarters, and v) quarter 5 contained dissolved trace element data, which was the most useful for the purposes of the present study.

5.1.4.2) Handling of data with multiple DLs

Due to the presence of multiple censored data during chemical analysis, the package non-detects and data analysis (NADA) (Lee, 2013) was used in the R statistical environment (R Development Core Team, 2017) based on methods from Helsel (2012). The empirical cumulative distribution function (ECDF) for each hydrochemistry variable was computed using the Kaplan-Meier method (Helsel, 2012).

5.1.4.3) Analysis by depth

Information in relation to well depth of some sampled sites was limited as only 39 sites had a depth value; therefore, wells were classified as being either a borehole (BH) or a dug well (DW) as a proxy for well depth (Table A2.1, Appendix 2). Descriptive statistics for variables for November 2005, taking account of censored values, were computed for BH/DW sites separately. For each hydrochemistry variable ECDF were computed separately for each depth category, BH and DW. To test for differences in ECDFs between the BH/DW variables, the log rank test was performed on the ECDFs.

The number of samples above guideline values are given as a percentage for each variable. In Ireland, these guideline values are not enforced for private groundwater supplies and as such they are used for informative and comparative reasons. The onus for checking if parameters are below guideline values falls to the homeowner of the private groundwater supply (Hooks et al., 2019).

5.1.4.4) Correlation analysis

Due to the presence of multiple DLs, the non-parametric correlation coefficient Kendall's tau (τ) was used to determine the strength of the monotonic relationship between pairs of variables, where pairs may be singly censored (one observation censored) or doubly censored (both observations censored) (Helsel and Hirsch, 2002; Helsel, 2012) using the *cenken* function in the NADA package (Lee, 2013). Strengths of correlation coefficients are described 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) with those deemed as significance relationships in the population denoted by * = p-value < 0.05, ** = p-value < 0.01, and *** = p-value < 0.001.

5.1.4.5) Multivariate methods

While univariate approaches use one variable at a time to perform statistical analysis, the application of multivariate techniques can be applied to understand the relationships of many parameters and observations (Grunsky, 2010; Wangkahad et al., 2017). These multivariate techniques can simplify the variation and relationships to a reduced number of dimensions which may be linked to a specific geochemical process (Grunsky, 2010). By implementing clustering algorithms distinct natural groupings within multi-dimensional data can be identified, i.e. based on similarities or differences (Grunsky, 2010; Wangkahad et al., 2010).

Hierarchical clustering was applied to cluster both variables (R-mode) and sampled sites (Q-mode) adopting Ward linkage between clusters. The distance matrix for wells was determined by calculating absolute difference in ECDF's, i.e. the distance between two individual wells, i and j , for the variable, v_k , is $d_{kij} = |F(v_{ki}) - F(v_{kj})|$, where $F(v_k)$ denotes the value of the Kaplan Meier estimated ECDF. The total distance between two individual wells, i and j , across all p variables considered is determined by Manhattan distance,

$$d_{ij} = \sum_{k=1 \dots p} d_{kij} = \sum_{k=1 \dots p} |F(v_{ki}) - F(v_{kj})| \quad (\text{Equation 5.1})$$

The distance matrix for variables was Kendall's tau correlation coefficient determined by the NADA *cenken* R command, i.e. the distance between two variables x and y , is

$$d_{xy} = \tau_{xy}(\text{Equation 5.2})$$

A heatmap was produced to display the values of the ECDFs and the resulting clustering dendrograms. This heatmap (or double dendrogram of parameters and sites) is a 2-D display of a data matrix showing magnitude as a colour (this colour is proportional to the magnitude along a colour gradient). Hierarchical clustering orders the rows and columns with similar rows and columns together on the heatmap.

5.1.4.6) *Spatial mapping*

Spatial mapping was completed for key parameters (As, pH, Fe, Mn, Se, Sb, NO_3^- and TC) with geology using a system of five classes (the class division depended on the parameter being investigated) using ArcGIS®10.2 (ESRI®, Colorado) in Irish National Grid (1965 Datum). Where non-detects were present they were binned into the first classification. In the case of microbiological parameters (i.e. TC), a detected value is classed as a failure so that the first intercal only contained non-detects, i.e. groundwater is free from microbial contamination. Thus, other classifications for microbiological parameters are designated as failures.

5.1.4.7) *Aqueous geochemical modelling*

As the redox state of the groundwater was not measured, Eh values were calculated ($\text{NO}_3^-/\text{NO}_2^-$ redox couple) in PHREEQCI V3.4 (Appelo and Postma, 2005) using the WATEQ4F database (Ball and Nordstrom, 1991). These calculated values were used to assist in the interpretation rather than being incorporated into statistical analysis. Saturation indices (SI) for minerals were also calculated for wells in November 2005. The SI is defined as the logarithm of the ratio of the ion activity product (IAP) of the component ions of the solid in solution to the solubility product (K) for the solid [$\text{SI} = \log \text{IAP}/\text{K}$]. The SI of a given mineral indicates whether the groundwater is undersaturated ($\text{SI} < 0$), at equilibrium ($\text{SI} = 0$), or supersaturated ($\text{SI} > 0$) (Naus et al., 2001; Appelo and Postma, 2005). If the groundwater is undersaturated with respect to a given mineral ($-\text{SI}$) then the groundwater would theoretically dissolve the mineral if present (Naus et al., 2001). If groundwater is supersaturated with respect to a given mineral ($+\text{SI}$), then the mineral would theoretically precipitate from the groundwater (Naus et al., 2001).

5.2) Results

5.2.1) Descriptive statistics

Results of the log rank test for differences in ECDF between the depth categories of BH and DW for different variables observed in November 2005 gives evidence of a difference for pH ($p < 0.001$) and water level ($p = 0.001$) only. Descriptive statistics (minimum, first quartile (Q_1), median, third quartile (Q_3) and maximum) with censoring rates and percentage of samples above the legal limit are provided for DW ($n=24$) and BH ($n=43$) samples for each of the variables for November 2005, in Tables 5.1-5.2. Table 3 shows the classification of microbiological parameters above certain thresholds for each parameter (where <1 CFU 100 mL^{-1} represents no microbiological contamination). Limit values were taken from the following references: interim guideline values (EPA, 2003) – total coliforms, faecal coliforms; groundwater regulations (EC, 2010) – NO_3^- , and drinking water regulations (EC, 2014) – pH, conductivity, *C. perfringens*, faecal Streptococci, F, SO_4^{2-} , Cl^- , BrO_3^- , Na, NO_2^- , NO_3^- , ammoniacal nitrogen, B, Al, Cr, Mn, Fe, Ni, Cu, As, Se, Sb, Pb and Hg. The pH of shallower groundwater of DWs (water level range of 0.29-4.64 m with median of 2.13 m) varied from acidic to weakly alkaline (6.11-7.47 pH units) to acidic to alkaline (6.37-8.19 pH units) for the deeper groundwater of BHs (water level range of 0-30 m with median of 3.82 m). Both groundwater depth categories contained sites which had a pH measured below the lower standard limit (6.5 pH units), while no sites from either depth category exceeded the upper limit (8.5 pH units). While the redox potential of groundwaters was not measured modelling using PHREEQC estimated that the Eh ranged from 385-602.9 mV (average, 507.1 mV; standard deviation, 44.8 mV). The correlation of water quality parameters is observed (Fig. 5.2 and Table A2.2, Appendix 2) with a censored scatterplot of pH and arsenic in Fig. 5.3.

Several transition series metals show a weak to moderate correlation with each other (e.g. Cr, Ni, Fe and Mn) (Fig. 5.2). Both Fe and Mn were generally measured at low concentrations in groundwaters, with observed median values for DWs (Fe $2 \mu\text{g L}^{-1}$ and Mn $1 \mu\text{g L}^{-1}$) and BHs (Fe $7 \mu\text{g L}^{-1}$ and Mn $1 \mu\text{g L}^{-1}$). The highest concentration of Fe was measured at $12820 \mu\text{g L}^{-1}$ in a borehole (W-57), with an alkaline pH (7.99 pH units) and an arsenic concentration of $9 \mu\text{g L}^{-1}$. The next highest value of Fe was recorded in a dug well (W-5) with an Fe concentration of 769 L^{-1} , with an acidic pH (6.75 pH units) and an arsenic concentration of $<1 \text{ L}^{-1}$. This well also had the highest Mn concentration of $584 \mu\text{g L}^{-1}$. In comparison to Fe and Mn, Al was detected at lower concentrations, with the maximum value being $119 \mu\text{g L}^{-1}$ (8.05 pH units) in a borehole (W-22). The concentration of detected mercury ranged from 0.5-

0.1 $\mu\text{g L}^{-1}$ in this study, which is lower than the naturally occurring concentration of 0.5 $\mu\text{g L}^{-1}$ in groundwater (WHO, 2005). In this study, arsenic is the most detected trace element above the legal limit of 10 $\mu\text{g L}^{-1}$ (8.3% for DWs and 18.6% for BHs). This observation has been seen in other studies (Bondu et al., 2017a).

5.2.2) Saturation indices

The SIs of several Fe, Mn, Al and Cu minerals was tabulated in Table 5.4.

Table 5.1. Summary statistics of groundwater parameters for November 2005 with notes on censoring and number of samples above parametric value for DW (n = 24) (where Q₁ is quartile 1 and Q₃ is quartile 3).

Parameter	Units	Min	Q ₁	Median	Q ₃	Max	%Cen	Limit	%> Limit
pH	pH units	6.11	6.63	6.73	7.13	7.47	0	≥ 6.5 and ≤ 9.5	12.5
Conductivity	mS cm^{-1}	0.20	0.39	0.48	0.65	0.84	0	2.5	0
Temperature	$^{\circ}\text{C}$	6.6	9.5	10.3	11.2	12.5	0	-	NA
Water level	m	0.29	1.77	2.13	2.9	4.64	8.3	-	NA
<i>C. perfringens</i>	CFU 100 mL^{-1}	1	2	18.5	28	213	33.3	0	66.6
F. coliforms	CFU 100 mL^{-1}	1	-	1	-	9	79.1	0	20.8
T. coliforms	CFU 100 mL^{-1}	0	10	50	142	346	8.3	0	91.6
F. Streptococci	CFU 100 mL^{-1}	1	-	1	-	11	70.8	0	29.1
F ⁻	mg L^{-1}	-	-	0.1	0.3	0.6	41.6	1.5	0
SO ₄ ²⁻	mg L^{-1}	8	20.5	28.5	34.5	71	0	250	0
Cl ⁻	mg L^{-1}	4	15	25.5	38	94	0	250	0
BrO ₃ ⁻	mg L^{-1}	-	-	-	-	-	100	0.01	0
TOC	mg L^{-1}	4	21	27.5	34	51	0	-	NA
Na ⁺	mg L^{-1}	8.5	11.75	13.5	16.75	26	0	200	0
NO ₃ ⁻	mg L^{-1}	0.3	10.5	18.6	34.6	134.1	4.1	50	8.3
No ₂	mg L^{-1}	-	-	0.05	0.06	7.05	70.8	0.5	12.5
Ammoniacal N	mg L^{-1}	-	-	0.20	0.26	-	100	0.3	0
Colour	Hazen	0	0.5	4	7	16	0	-	NA
Turbidity	NTU	0.1	0.15	0.25	0.4	1	0	-	NA
B	$\mu\text{g L}^{-1}$	3	17.5	29	37.5	74	4.1	1000	0
Al	$\mu\text{g L}^{-1}$	-	2	3.5	4	76	62.5	200	0
Cr	$\mu\text{g L}^{-1}$	1	-	4	6.5	33	29.1	50	0
Mn	$\mu\text{g L}^{-1}$	-	-	1	2.5	584	54.1	50	8.3
Fe	$\mu\text{g L}^{-1}$	-	-	2	23	769	54.1	200	4.1
Ni	$\mu\text{g L}^{-1}$	-	-	1	2	10	54.1	20	0
Cu	$\mu\text{g L}^{-1}$	1	2	3.5	5	60	37.5	2000	0
As	$\mu\text{g L}^{-1}$	-	-	1	-	11	79.1	10	8.3
Se	$\mu\text{g L}^{-1}$	-	-	1	-	2	70.8	10	0
Sb	$\mu\text{g L}^{-1}$	-	-	1	-	2	83.3	5	0
Hg	$\mu\text{g L}^{-1}$	-	-	0.05	-	0.09	87.5	1	0
Pb	$\mu\text{g L}^{-1}$	-	-	1	-	2	95.8	10	0

Table 5.2. Summary statistics of groundwater parameters for November 2005 with notes on censoring and number of samples above parametric value for BH (n = 43). (where Q₁ is quartile 1 and Q₃ is quartile 3).

Parameter	Units	Min	Q ₁	Median	Q ₃	Max	%Cen	Limit	%> Limit
pH	pH units	6.37	6.99	7.35	7.61	8.19	0	≥6.5 and ≤9.5	4.6
Conductivity	mS cm ⁻¹	0.11	0.38	0.43	0.54	0.91	0	2.5	0
Temperature	°C	6.4	9.45	10.2	11	15.5	0	-	NA
Water level	m	0	2.85	3.82	6.36	16.33	13.9	-	NA
<i>C. perfringens</i>	CFU 100 mL ⁻¹	-	-	1	3	167	51.1	0	48.8
F. coliforms	CFU 100 mL ⁻¹	-	-	1	-	3	90.6	0	9.3
T. coliforms	CFU 100 mL ⁻¹	1	1.25	31	92	530	23.3	0	76.7
F. Streptococci	CFU 100 mL ⁻¹	-	-	1	-	21	83.7	0	16.3
F ⁻	mg L ⁻¹	-	-	0.1	0.2	3.1	27.9	1.5	2.3
SO ₄ ²⁻	mg L ⁻¹	4	16.75	24	38.75	135	0	250	0
Cl ⁻	mg L ⁻¹	7	14.25	18	28.75	114	0	250	0
BrO ₃ ⁻	mg L ⁻¹	-	-	0.0	-	0.06	95.3	0.01	2.3
TOC	mg L ⁻¹	3	6.5	22	39.25	56	0	-	NA
Na ⁺	mg L ⁻¹	8	11.63	14.5	18.38	78	0	200	0
NO ₃ ⁻	mg L ⁻¹	0.3	5.43	13.2	21.9	88.1	16.3	50	7
No ₂	mg L ⁻¹	-	-	0.05	0.06	8.95	76.7	0.5	11.6
Ammoniacal N	mg L ⁻¹	-	-	0.20	0.26	2.7	88.3	0.3	9.3
Colour	mg L ⁻¹	0	0	0	2	16	0	-	NA
Turbidity	mg L ⁻¹	0.1	0.2	0.4	0.5	11.9	2.3	-	NA
B	µg L ⁻¹	3	17.25	27	36.75	76	9.3	1000	0
Al	µg L ⁻¹	-	-	2	6.73	119	51.1	200	0
Cr	µg L ⁻¹	1	3	5	7.75	334	16.2	50	2.3
Mn	µg L ⁻¹	-	-	1	3	148	48.8	50	6.9
Fe	µg L ⁻¹	2	-	7	23.75	12820	39.5	200	2.3
Ni	µg L ⁻¹	-	-	1	3	256	37.2	20	4.6
Cu	µg L ⁻¹	-	-	1	5	100	53.4	2000	0
As	µg L ⁻¹	-	-	1	3.5	25	60.4	10	18.6
Se	µg L ⁻¹	-	-	1	-	18	62.7	10	2.3
Sb	µg L ⁻¹	-	-	1	-	6	62.7	5	4.6
Hg	µg L ⁻¹	-	-	0.05	-	0.1	83.7	1	0
Pb	µg L ⁻¹	-	-	1	-	16	86.1	10	0

Table 5.3. Degree of contamination of microbiological parameters (n=67)

Microbe	Degree of contamination (CFU 100 mL ⁻¹)			
	<1	≥1 and ≤10	≥10 and ≤100	≥100
<i>Clostridium perfringens</i>	31	24	9	4
Faecal coliforms	58	9	0	0
Faecal Streptococci	53	11	3	0
Total coliforms	12	11	27	17

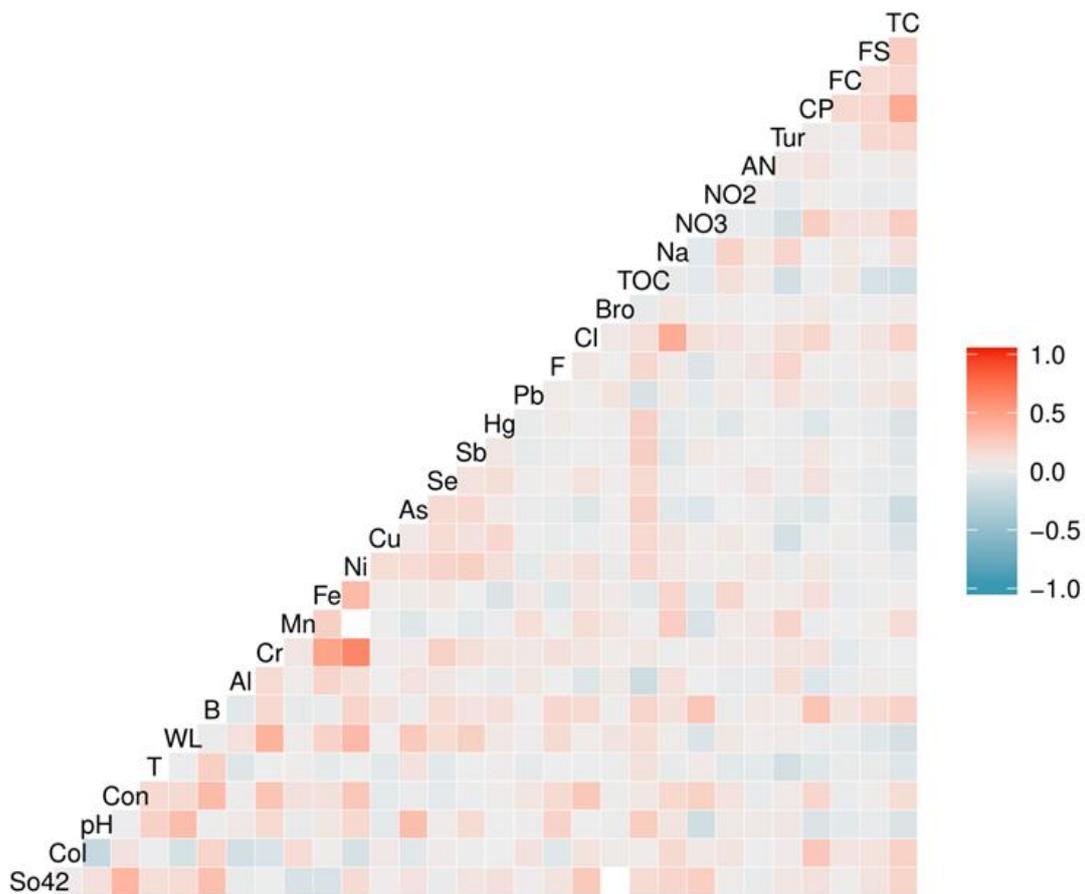


Fig. 5.2. Correlation matrix of Kendall's tau correlation calculated using NADA *cenken* function for November 2005. Red is indicative of a strong positive correlation (1.0), no colour is no correlation (0), and blue is a strong negative correlation (-1.0).

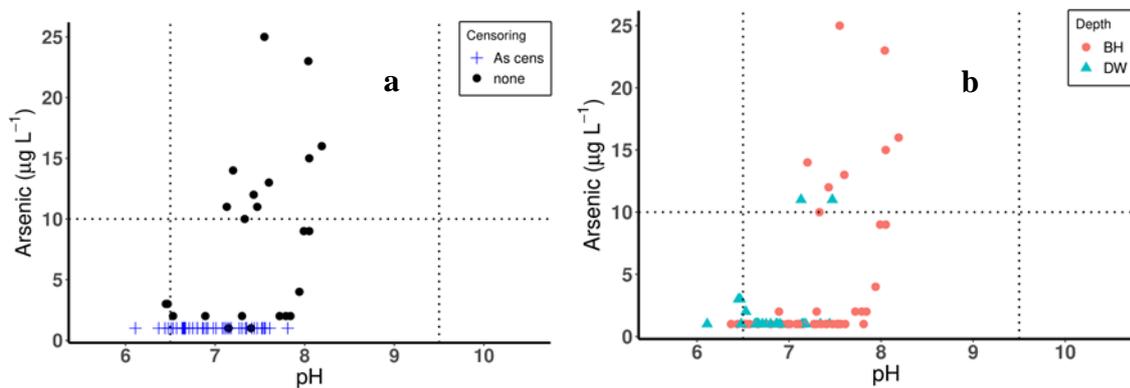


Fig. 5.3. Scatterplot of arsenic and pH, with (a) indication to the prevalence of censoring and (b) indication of depth.

Table 5.4. SIs for Fe, Mn, Al and Cu minerals

Name	Formula	Median	Average	SD	Min	Max
Basaluminate	Al ₄ (OH)10SO ₄	-0.77	-0.76	2.77	-7.83	6.82
Boehmite	AlOOH	0.27	0.30	0.52	-0.78	1.93
Cupric ferrite	CuFe ₂ O ₄	8.57	8.39	3.30	-0.42	18.02
Cuprous ferrite	CuFeO ₂	11.14	11.14	1.43	6.91	15.07
Diaspore	AlOOH	2.11	2.14	0.52	1.04	3.77
Fe(OH) ₂ .7Cl.3	Fe(OH) ₂ .7Cl.3	4.88	4.81	1.34	1.63	9.39
Fe(OH) ₃ (a)	Fe(OH) ₃	0.19	0.06	1.46	-3.54	4.86
Gibbsite	Al(OH) ₃	0.95	0.98	0.52	-0.13	2.62
Goethite	FeOOH	5.49	5.34	1.47	1.8	10.2
Hematite	Fe ₂ O ₃	12.92	12.62	2.96	5.53	22.33
Maghemite	Fe ₂ O ₃	3.61	3.42	2.93	-3.69	13.12
Magnetite	Fe ₃ O ₄	11.58	11.28	4.01	1.67	24.99

5.2.3) Spatial mapping

Interval mapping of groundwater quality parameters are illustrated in Fig. 5.4a-h with the corresponding number of values per classification illustrated in Table 5.5. As can be seen in the below table, many samples were below the legal limits. Similar spatial distributions were observed for the same groups of parameters. For example, arsenic shows a spatial cluster in the central to southern area in this study (Fig. 5.4a) with concentrations $\geq 10 \mu\text{g L}^{-1}$ with pH also showing high values in these locations (≥ 7.5 pH units). Similar spatial associations are seen with water level with some spatial overlap existing with selenium and antimony. Also, in this high arsenic cluster there are low concentrations of both Fe and Mn. There is another spatial cluster of high pH (≥ 7.5 pH units) to the south, but arsenic concentrations are $7.5 \mu\text{g L}^{-1}$.

For several parameters isolated high concentrations of trace elements were observed, e.g. Fe. By comparison, other trace elements had several spatial clusters, including Mn. There is a large variation in spatial distribution for NO₃⁻ showing the widespread contamination of this nutrient. Most other nutrients were detected at low concentrations with low sample numbers measured at concentrations above the legal limit, e.g. NO₂⁻ and ammoniacal nitrogen. While low numbers were detected for faecal coliforms and faecal streptococci, higher numbers were seen for total coliforms, and to a somewhat lesser degree for *C. perfringens* (Table 5.5).

Table 5.5. Number of monitoring sites for each classification (refer to Fig. 5.4a-h for classification)

Class	pH (pH units)		EC (mS cm ⁻¹)		T (°C)	
	Interval	Number	Interval	Number	Interval	Number
1	(6.11,6.5]	6	(0.11,0.2]	2	(6.4,8]	7
2	(6.5,7]	22	(0.2,0.4]	21	(8,10]	15
3	(7,7.5]	22	(0.4,0.6]	29	(10,12]	41
4	(7.5,8]	13	(0.6,0.8]	10	(12,14]	2
5	(8,8.19]	4	(0.8,0.909]	5	(14,15.5]	2

Table 5.5. (continued).

WL (m)		CP (CFU 100 mL⁻¹)		FC (CFU 100 mL⁻¹)		
Class	Interval	Number	Interval	Number	Interval	Number
1	(0,3]	28	(0,1]	30	(0,1]	58
2	(3,6]	19	(1,10]	24	(1,5]	8
3	(6,9]	7	(10,100]	9	(5,9]	1
4	(9,12.76]	3	(100,200]	3	-	-
5	(12.76,30]	3	(200,213]	1	-	-
TC (CFU 100 mL⁻¹)		FS (CFU 100 mL⁻¹)		SO₄²⁻ (mg L⁻¹)		
Class	Interval	Number	Interval	Number	Interval	Number
1	(0,1]	12	(0,1]	54	(4,10]	6
2	(1,10]	11	(1,10]	10	(10,30]	33
3	(10,100]	28	(10,21]	3	(30,50]	24
4	(100,200]	8	-	-	(50,70]	2
5	(200,530]	8	-	-	(70,135]	2
Cl (mg L⁻¹)		AN (mg L⁻¹)		Turbidity (NTU)		
Class	Interval	Number	Interval	Number	Interval	Number
1	(4,10]	6	(0,0.258]	62	(0.1,0.3]	28
2	(10,30]	47	(0.258,0.3]	1	(0.3,0.6]	26
3	(30,50]	9	(0.3,2.7]	4	(0.6,1]	5
4	(50,70]	4	-	-	(1,3.7]	6
5	(70,114]	1	-	-	(3.7,11.9]	2
TOC (mg L⁻¹)		NO₃⁻ (mg L⁻¹)		NO₂⁻ (mg L⁻¹)		
Class	Interval	Number	Interval	Number	Interval	Number
1	(3,10]	16	(0.3,25]	50	(0,0.05]	50
2	(10,20]	6	(25,50]	12	(0.05,0.5]	9
3	(20,30]	18	(50,75]	3	(0.5,1]	1
4	(30,40]	14	(75,100]	1	(1,5]	4
5	(40,56]	13	(100,134.1]	1	(5,8.95]	3
Colour (Hazen)		Na (mg L⁻¹)		F (mg L⁻¹)		
Class	Interval	Number	Interval	Number	Interval	Number
1	(0,1]	35	(8,10]	4	(0,0.1]	21
2	(1,2]	10	(10,20]	48	(0.1,0.2]	20
3	(2,5]	17	(20,40]	13	(0.2,0.5]	21
4	(5,10]	4	(40,60]	1	(0.5,1]	4
5	(10,16]	1	(60,78]	1	(1,3.1]	1
B (µg L⁻¹)		Al (µg L⁻¹)		Ni (µg L⁻¹)		
Class	Interval	Number	Interval	Number	Interval	Number
1	(3,10]	7	(0,10]	58	(0,1]	28
2	(10,30]	29	(10,20]	4	(1,5]	33
3	(30,50]	27	(20,50]	2	(5,20]	4
4	(50,70]	1	(50,100]	2	(20,50]	1
5	(70,76]	3	(100,119]	1	(50,256]	1
Cr (µg L⁻¹)		Mn (µg L⁻¹)		Fe (µg L⁻¹)		
Class	Interval	Number	Interval	Number	Interval	Number
1	(0,1]	14	(0,1]	34	(0,50]	60
2	(1,5]	15	(1,50]	28	(50,100]	3
3	(5,10]	28	(50,100]	2	(100,200]	2
4	(10,50]	9	(100,200]	2	(200,1000]	1
5	(50,334]	1	(200,584]	1	(1000,12820]	1

Table 5.5. (continued).

Cu ($\mu\text{g L}^{-1}$)			Pb ($\mu\text{g L}^{-1}$)		Sb ($\mu\text{g L}^{-1}$)	
Class	Interval	Number	Interval	Number	Interval	Number
1	(0,1]	32	(0,1]	60	(0,1]	52
2	(1,5]	16	(1,10]	6	(1,5]	13
3	(5,20]	15	(10,16]	1	(5,6]	2
4	(20,50]	2	-	-	-	-
5	(50,100]	2	-	-	-	-

As ($\mu\text{g L}^{-1}$)			Se ($\mu\text{g L}^{-1}$)		Hg ($\mu\text{g L}^{-1}$)	
Class	Interval	Number	Interval	Number	Interval	Number
1	(0,1]	43	(0,1]	49	(0,0.05]	57
2	(1,7.5]	12	(1,10]	17	(0.05,0.09]	7
3	(7.5,10]	3	(10,18]	1	(0.09,0.10]	3
4	(10,20]	7	-	-	-	-
5	(20,25]	2	-	-	-	-

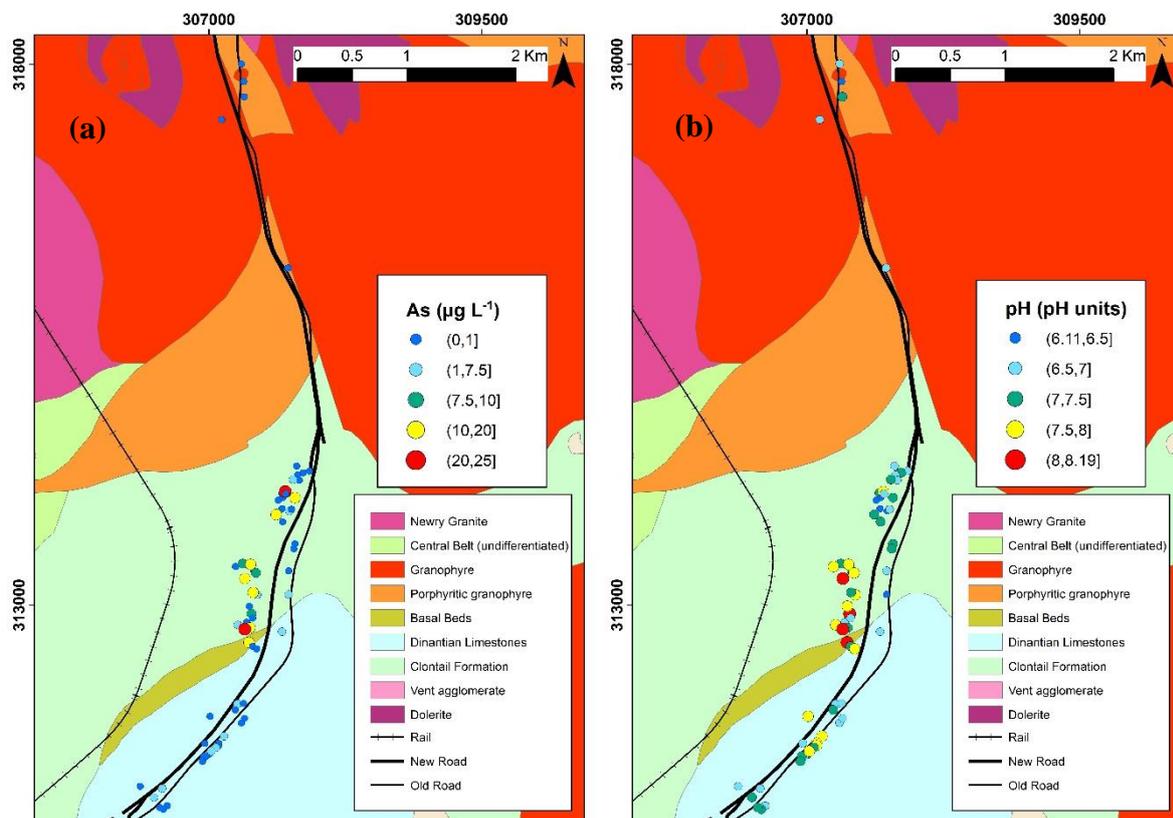


Fig. 5.4. Spatial distribution of parameters divided into five classifications for (a) arsenic, (b) pH, (c) iron, (d) manganese, (e) antimony, (f) selenium, (g) nitrate, and (h) total coliforms.

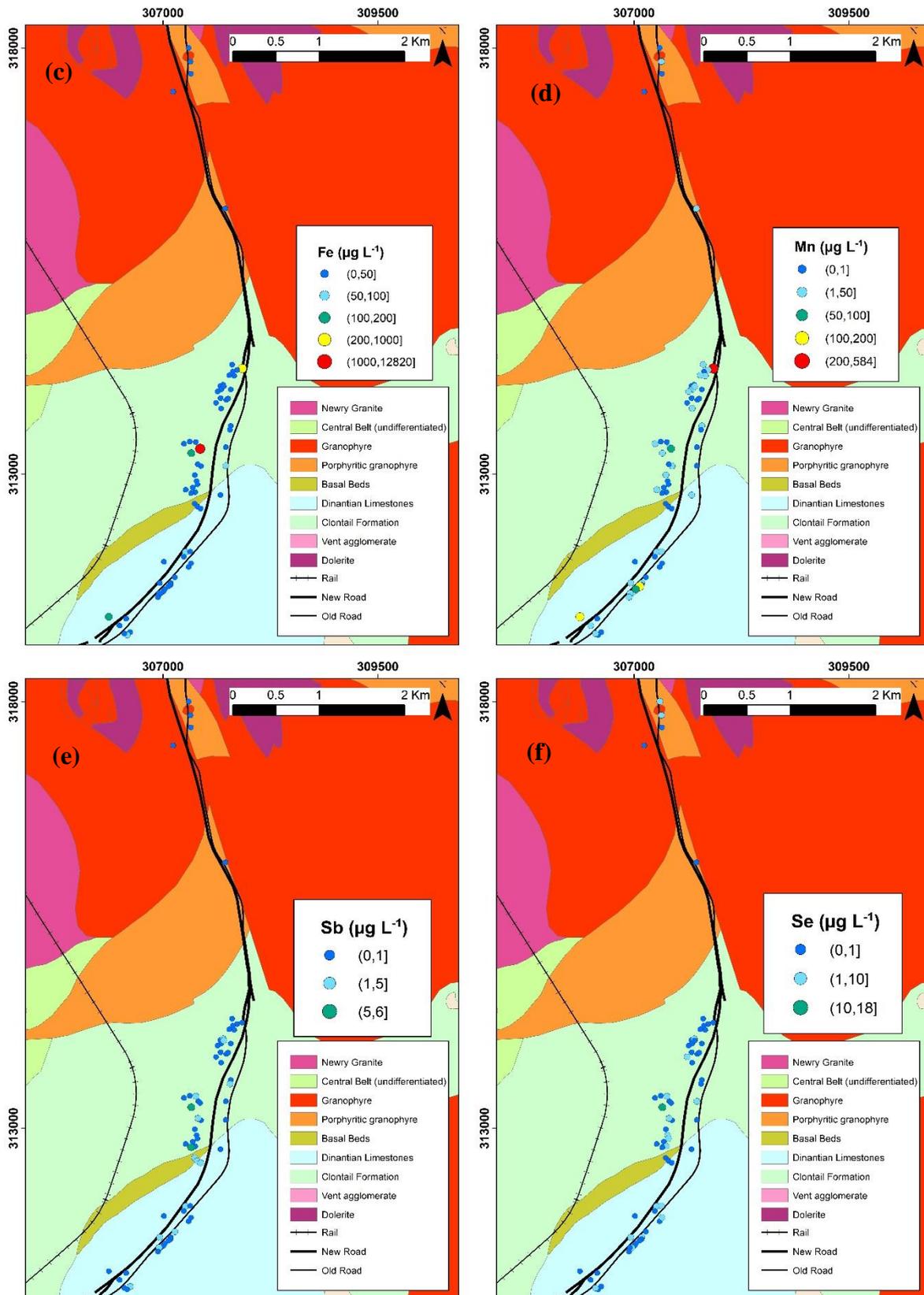


Fig. 5.4. (continued).

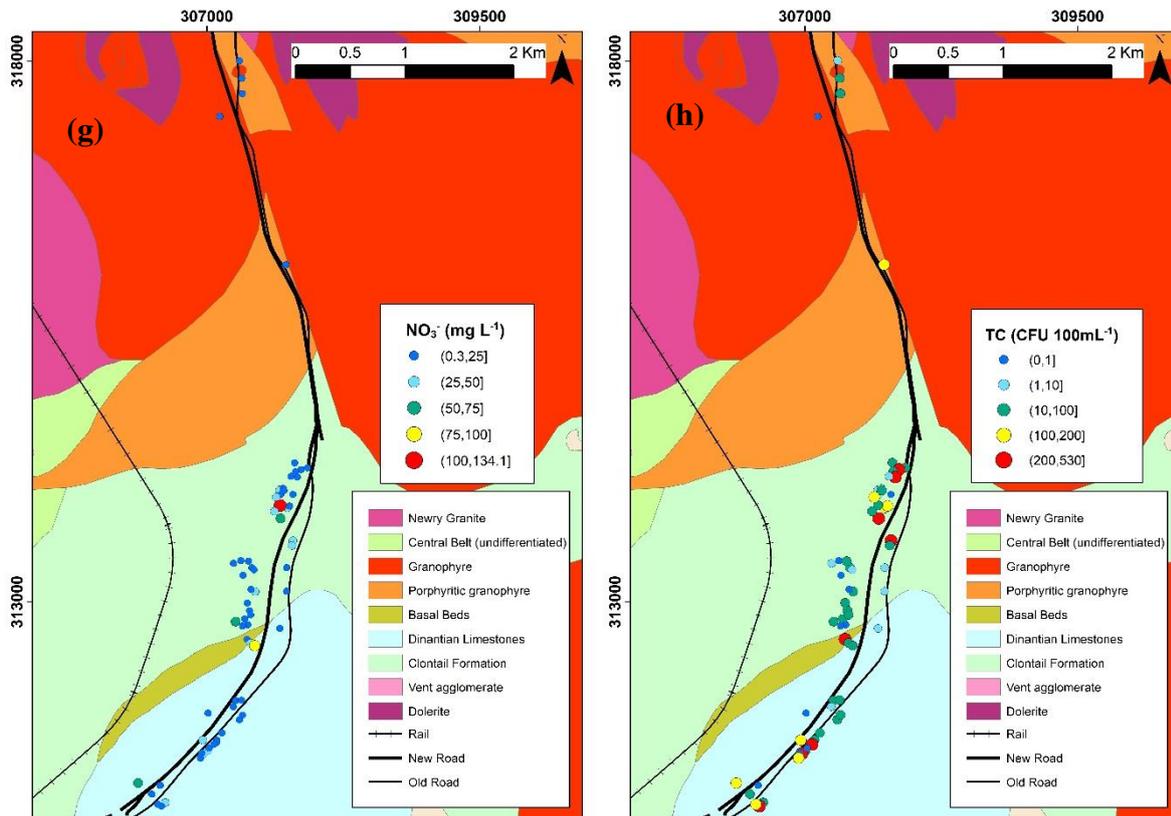


Fig. 5.4. (continued).

5.2.4) Hierarchical clustering

Table 5.6 shows the partition of variables at the specification of five clusters with the combined dendrogram of both variables and sites illustrated in Fig. 5.5. Table 5.7 shows the partition of sites at the specification of three clusters, resulting in clusters of 32, 21 and 14 sites which are subsequently spatially mapped in Fig. 5.6.

Table 5.6. Variables in clusters from heatmap

Cluster	Variables
1	Fe, Cr, and Ni
2	Se, Cu, Hg, pH, As, Sb, and TOC
3	NO ₂ ⁻ , Cl, and Na
4	F, ammoniacal N, Pb, Mn, turbidity, Al, and BrO ₃ ⁻
5	temperature, NO ₃ ⁻ , B, SO ₄ ²⁻ , conductivity, Colour, <i>C. perfringens</i> , total coliforms, faecal coliforms, and faecal streptococci

Table 5.7. Sites in clusters from heatmap

Cluster	Sites
1	W-2, W-6, W-11, W-16, W-18, W-19, W-21, W-23, W-24, W-25, W-26, W-27, W-28, W-30, W-31, W-33, W-34, W-35, W-38, W-46, W-48, W-49, W-50, W-51, W-53, W-54, W-55, W-56, W-57, W-58, W-60, and W-61
2	W-1A/1B, W-1C, W-3, W-5, W-7, W-8, W-9, W-10, W-12, W-13, W-14A, W-14B, W-15A, W-15B, W-29, W-32, W-37, W-39, W-47, W-52, and W-66

Table 5.7. (continued).

Cluster	Sites
3	W-17, W-22, W-36, W-40, W-41, W-42, W-43, W-44, W-45, W-59, W-62, W-63, W-64, and W-65

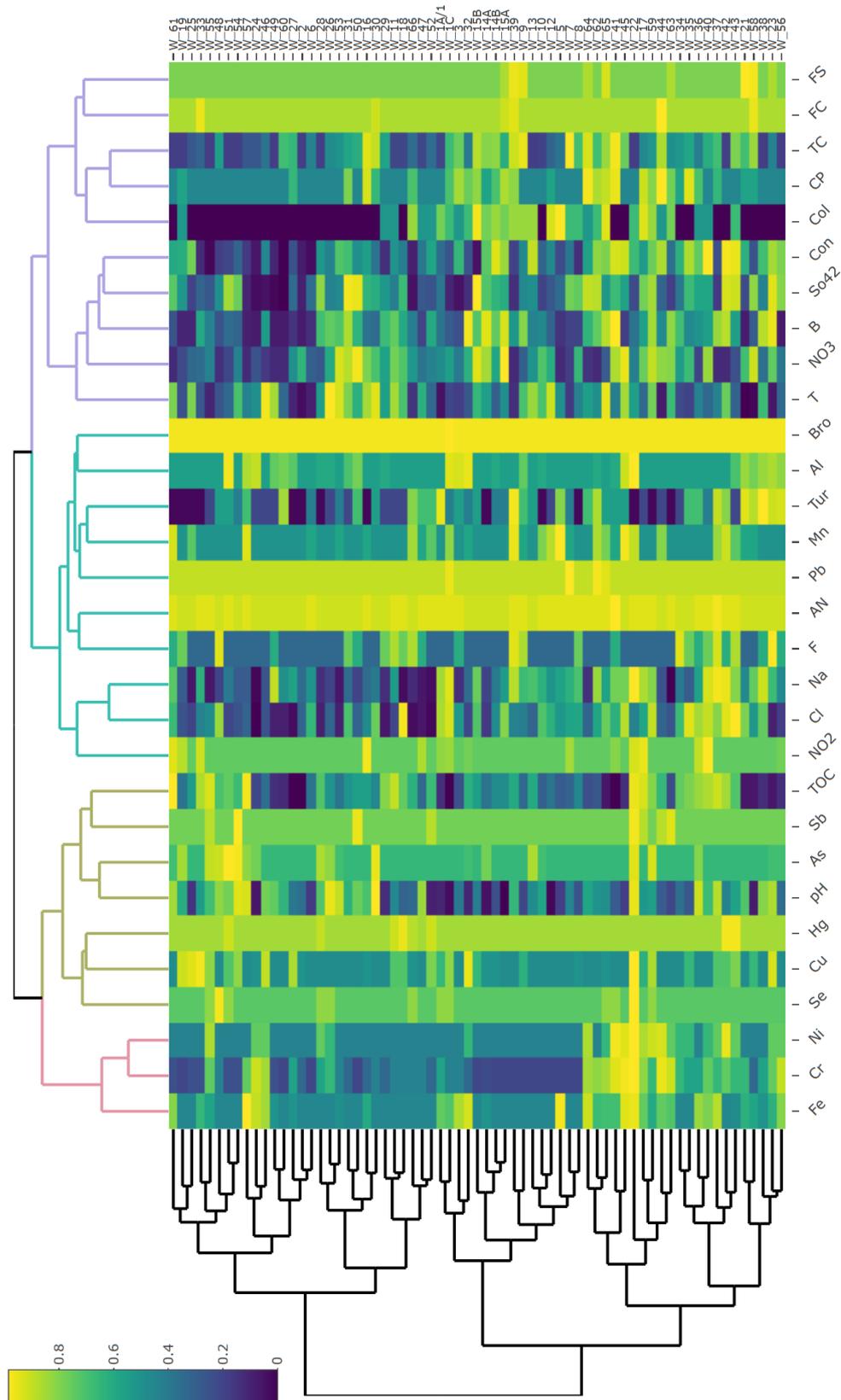


Fig. 5.5. Heatmap of relative standing ECDF values for November 2005, with variables on the X-axis clustered by Kendall's tau using *cenken* function and sites on the Y-axis clustered by interval distances of on ECDF values.

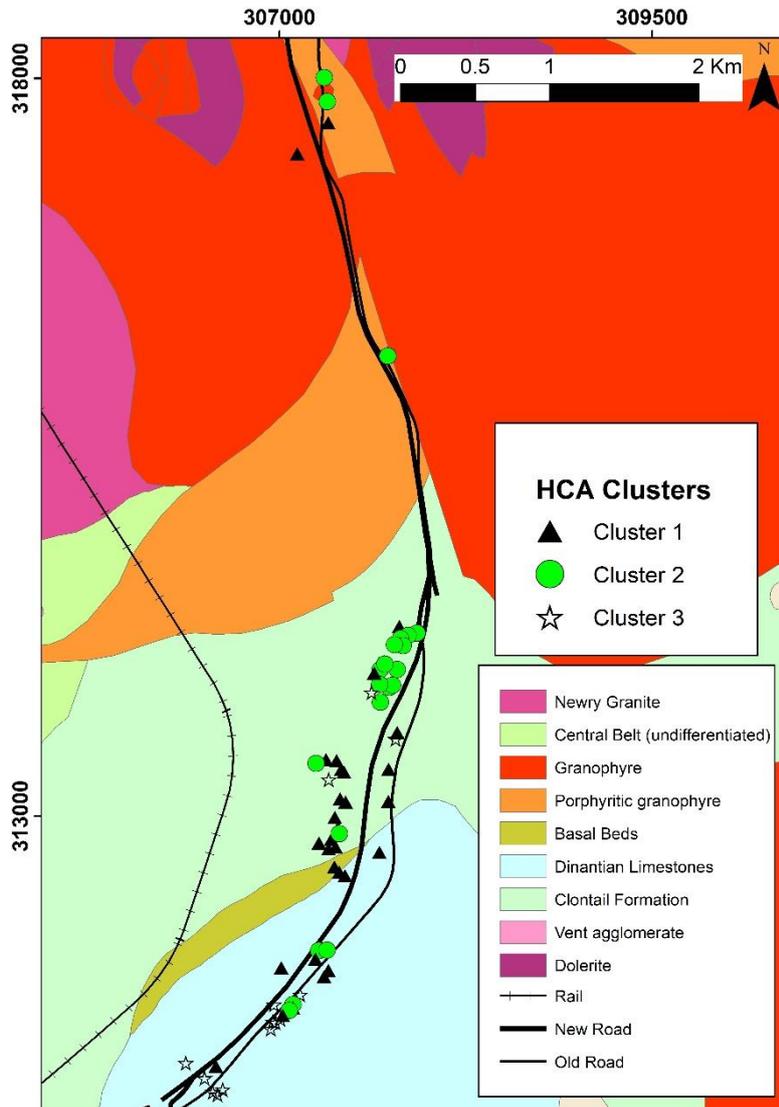


Fig. 5.6. Spatial distribution of three clusters of groundwater wells where sites within the same cluster are deemed to have similarity with respect to the variables measured in November 2005.

5.2.5) Organic geochemistry

No incidences of pesticides or PAHs were detected in any wells in November 2005 with only a small number of VOCs were detected in one well (W-7): methyl tert-butyl ether (MTBE) and carbon disulphide (58 and 14 $\mu\text{g L}^{-1}$ respectively).

5.3) Discussion

5.3.1) Trace element and arsenic groundwater geochemistry

Several geological and environmental settings (such as deltas, crystalline bedrock, unconsolidated sediments, mineralisation, etc) in combination with geochemical processes (geothermal, sulphide oxidation, alkali desorption and reductive dissolution) can contribute to

the mobilisation of arsenic from the host material into the surrounding groundwater (Ravenscroft et al., 2009; Smedley and Kinniburgh, 2013). Based on the geochemistry of this present study, arsenic is being mobilised through the process of alkali-desorption as shown from the various statistical analysis. Mobilisation of arsenic arising from alkali desorption often produce groundwaters that give rise to elevated arsenic in addition to other oxyanion-forming elements (such as antimony, selenium and uranium) through desorption from amorphous or crystalline oxyhydroxides (Ravenscroft et al., 2009; Smedley and Kinniburgh, 2013). This geochemical process can be inferred from several key geochemical signatures of this process. While pH is a key indicator of metal mobility and of alkali desorption, it shows a weak increasing association with arsenic in the present study ($\tau=0.27^{***}$) (Fig. 5.2 and Table A2.2), which may be lower than expected due to a high number of more acidic dug wells in this study and potential outliers (see below). While the pH values have a narrow range in this study (6.11-8.19 pH units) elevated arsenic concentrations occur at an alkaline pH (> 7.5) (Fig. 5.3a-b). Several locations in this study which had elevated concentrations of arsenic also contained detected selenium and/or antimony (Fig. 5.4e-f). In these groundwaters arsenic shows a positive correlation with selenium ($\tau=0.11^*$) (see cluster two, Table 5.6). The presence of elevated oxidised N species such as NO_3^- is also indicative of this mobilisation process (Ravenscroft et al., 2009) as alkali-oxic groundwaters are needed for this geochemical process. While Eh was not measured, thermodynamic calculations indicate that the groundwater is oxic. Several metal oxides (e.g. cuprous ferrite, diaspore, goethite and gibbsite) are supersaturated in these groundwaters, which is indicative of precipitation or desorption (Table 5.4). These supersaturated mineral phases indicate that these Fe and Mn oxides (and to a lesser extent Al and Cu) may be responsible for release and transport of arsenic in groundwaters through the process of alkaline desorption as observed in the bedrock aquifers of Argentina, USA, and Spain (Smedley et al., 2002; Ravenscroft et al., 2009; Smedley and Kinniburgh, 2013). These observations are supported from cluster two (Table 5.6) from the HCA. Furthermore, the lack of a correlation between arsenic and iron in this study is indicative of reductive dissolution or desorption processes (Levitt et al., 2019). Interestingly, arsenic is also clustered with TOC (cluster two, Table 5.6) with these two variables showing a weak positive correlation ($\tau=0.16^*$) (Fig. 5.2), suggesting that the source of arsenic may be organic, however further work would need to be carried out to assess this. Generally arsenic mobilisation through alkali desorption produces waters with arsenic concentrations $< 100 \mu\text{g L}^{-1}$ (Ravenscroft et al., 2009) with concentrations in this study having a maximum concentration of $25 \mu\text{g L}^{-1}$. Groundwaters with elevated arsenic concentrations ($\geq 10 \mu\text{g L}^{-1}$) are associated with alkaline pH (7.13-8.19 pH

units), detection of antimony and/or selenium, moderate SO_4^{2-} ($\leq 42 \text{ mg L}^{-1}$), low Fe and Mn ($\leq 14 \text{ }\mu\text{g L}^{-1}$ for Fe and $\leq 2 \text{ }\mu\text{g L}^{-1}$ for Mn) and low or no microbial contamination. In contrast when Fe and/or Mn concentrations are $\geq 20 \text{ }\mu\text{g L}^{-1}$ then low arsenic concentrations are measured (maximum arsenic concentration of $3 \text{ }\mu\text{g L}^{-1}$) with a mixed a pH of 6.38-8.04. Based on threshold values of key parameters (e.g. NO_3^- , Fe and Mn and SO_4^{2-}) it is likely that there are mixed redox processes occurring in these groundwaters (McMahon and Chapelle, 2008). Most sites exhibiting elevated arsenic concentrations are observed in the Clontail Formation with corresponding lower concentrations in the Dinantian Limestones (Fig. 5.5a).

Whilst most of the elevated arsenic in groundwater is inferred from alkali-desorption, other processes may be having a greater influence on two distinct wells: W-57 and W-23. The process of reductive dissolution is the most commonly encountered arsenic mobilisation mechanism encountered worldwide in groundwaters which affects many regions in southeast Asia (e.g. West Bengal and Bangladesh) through the microbial mediated process of reductive dissolution of arsenic from metal oxides (e.g. Fe) (Smedley and Kinniburgh, 2013; Ali et al., 2019). This process may be occurring in W-57 (dissolved Fe was $12820 \text{ }\mu\text{g L}^{-1}$), but as an isolated incident it may have occurred from contamination from sampling or specific well conditions (i.e. stagnant water).

Oxidising conditions (using theoretically calculated Eh values) are prevalent in these groundwaters and as such the elevated arsenic can also result from sulphide oxidation, i.e. W-22. Although not as prevalent as reductive dissolution, the processes of sulphide oxidation (and alkali desorption) have given rise to elevated arsenic concentrations in groundwater particularly in fractured bedrock aquifers (Smedley et al., 2002; Ayotte et al., 2003; Hudson-Edwards and Archer, 2012; Ryan et al., 2015a; Bondu et al., 2017b). Under the process of sulphide oxidation, the oxidation of sulphide minerals such as arsenopyrite, pyrite and pyrrhotite occurs to produce SO_4^{2-} rich (often up to hundreds of mg L^{-1}) acidic groundwaters, in addition to increased concentrations of other trace elements (e.g. Ni, Pb, Cu, Zn, and Cd) (Ravenscroft et al., 2009; Smedley and Kinniburgh, 2013). Besides one anomaly (e.g. W-22) concentrations of these trace elements were generally low. In W-23 several trace elements were measured at elevated values: Al ($119 \text{ }\mu\text{g L}^{-1}$), Cr ($334 \text{ }\mu\text{g L}^{-1}$), As ($15 \text{ }\mu\text{g L}^{-1}$), Fe ($133 \text{ }\mu\text{g L}^{-1}$), Mn ($33 \text{ }\mu\text{g L}^{-1}$), Ni ($256 \text{ }\mu\text{g L}^{-1}$), Cu ($100 \text{ }\mu\text{g L}^{-1}$) and Se ($18 \text{ }\mu\text{g L}^{-1}$), however, the values reported for SO_4^{2-} and pH are inconsistent with this process and may represent dissolved mineral phases. It also must be noted that W-22 was not sampled directly from the well, but from a tap sample (Table A2.1). However other samples taken from taps did not have elevated values of trace elements as per W-22.

Mercury concentrations recorded in this study ranged 0.05-0.1 $\mu\text{g L}^{-1}$ which is below the regulatory value of 1 $\mu\text{g L}^{-1}$ in Ireland which is indicative that road construction did not affect Hg concentrations (WHO, 2005, EC, 2007).

5.3.2) The source of nutrient, microbial and organic contamination

The majority of groundwaters shows contamination of both nutrients and/or microbes as evident from cluster five in Table 5.6 and Fig. 5.5. Microbiological parameters had the greatest number of samples above the legal limit with total coliforms showing the greatest proportion in both groundwater depth types. Generally total coliforms and faecal coliforms were more elevated when compared to *C. perfringens* and faecal streptococci (Table 5.3). Spatially, most elevated microbiological parameters intersect the poorly productive aquifers (PI) of the study area. In addition, the land use of this area is pastures with a moderate to extreme groundwater vulnerability, illustrating how these microbiological parameters may enter the groundwater system via flow patterns as the north of this locality has a high elevation. The presence of these faecal microbiological bacteria indicates that some input of faecal waste or sewage to these groundwater sources. Elsewhere it has been shown that septic tanks were responsible for the prevalence of bacteria within groundwater with dug wells being twice as susceptible to this bacterial contamination when compared to boreholes due to surface contamination (Hynds et al., 2012 and 2014). When improperly installed or maintained, these DWWTs may represent a source of nutrients and enteric pathogens which can affect water quality (Naughton and Hynds, 2014; Withers et al., 2014). Total coliforms have been detected in groundwater in the absence of faecal streptococci or coliforms. As total coliforms are present in soil, bacteria in groundwater may result from the overburden or subsoils moving into the borehole as a result of poor well construction practices. In Ireland, older boreholes were constructed in order to maximise the flow of groundwater into the borehole, resulting in a blend of deep groundwater and the more polluted shallow groundwater (refer to Section 4.1.1.1, Fig 4.2a-b, Chapter 4). Modern borehole design (i.e. IGI, 2007; EPA, 2013) excludes this easily polluted shallow groundwater (Chapter 4). If bacteria were resulting from soils, then after a dry summer the bacterial quality would improve as the shallow groundwater (containing bacteria) would be depleted and thus is making a negligible contribution to the borehole flow (EPA, 2013).

Elevated concentrations of nitrate were detected in wells, particularly above the limit of 50 mg L^{-1} with concentrations approaching 134.1 mg L^{-1} . Nitrate in groundwater can arise from both point and non-point sources such as septic tanks, oxidation of organically bound N in soils, agricultural activities and animal feed with elevated concentration giving rise to health

conditions (e.g. methemoglobinemia) (Appelo and Postma, 2005; Bondu et al., 2017a). In shallow groundwaters, contamination can originate from the excessive application of fertilisers and manure from agricultural practices. Both shallow and deeper groundwaters had similar values of elevated NO_3^- with < 10% of sites having a NO_3^- concentration greater than the drinking water limit of nitrate (i.e. 50 mg L^{-1}). In contrast, both nitrite (NO_2^-) and ammoniacal nitrogen ($\text{NH}_3\text{-N}$) are not present in detectable quantities in many samples, which is likely as a result of the rapid conversion to NO_3^- in a suspected oxygenated environment with denitrification as a result (Petrunic et al., 2012). Given that concentrations of NO_3^- generally exceed 25 mg L^{-1} , anthropogenic nutrient activity represents a major impact on groundwater in this study either from organic waste (i.e. septic tank and slurry) and/or inorganic fertilizer sources. Also, the evidence of a moderate positive correlation of nitrate with *C. perfringens* and total coliforms (a FIB) ($\tau=0.38^{***}$) supports the rationale that these nutrients originate from septic tank sources (Table A2.2 and Fig. 5.2). Indeed, septic tanks may be one potential source of anthropogenic nutrients as boron shows a correlation with NO_3^- ($\tau=0.25$), *C. perfringens* ($\tau=0.24$), and total coliforms ($\tau=0.16$) (and to a lesser degree TOC ($\tau=0.14$) which is also evident from cluster 5 from the HCA analysis presented in Table 5.6. However, NO_3^- shows a weak correlation with Cl, illustrating how domestic sewage is not a major source of nitrate in this study (Zhang et al., 2020). This response is further supported as boron is a common component in many household detergents which moves through septic systems and thus a potential indicator of domestic waste in the environment (Thurman et al., 1984; Wang et al., 2000; EPA, 2003). The concentrations of boron observed in this study (maximum $76 \mu\text{g L}^{-1}$) are generally above the natural background level of $15 \mu\text{g L}^{-1}$, potentially indicating an urban pollution source (Buss et al., 2004; Tedd et al., 2017). While boron may behave conservatively in aqueous systems, it can sorb onto oxyhydroxides and clay surfaces and ultimately this sorption is a mechanism to remove boron from groundwater (Table 5.4) (Wang et al., 2000). In addition, boron is also a minor component of fertilizers (Tedd et al., 2017). However, if organic waste (i.e. septic tanks) was responsible for all instances of elevated nutrients, then concentrations of ammoniacal nitrogen $> 0.1 \text{ mg L}^{-1}$ would be expected to be observed if septic tanks were in close proximity to the well (Cronin and Deakin, 2000), however only five wells had concentrations $0.2\text{-}2.7 \text{ mg L}^{-1}$ with the remaining wells being below the DL (<0.2 or $<0.258 \text{ mg L}^{-1}$). It must be noted that detected ammoniacal nitrogen was observed in only boreholes, and not in dug wells as expected from a septic tank source. For the remaining microbiological parameters there appears to be a weak correlation except a moderate relationship exists with total coliforms and *C. perfringens* ($\tau=0.38^{***}$). In contrast, given that

the groundwater vulnerability of the study ranges from moderate to extreme, the groundwater may be susceptible to this nutrient contamination as a result of land spreading of fertilizers (inorganic and organic slurry) given that the main hydrological pressure is agricultural land and one third of sampling locations are surface dug wells. While this diffuse source may be occurring in the study area, as it is predominately an agricultural area, detailed information on where land spreading is occurring remains unknown. However, given the high level of contamination from total coliforms in these groundwaters it is possible that the source of groundwater nitrate results from organic waste, i.e. slurry or septic tank (Cronin and Deakin, 2000). However, low instances of faecal coliforms (including *Escherichia coli*) were detected in this study (15 shallow and deep groundwater wells), suggesting that organic waste from septic systems is not a source for most sites (Cronin and Deakin, 2000). Based on this, and other data, it is expected that the majority of elevated nitrate results from inorganic fertilizer practices due to absence of faecal coliforms, with minor contribution from organic waste (both slurry and septic tank sources). However, it must be noted that even though faecal coliforms were not detected in 52 wells, this may result from the bacteria not surviving due to either attenuation or time of travel to well is greater than 100 days (Cronin and Deakin, 2002). Variations in groundwater nitrate concentrations are affected by complex physical and chemical processes within the soil, subsoil and aquifers, which result in some areas been more susceptible to contamination when compared to others (Tedd et al., 2014). Reduction of nitrate to nitrite is expected to occur only in a small percentage given the high rate of non-detects for nitrite. Organic N can be converted to nitrate through the process of ammonification (organic matter converted to ammonia) and nitrification (ammonia converted to nitrate) under aerobic processes (Wang et al., 2000). While other key indices may help constrict the nutrient source such as K:Na ratio and Cl concentrations (Cronin and Deakin, 2000) these could not be used in this study as K was not measured and this study area is within 20 km of the coast so sea spray may be a contributing factor. In this study area, contamination of the nutrient nitrate, is likely occurring from multiple sources.

In addition to the above observation with nutrients a correlation is observed with Na and Cl ($\tau=0.37^{***}$). For many samples, the Na:Cl ratio nearly equals 1:1 indicative of halite dissolution in groundwater (Chenini et al., 2010) with geochemical modelling illustrating that halite is undersaturated in the groundwater (cluster 3, Table 5.6. Fluoride was only detectable above the legal value in one location, W-23, measured at a value of 3.1 mg L⁻¹).

While groundwater showed anthropogenic contamination of nutrients (i.e. nitrate), negligible contamination of organic geochemistry (i.e. PAHs, VOCs and pesticides) occurred

with only CS₂ and MTBE being detected. It is expected that these VOCs originated from a pyrolytic origin (i.e. from fossil fuels such as diesel) from point pollution. However, the low number of detected VOCs could have resulted from contamination not reaching the zone of contribution of the borehole. Overall groundwater shows negligible contamination resulting from organic geochemistry parameters, however, point pollution indicative by excessive nutrient and microbes illustrates that anthropogenic activities are occurring in this area.

5.3.3) *Multivariate analysis*

All clusters isolated from hierarchical cluster analysis contained a mixture of both DWs and BHs (Fig. 5.1a). The first cluster for variables shows similarity amongst transition series metals (i.e. Fe, Cr and Ni) illustrating a common mineral source. Arsenic is clustered in the same group as other oxyanions; selenium and antimony, in addition to pH further showing the key geochemical parameters in alkali desorption processes as discussed in earlier sections. The 4th and 5th clusters contain the microbiological based parameters, nutrients, and the remaining trace elements, including boron, illustrating the widespread nutrient (i.e. NO₃⁻) and microbial contamination present in wells of this study area. While nitrate was grouped in this cluster, elevated nitrate was also seen in the remaining clusters. This hierarchical clustering analysis was able to discern the two dominant water processes occurring: alkali desorption of arsenic from Fe oxyhydroxides and microbial and nutrient contamination of wells resulting from fertilizer and organic waste. This analysis showed that arsenic concentrations are also associated with redox-sensitive elements (e.g. antimony and selenium) (Jiang et al., 2015). By using these clustering techniques, it is possible to identify distinct natural groupings within multi-dimensional data (Grunsky, 2010).

In contrast, sites clustered from the heatmap in cluster 1 (n=32) are present within the centre to south of the study area with cluster sites identified in cluster 2 (n=21) are located within the centre of the study area, and; the remaining sites, cluster 3 (n=14), mainly present to the south of the study area. Cluster 1 represents groundwater wells mainly associated with elevated arsenic concentrations, alkaline pH, and detection of antimony and/or selenium. This cluster is contained within a spatial scale that extends to the whole study area and may be constrained by groundwater flow. While cluster 1 extends to the whole study area both cluster 2 and 3 are generally more isolated. Cluster 2 generally contains more total coliforms in addition to Fe and Mn with low arsenic concentrations. The main sampling sites within this cluster are north west of a hill within the Porphyritic granophyre bedrock geology which may represent surface runoff from an agricultural pressure. Cluster 3 represents groundwater wells

with low microbial contamination, but with elevated trace elements (e.g. Cr, Al, Fe, Ni, Cu and Mn). While cluster 1 and 2 are mainly present in sampling sites within the Clontail Formation, cluster 3 contains sites within the Dinantian Limestones.

5.3.4) Strengths and recommendations

The findings of this study show the presence of elevated arsenic in a rock type which was previously described as containing elevated arsenic (Chapter 3). As this data was collected as part of an EIA for a new road construction it is likely there are more of this type of datasets in Ireland and elsewhere. These methods described here can be applied to other areas with similar EIA datasets where data on arsenic and other environmentally relevant trace elements is sparse. This study examines elevated arsenic in a fractured bedrock aquifer in Ireland and provides a footprint of further research in other areas and several recommendations can be made;

- As a result of the high censoring it is recommended that for new work the objectives and deliverables of the sampling campaign need to be fully considered at the planning phase. For example, a more rigid sampling and analytical protocol could be adopted to quantify sub- $\mu\text{g L}^{-1}$ concentrations of trace elements.
- This work did not examine the influence of mitigation measures (e.g. filters) at the point of use in dwellings for elevated arsenic and would be of benefit to include in future works for health evaluation.
- Future works would need to include other oxidised species, i.e. dissolved oxygen into the sampling strategy to assist with this interpretation.
- To understand the complex processes of sewage in more detail sewage-specific microbial source tracking methodologies adopted elsewhere, e.g. Wangkahad et al. (2017) would need to be completed in addition to B isotopic data (Widory et al., 2005).
- Inclusion of a depth data category in the sampling protocol. Elsewhere depth has been linked as a factor explaining elevated arsenic concentrations (Thomas, 2007; Kim et al., 2011b).

5.4) Conclusions

Groundwater were sampled and analysed for several relevant parameters of environmental concern. The main conclusions of this work in this study area are summarised below;

- The source of trace elements, particularly arsenic, arise from geogenic sources rather than anthropogenic activities with alkali desorption causing the mobilisation of arsenic in groundwater in most of the sites.

- Groundwaters with elevated arsenic concentrations ($\geq 10 \mu\text{g L}^{-1}$) are associated with alkaline pH (7.13-8.19 pH units), detection of antimony and/or selenium, moderate SO_4^{2-} , low Fe and Mn with low or no microbial contamination.
- High Fe and/or Mn groundwaters are associated with low concentrations of arsenic.
- There are low instances of organic contaminants in groundwaters and contamination of these are most likely representative of point source fuel spills. (i.e. MTBE).
- Elevated nitrate potentially results from inorganic fertilizer with less contribution from organic waste (both slurry and septic tank sources), however this environmental process warrants further research to understand these complex behaviours.
- This study showed that both censored chemical and biological data can be integrated for the application of multivariate statistical analysis.
- It is expected that the inclusion of similar EIA datasets in Ireland and elsewhere can be applied to understand the distribution of trace elements in groundwater systems where data is available.

5.5) Summary

While the previous two chapters dealt with arsenic at larger spatial scales, this present chapter focuses on understanding arsenic geochemistry at a local setting. In addition, other parameters including microbiology, nutrients, physical, and organic geochemistry were collated and analysed using MSA whilst incorporating censored data to understand groundwater processes.

Chapter 6

Investigation of elevated geogenic arsenic concentrations and speciation in groundwater of a fractured bedrock aquifer in the Southern Uplands-Down-Longford Terrane in northeast Ireland

Abstract

The presence of elevated arsenic concentrations ($\geq 10 \mu\text{g L}^{-1}$) in groundwaters has been widely reported in areas of south east Asia, and it has been recently detected in fractured bedrock aquifers, particularly in regions of north eastern United States, however data from within Europe remains limited. The objective of this work was to build upon previous results from the national-scale approach in Chapter 3 to understand the precise geochemical mobilisation mechanism of arsenic and other oxyanion-forming elements in the Southern Uplands-Down-Longford Terrane of north eastern Ireland. An initial hydrogeological survey revealed elevated arsenic concentrations in deeper boreholes and subsequently, a subset of wells was targeted for more detailed geochemical investigations ($n=43$). Physiochemical, trace element, major ion and arsenic speciation samples were collected and analysed using a variety of field and laboratory-based techniques. Detailed statistical approaches incorporating multivariate statistical analysis, spatial analysis, and thermodynamic calculations were conducted. Elevated dissolved arsenic concentrations (up to $73.95 \mu\text{g L}^{-1}$) 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 rather than both pH and Eh controlling the speciation. The source of arsenic is expected to be sulphide minerals within fractures of the bedrock aquifer with transportation of As and other oxyanion-forming elements facilitated mainly by secondary Fe mineral phases. However, given the presence of methylarsenical compounds detected in the groundwaters, it is likely that microbially mediated mobilisation processes were also occurring. While As concentrations were reduced at the drinking water source (taps) due to filtration devices, several sources had no such mitigation measures and represent an exposure pathway to inorganic arsenic. This study confirms and adds to previous datasets showing arsenic in groundwater and contributes to understanding the precise geochemical controls of arsenic in groundwater. In addition, this study also successfully 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.

Keywords: arsenic, aqueous geochemistry, speciation, groundwater, health, oxyanions

6.0) Introduction

Globally, 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 thus is a critical exposure pathway for arsenic.

The International Agency for Research on Cancer (IARC) classes arsenic as a Group I carcinogen (IARC, 2012). Short-term exposure or acute exposure to elevated arsenic concentrations can lead to the development of arsenicosis, a term used to describe diseases related to arsenic exposure (van Halem et al., 2009; Naujokas et al., 2013). Recently, it has been demonstrated that long term exposure (chronic) of low-to-medium levels of arsenic in drinking water (i.e. 1 – 100 $\mu\text{g L}^{-1}$) 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), suggesting that the World Health Organisation (WHO) limit of 10 $\mu\text{g L}^{-1}$ may not be sufficiently protective of human health (Saint-Jacques et al., 2014; Roh et al., 2017).

Arsenic exists in four oxidation states including +V (arsenate – As^{V}), +III (arsenite – As^{III}), 0 (elemental – As^0) and –III (arsenide – $\text{As}^{-\text{III}}$), with both the pentavalent arsenates (As^{V}) and trivalent arsenites (As^{III}) being 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 (i.e. high Eh values of oxygenated water), while arsenite forms the oxyanions H_3AsO_3^0 and H_2AsO_3^- in reducing (i.e. low Eh values) environments (Stolz et al., 2006; Garelick et al., 2009). The degree of protonation of the arsenic species depends on the pH of the groundwater (Sharma and Sohn, 2009). The ratio of As^{III} to As^{V} in natural waters depends upon several factors including organic carbon concentrations, flux of potential oxidants (oxygen, nitrate and sulphate), presence or absence of redox-active solids, microbial activity and iron/manganese oxides (Smedley and Kinniburgh, 2013). Organic arsenic species may be present in groundwater as a result 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 and their presence in the environment (MMA as sodium salts) could result from their use as herbicides (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; Gupta et al., 2012). 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, i.e. arsenic, selenium, boron, molybdenum, uranium and antimony (Smedley and Kinniburgh, 2002; Sanexa et al., 2004). For the mobilisation of arsenic from the host rock into the groundwater system, it is acknowledged that there needs to be two specific geochemical triggers: 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 can also be elevated.

In Asia, groundwater with elevated arsenic are generally associated with Quaternary unconsolidated alluvial sediments, with geochemical and hydrogeological conditions favouring the mobilisation of arsenic (Ravenscroft et al., 2005; The World Bank, 2005; Benner and Fendorf, 2010; 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, Europe and certain regions of Asia (Ayotte et al., 2003; Smedley et al., 2007; Verplanck et al., 2008; Drummer et al., 2015; Ryan et al., 2011 and 2015; Reyes et al., 2015; Zkeri et al., 2015; Andy et al., 2017). This is an important consideration as many people rely on private bedrock wells for drinking water (Ryan et al., 2013; Bondu et al., 2017a). Indeed, a large proportion of rural communities globally have low-to-moderate concentrations (i.e 10-100 $\mu\text{g L}^{-1}$) of arsenic due to dispersed occurrence of arsenic in the environment and frequent reliance on private wells (Zheng et al., 2017).

In Ireland, these hard rock aquifers, or poorly productive aquifers (PPA) underlie 60% of the island (Robins and Misstear, 2000) and provide an important water source for domestic, commercial and industrial settings. 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 has been observed in clusters around Ireland with certain lithology groupings (Sandstone and Shale (Greywacke), Impure Limestones and Rhyolite) posing a potentially greater risk of elevated arsenic (Chapter 3). While concentrations of arsenic $\geq 10 \mu\text{g L}^{-1}$ in groundwaters are considered elevated (i.e. above the WHO and EU limit), in Ireland a lower concentration of $7.5 \mu\text{g L}^{-1}$ is used (the arsenic groundwater threshold value) which is the concentration at which action is taken. It must be noted that Ireland uses the EU limit of $10 \mu\text{g L}^{-1}$.

The traditional practice of determining only total arsenic concentrations in water quality testing fails to provide information regarding the various physicochemical forms of arsenic, so that information regarding metabolism, toxicity, ecotoxicity and potential mobility in the environment remain unknown (Fodor, 2001; Michalke, 2003). In order to overcome this, speciation analysis can be undertaken using laboratory separation and detection techniques 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). As 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; Lord et al., 2012; Sugař et al., 2012; Ullrich et al., 2016; Bondu et al., 2017a).

The aims of this study were to i) understand the regional geochemistry of arsenic in groundwater, ii) elucidate the geochemical triggers which are responsible for the mobilisation of arsenic within the study site, iii) understand the mobility and toxicity of arsenic through speciation studies, iv) assess the concentration of arsenic in drinking water taps, and v) compare findings with previous observations in both Ireland and elsewhere.

6.1) Study area

The study site is located north of Dundalk town along the border of the Republic of Ireland and Northern Ireland beside the A1/N1 motorway (Fig. 6.1). Most residential homes in the area consist of one-off dwellings with a private well as their primary source of drinking water and with a domestic wastewater treatment system (DWWTS) for wastewater treatment. The surrounding area is primarily agricultural (pastures) with forestry to the north based on CORINE land use classification data. Detailed information on land use is presented in Section 5.1.

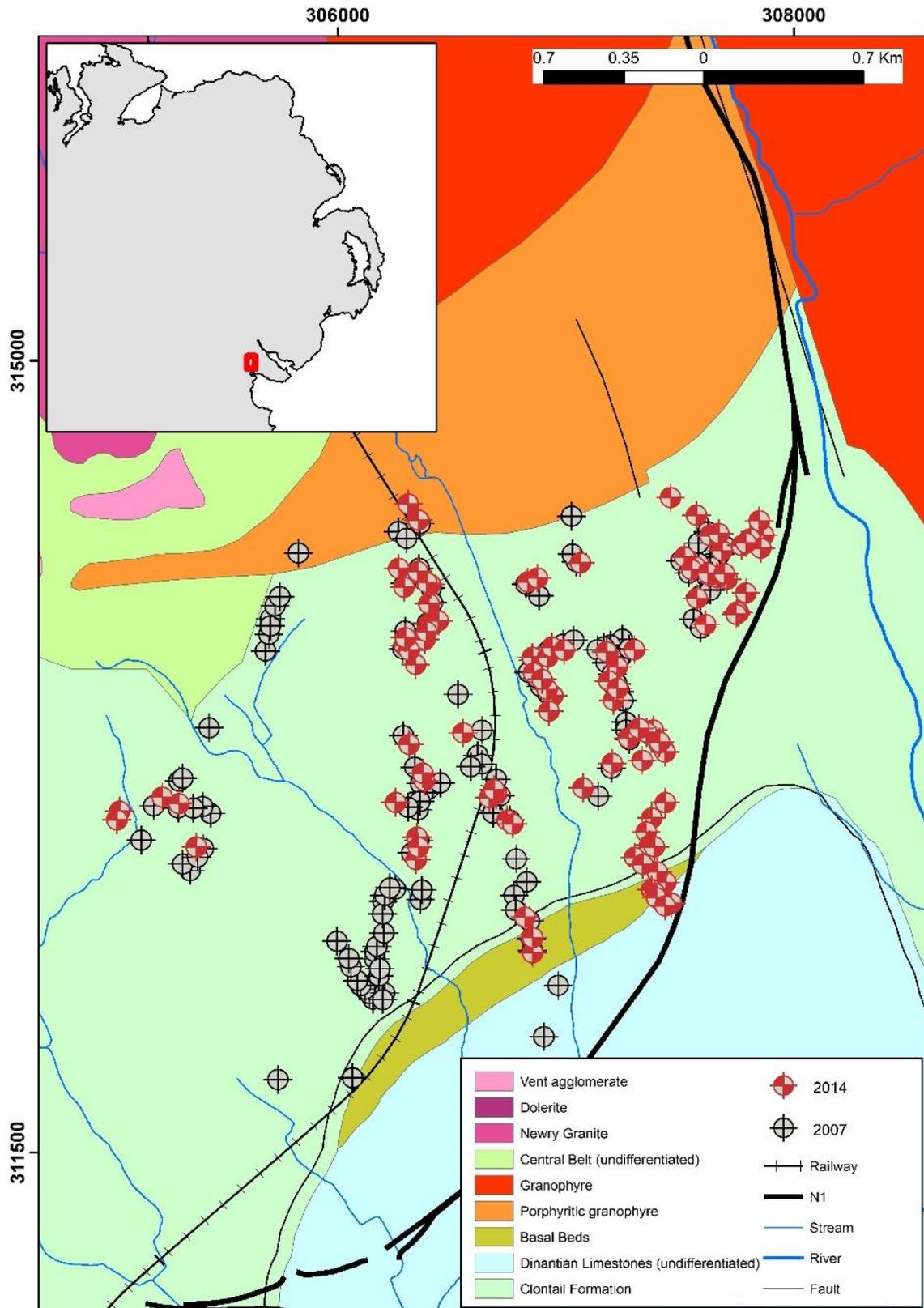


Fig. 6.1. Spatial distribution of historical data (2007) and data collected as part of this work (2014) overlaid on bedrock geology (1:100K).

6.1.1) Geological setting and hydrogeology

The study area is contained within the Southern Uplands-Down-Longford terrane (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). This terrane was created by orogeny in the Ordovician, Silurian and Devonian periods. The Southern 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). The stratigraphy of the terrane has a ENE-WSW strike, with a consistent steep dip (Anderson, 2004). The SUDLT has been sub-divided into three strike-parallel belts: Northern, Central and Southern Belts (Lusty et al., 2012). Only the Northern and Central Belts of the SUDLT occur in the study area (Anderson, 2004). Several major strike-parallel faults spaced at 1 and 5 km distance apart, dissect the terrane into a series of fault-bounded tracts (Morris et al., 1986; Anderson, 2004; Lusty et al., 2012).

The SUDLT contains gold mineralisation including an area in the north east of Ireland (Clontibret, Monaghan) with Sb-As-Au vein-hosted deposits within Ordovician felsic greywackes (Morris et al., 1986; Steed & Morris, 1986; Geraghty, 1997; Lusty et al., 2012). Previous research (Chapter 3) found a borehole within the greywackes containing elevated levels of both antimony and arsenic (As, 9.7-17.76 $\mu\text{g L}^{-1}$; Sb, <1-132.65 $\mu\text{g L}^{-1}$). To the north of the SUDLT, Late Palaeozoic intrusives of the Newry Igneous Complex are observed. This igneous complex intruded into the Silurian greywacke and mudstone, and is found in the area extending from Slieve Croob to Forkhill (west of study site) (Cooper and Johnston, 2004). During recent construction of the A1/N1 motorway, a 300 m section was excavated showing metasediments of the SUDLT in contact with the Newry Igneous Complex porphyritic microgranite along a steep, and locally intensely crushed, contact zone that dips away from the ring-complex (Troll et al., 2008). The Slieve Gullion ring-complex was formed of silica-rich rocks of fine-grained porphyritic rhyolite and medium-grained porphyritic microgranite (Meade et al., 2010). Surrounding the study area there are also Lower Carboniferous limestones, which include a variety of limestones, shales and dolomites (Geraghty, 1997).

Groundwater sampling boreholes and wells penetrate the following geological formations: Porphyritic granophyre (Pg), Dinantian Limestones (undifferentiated) (DIN), Basal Beds (BAS) and Clontail Formation (CL). Most sampling sites are contained within the Clontail Formation. The Clontail Formation is a calcareous red-mica greywacke. It is present in Tract 7 of the Central Belt and is made up of grey-green, medium to thick-bedded, coarse

and very fine-grained greywackes, with dark grey, thin-bedded, poorly graded, quartzose fine sandstone to siltstone units (Vaughan, 1991; McConnell et al., 2001). The Clontail Formation contains distinctive brown-red coloured biotite indicating a correlation with the Hawick Group on the Southern Uplands (Rust, 1965; Kemp, 1987) and the Inniskeen Formation to the northwest (McConnell et al., 2001). Based on correlation to the Hawick Group, the formation is thought to be Llandovery to Wenlock in age (McConnell et al., 2001). This formation is bounded to the south by the Salterstown Formation which consists of calcareous white-mica bearing greywacke (Vaughan and Johnston, 1992).

There are several Quaternary deposits within the study area with most of the monitoring sites located in areas where the bedrock is overlain by till derived from granites (TGr). Some sites are in areas, of bedrock outcrop or subcrop (Rck), cut-over raised peat (Cut), and alluvium (A) scattered to the north, east and in the middle. To the west of the monitoring location the bedrock is overlain by till derived from Lower Palaeozoic sandstones and shales (TLPSsS). To the north (in Northern Ireland) quaternary sediments are described as till (diamicton).

The term aquifer is often used for convenience in the Republic of Ireland, even though unaltered bedrock usually does not either store or transmit groundwater. Bedrock below the Republic of Ireland is older than 300 million years. The bedrock is essentially impermeable. However, the Republic of Ireland has considerable groundwater resources. Groundwater is contained in, and moves through, fractures, joints, faults and conduits formed by solution weathering. In other words, water moves underground through the breaks in the rock rather than the rock matrix. The flow through the network of interconnected narrow and wide breaks in the bedrock could be best described as a groundwater flow system (IGI, 2007; EPA, 2013). Irish water supply boreholes are predominantly shallow; few wells are deeper than 120 m. The water table in the bedrock and the overburden is usually close to ground surface, due to elevated rainfall (Collins et al., 2001). The Lower Palaeozoic 'aquifers', although fractured, generally do not contain numerous or wide breaks in the rock and are classified as poor aquifers (Geraghty, 1997; McConnell et al., 2001). Water can also be obtained from a weathered zone in the shallow bedrock. Sometimes, the top of the weathered bedrock and the bottom of the overburden are indistinguishable, and this zone is commonly termed the transition zone. Generally, the groundwater flow system in the bedrock and transition zone will yield sufficient water to supply a house or a small farm ($0.2-0.5 \text{ L s}^{-1}$). The yield occasionally is higher in major fracture zones (Geraghty, 1997). The yield of shallow wells and boreholes sometimes will depend almost entirely on the groundwater resources in the transition zone, and as a result borehole yields may decrease significantly in dry spells as the water table falls. Supplies of

water from wells and boreholes are dependent on the resource in the transition zone may be unreliable (Geraghty, 1997; McConnell et al., 2001). Much of the Lower Carboniferous clastic rocks (sandstones, siltstones, and mudstones) are fractured enough to have a better groundwater flow system, but the yields are still insufficient for the rock types to be regarded as regionally important aquifers (yields of $0.5\text{-}3\text{ L s}^{-1}$) (McConnell et al., 2001).

The heterogenous, anisotropic nature of the groundwater flow systems in the bedrock under the Republic of Ireland also means that there can be different flow systems or preferential flow paths at different depths in the rock. These flow systems may be connected to each other or disconnected. Groundwater chemistry and bacteriology can also change with depth. Modern boreholes in the Republic of Ireland are designed and constructed with this consideration in mind (IGI, 2007; EPA, 2013). Older, or simply constructed boreholes will often yield water that is an uncontrolled blend of shallow groundwater from the overburden and the transition zone and deep groundwater from one or more open joints, fractures or faults in the deep bedrock (see Section 4.1.1.1).

6.2) Materials & Methods

6.2.1) Desk study

Due to elevated arsenic concentrations above the guideline value ($10\text{ }\mu\text{g L}^{-1}$) during a previous study (Chapter 5), a survey focusing solely on arsenic concentrations in groundwater was undertaken in May 2007 by Louth Country Council (LCC) to cover the board area (regional-scale historical data collected as part of Chapter 3. In total 168 wells, north-west of the N1 were sampled. 164 measurements were taken at unique locations, with 158 being used as 6 had no arsenic data. Only 127 of these had coordinate metadata associated with arsenic measurements (31 missing coordinate data).

For comparative purposes, summary statistics were calculated using the robust regression on order statistics (ROS) (due to the presence of censored data) in Minitab[®] 17 (Location) using the %*Cros* macro (Helsel, 2012). The detection limit was either $0.37\text{ }\mu\text{g L}^{-1}$ or less commonly $1\text{ }\mu\text{g L}^{-1}$. Censored data were encountered in this present study as a result of the sensitivity of instrumentation which is usually expressed as $<x\text{ }\mu\text{g L}^{-1}$ (where x is a numerical value), i.e. data that are below the detection limit of the instrument (Helsel, 2012). Excluding this historical data, the analytical sensitivity of instrumentation used as part of this study was much lower as a result of improved sampling and bottle washing procedures in addition to improved analytical measuring capability (see Section 6.2.4.1).

6.2.2) Reconnaissance hydrogeological survey

In order to determine potential hot spots of metal contamination and groundwater flow patterns for further study, an initial reconnaissance hydrogeological survey was undertaken in May and June 2014 with boreholes (BH), springs (SP) and shallow groundwater sources i.e. dug wells (DW), sampled (n=107). For each sampling site, a hydrogeological questionnaire was completed with the homeowner and a screening sample was obtained (where appropriate) from unfiltered tap locations, or at well source. The tap was run for several minutes where the 50 cm³ DigiTUBE (SCP Science, USA) was rinsed several times with water, filled and acidified to pH <2 (*Optima* HNO₃, Fisher Scientific, Dublin) and packed (Bryson Packaging™ Minigrip™ PE Bags, Fisher Scientific, Ireland). Samples were stored at 4°C until returned to the laboratory. To ensure trace element clean sampling conditions, field blank samples of Milli-Q were taken.

GPS coordinates were measured at the top of the well using a Trimble XRS Pathfinder Pro differential global positioning (DGPS) system using VRS (virtual reference station) and corrected to the nearest active global navigation satellite system (GNSS) station (Markethill, OSi) by using the appropriate RINEX files on the day of sampling for post-processing. Recording time was 20 minutes. Septic tanks at each location were also recorded using a handheld unit (Garmin GPSMAP 62 Handheld GPS, Ireland).

6.2.3) Extensive water chemistry

An extensive water sampling campaign (locations identified from the reconnaissance hydrogeological survey) was conducted to in June 2015 (n=43) (Fig. 6.1). Subsequently, a smaller subset of these monitoring locations (n=20) was sampled in July 2016 in order to understand arsenic speciation in the groundwater (both laboratory and field-based methodologies). So, this study is comprised of the following three sampling campaigns.

- May-June 2014 (n=107) – reconnaissance hydrogeological survey.
- June 2015 (n=43) – extensive water chemistry.
- July 2016 (n=20) – extensive water chemistry (with arsenic speciation).

6.2.3.1) Sample bottle decontamination

Refer to Chapter 2 (Section 2.1).

6.2.3.2) *Sampling*

Samples were collected using the “clean hands dirty hands” methodologies to reduce sample contamination (Fitzgerald, 1999). Groundwater sampling was conducted using depth specific sampling (Appelo and Postma, 2005) and was conducted at around 8-10 mbgl. While the collection of groundwater samples at a monitoring well may not fully represent the composition of the water in the vertical section, it is a good indicator of the average composition (Hem, 1985). The method of low-flow groundwater sampling has been recently used to gain representative groundwater samples for trace elements evaluation of the aquifer while avoiding the pitfalls of standard techniques (Puls et al., 1992; Creasey and Flegal, 1999). In addition, the employment of trace element clean techniques limits the introduction of contaminants during sampling, storage and analysis (Creasey and Flegal, 1999). In order to achieve low-flow conditions, a 42mm stainless steel bladder pump was used with a PCU ProPlus control unit (100 PSI) /Geotech Geocontrol Pro™ (In-Situ, UK) powered by 12V 18AH batteries (RS Hydro, Ireland). Bladders used were made from PE. Low-density polyethylene (LDPE) tubing was used for both the sample line (6x10mm/0.38” OD) and air line (4x6mm/0.25” OD) and appropriate lengths were cut using a PTFE coated steel cutter.

Electrochemistry was monitored using the Sheffield low-flowcell (Waterra In-Situ®, Shirley, UK) which allows these constituents to be measured without atmospheric exposure and under laminar flow conditions (Fig. 6.2). This is a critical step especially for pH and Eh when investigating arsenic speciation as separation from the atmosphere facilitates accurate measurements of these parameters. Temperature (Orion™ 972005MD, Star ATC Probe) and Eh (platinum electrode using Ag/AgCl as reference Orion™ 9678BNWP, Sure-Flow Comb. Rexox/ORP) were monitored using an Orion™ 3 Star meter (Thermo Scientific), while dissolved oxygen (d-O₂) (Orion™ 083010MD Dissolved Oxygen Probe), pH (Orion™ 9107WMMD, Triode Waterproof pH) and conductivity (Orion™ 01310MD, Conductivity Cell [4 Cell Conductivity Electrode Graphite, K = 0.475]) were measured using an Orion™ 5 Star meter (Thermo Scientific). Probes were calibrated at each field station; conductivity (Reagecon Conductivity Standard 1413 $\mu\text{S cm}^{-1}$ at 25°C), pH (Orion™ pH 4.01, 7.01 and 10.01 pH buffer solutions [Orion 910110, Thermo Scientific]), ORP (ORP Standard [Orion™ 967961, Thermo Scientific]). ZoBells solution was used for calibration of the Eh electrode (Nordstrom, 1977; Weight, 2008). Relative values for redox potential measured in mV were corrected for temperature and adjusted to a potential relative to the standard hydrogen electrode (SHE) (Nordstrom, 1977). Groundwater electrochemical parameters were recorded every five minutes while drawdown/static water level (SWL) was monitored using a water-level contact gauge in

parallel (Solinst[®] Model 101 30 m and/or OTT Hydrometry KL010 100 m). Sampling pumping parameters were altered to minimise drawdown, i.e. ≤ 10 cm and to maintain low-flow conditions. A drawdown of >10 cm occurred during sampling for five wells in 2015 (BH-41, BH-17, BH-67, BH-29, and BH-39) and four wells in 2016 (BH-20, BH-74, BH-60, and BH-39).

Triplicate groundwater samples were collected once the electrochemical parameters stabilised and were filtered using 20 cm³ BD Discardit[™] II PP/PE syringes (VWR, Dublin, Ireland) and Millex[®]-LCR 25 mm 0.45 μ m hydrophilic polytetrafluoroethylene (PTFE) filter (Merck Millipore Ltd., Cork, Ireland) and acidified to $\text{pH} < 2$ using 16 N HNO₃ (either using *Optima* HNO₃ (Fisher Scientific, Dublin) or Romil UpA HNO₃ (Lennox, Dublin)) in 60 cm³ bottles. Additionally, one 250 cm³ bottle was used to collect an anion sample. Samples for hydrogen carbonate (HCO₃⁻) analysis were collected in three 125 cm³ 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). Where possible a tap sample was also collected for both filtered and unfiltered metals as described in Section 6.2.2.

While total dissolved salts (TDS) were not directly measured gravimetrically, this water quality parameter can be estimated from the direct EC measurement of groundwater. At low EC concentrations, the relationship between EC and TDS is generally linear and this relationship is reasonably well defined to be of good practical value (Hubert & Wolkersdofer, 2015; Hem, 1985). This conversion formula is provided in Equation 6.1 (Hubert & Wolkersdofer, 2015).

$$TDS = EC \cdot f \quad (\text{Equation 6.1})$$

Where f is the conversion factor and can vary due to the differing composition of natural waters. The value of f for natural waters is given to lie between 0.54 and 0.96, but generally, most factors lie between 0.55 and 0.75 (McNeil and Cox, 2000; Hem, 1985). Given that the median conductivity for this study resides within the range of 300 – 400 $\mu\text{S cm}^{-1}$ the conversion factor (median value) of 0.69 was used (McNeil and Cox, 2000).

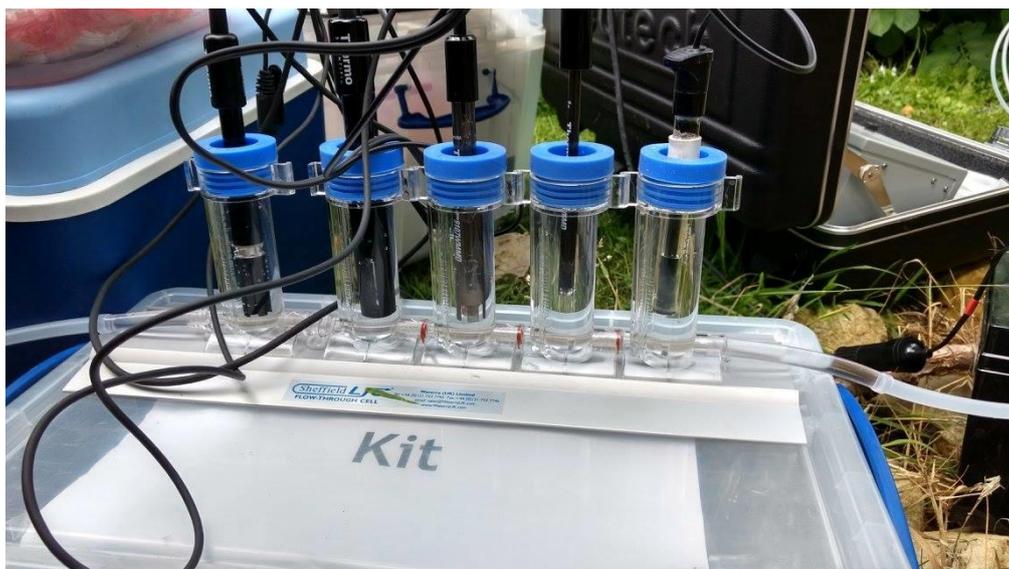


Fig. 6.2. LFC groundwater flow-cell with groundwater moving from the right inlet to the left outlet. Electrochemical probes from right to left: Eh, temperature, pH (with temperature), conductivity and dissolved oxygen. The PCU control plus unit is evident in the top right of image (source: authors own image).

6.2.3.3) *Field determinations*

Alkalinity was titrated in the field with aliquots of known volume (either 25 cm³ 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 H₂SO₄ cartridge using bromocresol green–methyl red indicator on the day of collection (Hach-Lange, Dublin, Ireland).

6.2.3.4) *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. In order to speciate arsenic in the field the solid-phase extraction (SPE) methods of O’Reilly et al. (2010) and Watts et al. (2010) were adopted for this study. This methodology has been previously adopted in the literature to study the speciation of arsenic in groundwaters (Christodoulidou et al., 2012; Farnfield et al., 2012; Lord et al., 2012; Bondu et al., 2017a; Richards et al., 2017).

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). Cartridge conditioning was carried out to promote the adsorption of the arsenic species onto the resin (silica-based). Firstly, the SCX cartridge was preconditioned using 50% CH₃OH (LC-MS Chromasolv[®], Fluka Analytical), 15 cm³ of 1 M H₃PO₄ (Fluka Analytical 85% TraceSELECT[®], Sigma-Aldrich, Ireland) and finally 10 cm³ of

ultra-pure water. The SAX cartridge was conditioned using 15 cm³ 50% CH₃OH followed by 10 cm³ of ultra-pure water. After the conditioning process, both cartridges were connected in series (with SCX on top and SAX on bottom) with a 0.45 µm filter at the top. The sample (25 cm³) was passed through the assembly with an Agilent 20 cm³ disposable syringe (Apex Scientific, Maynooth, Ireland). Arsenite was retained within the effluent and was collected in a 60 cm³ bottle. Both SCX and SAX SPE cartridges were separated and 1 M HNO₃ (Romil, SpA) was passed through the SCX cartridge to collect DMA^V. For the SAX cartridge, 5 cm³ of CH₃CO₂H (Fluka Analytical, TraceSELECT[®], Sigma-Aldrich, Ireland) was used to collect MA^V while iAs^V was collected using 1 M HNO₃. In order to maximise recovery of the species, air was passed through the cartridge after each elution (Lord et al., 2012). As this is a pre-concentration technique the detection limits for this method are generally much lower when compared to analysis of total concentrations of trace elements in water.

6.2.3.5) *Samples for laboratory speciation of arsenic*

Confirmatory analysis by HPLC-ICP-MS was completed to validate the SPE field speciation procedure (Reilly et al., 2010). However, inorganic arsenic species are generally more prone to species redistribution than the methylated species. In the absence of preservation, the complete oxidation of As^{III} standards and reduction of As^V standards occurs within 36 hours at room temperature (Franscesconi and Kuehnelt, 2004). Prevention of arsenic species redistribution involved: i) sample filtration (for the removal of microorganisms and colloids), ii) reagent addition to prevent oxidation and precipitation of dissolved iron and manganese, and iii) isolation of sample from solar radiation (McCleskey et al., 2004). Preservation methods for arsenic speciation have included HNO₃, HCl, ethylenediaminetetraacetic acid (EDTA), H₂SO₄, phosphoric acid (H₃PO₄), ascorbic acid and ethanoic acid. Generally, EDTA is the preferred preservative, (Gallagher et al., 2001; Bednar et al. 2002; McCleskey et al., 2004; Pandey et al., 2004; Samanta and Clifford, 2005), however the use of EDTA can be problematic in groundwaters with high iron concentrations (McCleskey et al., 2004). When methylarsenicals are present EDTA is the preferred preservative (McCleskey et al., 2004).

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 (EDTA dipotassium dihydrate, Fluka Analytical, Sigma-Aldrich, Ireland) and stored in the dark at 4°C (Ujević et al., 2010).

6.2.4) Instrumental analysis

Details of instrumental analysis used for the detection of trace elements, anions, and arsenic species are provided in full, in Appendix A3.

6.2.5) Health implications

Using trace element concentrations from groundwater and taps, comparison can be made on the effectiveness of arsenic and other trace element removal using a treatment system that was pre-existing at the sampling location. This is denoted in Equation 6. 2.

$$\text{Percentage removal (\%)} = \frac{(M_W - M_T) * 100}{M_W} \quad (\text{Equation 6.2})$$

Where M_W = initial concentration of metal analyte in groundwater well and M_T = concentration of analyte in treated tap.

6.2.6) Data and spatial analysis

Due to the presence of data below the limit of quantification (LOQ) 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). For the purposes of this study the classification of arsenic concentrations was denoted as high ($> 50 \mu\text{g L}^{-1}$), moderate (>10 to $\leq 50 \mu\text{g L}^{-1}$), low ($\leq 10 \mu\text{g L}^{-1}$) (Welch et al., 2000).

6.2.6.1) Summary statistics

Summary statistics (mean, standard deviation, min, max, median, Q1 and Q3) were computed for each season based on different groundwater types (i.e. DW, BH and SP). Several methods exist for calculation of summary statistics in the presence of censored data: maximum likelihood estimation (MLE), Kaplan-Meier (KM) and regression on order statistics (ROS) (Helsel, 2012). While KM has been often used in survival analysis, it can introduce bias where one DL exists like in this study (Helsel, 2009). An advantage of ROS is that it can be computed for small datasets and can work up to a censoring rate of 80% (Helsel, 2012). ROS require data to follow a lognormal distribution (or any known distribution) where a probability plot is created and a probability plot correlation coefficient (PPCC) is generated (Helsel, 2012). In order to avoid transformation bias however, the summary statistics are computed by imputing

numbers for the censored observations based on a parametric model, i.e. “robust” ROS (Helsel, 2012). Where censored data were present summary statistics were computed using robust ROS using %*Cros* macro (Helsel, 2012). Where censoring is above 80% then these procedures are not accurate. In these cases, and/or where only two detects are observed then only the maximum value and censoring rate are presented. Number of samples above legal limits were also presented using data from Chapter 5 (Table 5.1) for information purposes.

6.2.6.2) *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 (Helsel and Hirsch, 2002; Helsel, 2012) using the %*Ckend* macro. The analysis from Kendall’s tau uses a rank-based measure of association which facilitates one or both parameters to be censored and requires no assumption on the distribution of the data (Goodwin et al., 2012). One feature to note is that Kendall’s tau is generally 0.15-0.20 lower than Spearman’s rho and Pearson’s r given the same strength of correlation as it is measured on a different scale (Helsel and Hirsch, 2002; Goodwin et al., 2012). Where censoring was $\geq 80\%$ for a variable then it was not included in 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). The advantage of this type of linear regression is that it can account for doubly censored data (Helsel, 2012). All tests were computed at the 0.05 significance level.

6.2.6.3) *Multivariate statistical analysis (MSA)*

To account for censored data, multivariate techniques were employed (Helsel, 2012). Due to presence of one LOQ ordinal methods were employed using the %*ordranks* macro in Minitab to get ranks of data (Helsel, 2012). Ranks of data 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® Statistics V25. 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 (Bartlett, 1950; Kaiser and Rice, 1974). For each analysis, principal components (PCs) with an eigenvalue greater than one were retained

(Kaiser, 1960). To complement PCA, hierarchical cluster analyses (HCA) was 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 (sites) to assess spatial clustering of parameters. Due to many non-detects for parameters certain parameters were not included in the MSA analysis: 2015 (Sn).

6.2.6.4) 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). The SI is defined as the logarithm of the ratio of the ion activity product (IAP) of the component ions of the solid in solution to the solubility product (K) for the solid [$SI = \log IAP/K$]. The SI of a given mineral indicates whether the groundwater is undersaturated (SI<0), at equilibrium (SI=0), or supersaturated (SI>0) with respect to that given mineral (Naus et al., 2001; Appelo and Postma, 2005). If the groundwater is undersaturated with respect to a given mineral (negative SI) then the groundwater would theoretically dissolve the mineral (Naus et al., 2001). If groundwater is supersaturated with respect to a given mineral (positive SI), then the mineral would theoretically precipitate from the groundwater (Naus et al., 2001). Due to several uncertainties (i.e. pH measurement, ionic strength, equilibrium constants, and laboratory analysis) the range that equates to equilibrium generally is denoted with a SI of -0.3 to +0.3.

6.2.6.5) Spatial analysis

All data were in the same projection and datum (TM65 Irish Grid and D-TM65). Groundwater contour lines (mOD) were mapped using ArcGIS 10.2 by creating by interpolation and subsequent transformation to contour lines (5 m interval).

6.3) Results and Discussion

6.3.1) Quality control

Overall, CRM 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 6.1. The result of this CRM is comparable with published data (Cotta and Enzweiler, 2014; Dial et al., 2015; Andy et al., 2017; Gafur et al., 2018).

Field duplicate samples were generally within $\pm 10\%$ relative standard deviation (RSD) for all samples with the new sampling method in 2015 and 2016 producing lower RSDs for certain elements (As, Na, and Ca). Where the RSD was higher these concentrations were low or near DLs and caused a higher RSD, i.e. for manganese. Both field and laboratory blanks showed that metal concentrations were low. After acid washing, water contained in bottles were all below the LODS for each parameter (data not shown). For some trace elements that were present in greater concentrations in groundwater (Fe, Mn, Ba, As and Cu), some concentrations were detected in the field blanks while they were below LOQs for laboratory blanks. While the concentrations in field blanks for the 2014 survey are lower, this method would not yield a truly representative groundwater sample. Comparatively, for trace elements quantified in groundwater at low concentrations, these were also found at low concentrations for field blanks (Ag and Cd).

Charge balances were generally within 10.5% for all samples; however, some were higher, BH-27 (15.3%), DW-7 (15.5%), and BH-46 (12.1%). Given some of these higher charge balances coincided with lower milliequivalents for anions, NO_3^- should have been included in the analysis as an anion based on its presence in groundwater in this general location (as given in Section 5.3.2).

6.3.2) Initial site characterisation

Historical data from 2007 (Table 6.2) and data collected as part of this study in 2014 (Table 6.3-6.5) show that groundwater arsenic concentrations are elevated. Trace element data from 2014 was separated out based on well type: DW and BH. Groundwater arsenic concentrations are higher in the deeper boreholes which ranged from 0.07-77.74 $\mu\text{g L}^{-1}$ (mean $9.05 \pm 13.09 \mu\text{g L}^{-1}$) when compared to the shallow dug wells which ranged from 0.071-3.135 $\mu\text{g L}^{-1}$ (mean $0.728 \pm 0.759 \mu\text{g L}^{-1}$). Indeed, a strong correlation ($\tau=0.5$) between arsenic and depth is evident. Arsenic also shows both moderate and weak positive correlations with other redox-sensitive oxyanions such as Mo ($\tau=0.44$), Sb ($\tau=0.39$), ($\tau=0.32$) and Se ($\tau=0.18$) with these oxyanions also being correlated with depth. With respects to elevated trace elements, arsenic exhibits the most exceedance of all the parameters (34.6%). Both arsenic distribution maps show general contamination hot-spots in the south east which may be as a result of groundwater flow (Fig.

6.3a-b). One well in the north-west displayed very elevated arsenic levels in 2007 ($139 \mu\text{g L}^{-1}$), however access to this location was prohibited in 2014 and later sampling campaigns.

Using these data, more detailed studies were completed in 2015 and 2016 (explored in greater detail below). While spring locations were monitored concentrations were generally low and due to their small sample number were not included in further monitoring.

Table 6.1. Recovery of CRM 1643f from 2016 (n=6) showing average concentration and average recovery. Values are represented by mean \pm standard deviation. All parameters reported in $\mu\text{g L}^{-1}$ except for Mg, Na, Sr, K and Ca where parameters are reported in mg L^{-1} .

Parameter	Certified value	Average concentration	Average Recovery (%)
B	152.3	175.19 \pm 33.02	115.03 \pm 21.68
Al	133.8	165.69 \pm 35.01	123.83 \pm 26.16
V	36.07	37.88 \pm 1.89	105.04 \pm 5.25
Cr	18.5	20.15 \pm 1.55	108.92 \pm 8.39
Mn	37.14	37.81 \pm 1.01	101.79 \pm 2.72
Fe	93.44	100.10 \pm 7.47	107.12 \pm 7.99
Co	25.3	25.51 \pm 0.94	100.86 \pm 3.72
Ni	59.8	60.60 \pm 2.74	101.34 \pm 4.59
Cu	21.66	21.48 \pm 1.07	99.21 \pm 4.96
Zn	74.4	79.04 \pm 6.02	106.24 \pm 8.10
As	57.42	61.64 \pm 0.79	107.35 \pm 1.38
Se	11.7	14.02 \pm 1.48	119.87 \pm 12.66
Mo	115.3	117.26 \pm 2.76	101.71 \pm 2.40
Ag	0.9703	0.45 \pm 0.04	46.91 \pm 4.39
Cd	5.89	6.49 \pm 0.21	110.18 \pm 3.69
Sb	55.45	58.71 \pm 1.71	105.87 \pm 3.09
Te	0.977	0.77 \pm 0.17	79.27 \pm 18.36
Ba	518.2	512.81 \pm 25.35	98.96 \pm 4.89
Tl	6.892	7.11 \pm 0.42	103.29 \pm 6.16
Pb	18.488	19.19 \pm 1.17	103.81 \pm 6.33
Bi	12.62	11.83 \pm 0.99	93.81 \pm 7.87
Mg	7.454	7.85 \pm 0.60	105.42 \pm 8.06
Na	18.83	21.01 \pm 1.81	111.61 \pm 9.61
Sr	0.314	0.33 \pm 0.01	106.13 \pm 5.97
K	1.9326	2.04 \pm 0.18	105.95 \pm 9.73
Ca	29.43	27.02 \pm 2.21	91.84 \pm 7.49

Table 6.2. Summary statistics of arsenic data (both referenced, non-georeferenced and combined arsenic geochemistry data).

Data	Georeferenced data	Non-georeferenced data	Combined
Count (n)	127	31	158
Mean	5.56	5.57	6.36
SD	16.87	9.9	15.73
Min	0.01	0.01	0.01
Q1	0.28	0.2	0.28
Median	0.91	0.88	0.91
Q3	5.70	4.7	5.17
Max	139	43	139
Censoring rate (%)	25.2	25.8	25.5
% > limit (7.5)	20.5	22.6	26.0
% > limit (10)	16.5	16.1	20.5

Table 6.3. Statistical summary of hydrochemistry data on bedrock boreholes sampled in 2014 (n = 75) (Limit values taken from the following references: interim guideline values (EPA, 2003), drinking water regulations (EC, 2014), and groundwater regulations (EC, 2010).

Variable	Mean	SD	Min	Q1	Median	Q3	Max	Cen (%)	Limit	% > Limit
Depth (m)	68.75	36.12	4.05	42.80	70.00	91.60	185.00	0	-	NA
Be ($\mu\text{g L}^{-1}$)	0.051	0.091	0.0009	0.0081	0.0209	0.0536	0.6590	86.6	-	NA
B ($\mu\text{g L}^{-1}$)	18.21	10.44	7.14	11.51	14.23	20.98	55.37	0	1000	0
Al ($\mu\text{g L}^{-1}$)	96.0	447.7	1.0	1.7	4.5	48.2	3855.5	0	200	9.33
Ti ($\mu\text{g L}^{-1}$)	31.49	22.12	0.33	19.11	26.55	38.09	139.13	0	-	NA
V ($\mu\text{g L}^{-1}$)	2.385	5.836	0.122	0.294	0.793	1.699	42.773	0	-	NA
Cr ($\mu\text{g L}^{-1}$)	0.719	1.877	0.031	0.174	0.350	0.476	14.439	2.6	50	0
Mn ($\mu\text{g L}^{-1}$)	39.5	136.5	0.0	0.2	0.6	2.7	840.3	10.6	50	9.3
Fe ($\mu\text{g L}^{-1}$)	2232	13230	2	10	18	70	112397	0	200	16
Co ($\mu\text{g L}^{-1}$)	0.2045	0.4399	0.0026	0.0249	0.0930	0.1360	2.634	44.0	-	NA
Ni ($\mu\text{g L}^{-1}$)	2.033	1.607	0.463	1.228	1.716	2.286	9.997	4.0	20	0
Cu ($\mu\text{g L}^{-1}$)	31.9	52.18	0.47	6.94	15.62	35.22	379.55	0	2000	0
Zn ($\mu\text{g L}^{-1}$)	112.8	192.4	3.0	13.2	30.8	118.6	879.3	0	5000	0
As ($\mu\text{g L}^{-1}$)	9.05	13.09	0.07	0.90	4.74	11.62	77.74	0	10	34.6
Se ($\mu\text{g L}^{-1}$)	0.833	1.276	0.132	0.362	0.510	0.657	9.525	0	10	0
Nb ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.109	98.6	-	NA
Mo ($\mu\text{g L}^{-1}$)	1.350	1.855	0.020	0.169	0.715	1.815	10.052	17.3	-	NA
Ag ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.2280	97.3	-	NA
Cd ($\mu\text{g L}^{-1}$)	0.0212	0.0416	0.0004	0.00351	0.00883	0.02214	0.331	78.6	5	0
Sb ($\mu\text{g L}^{-1}$)	0.3180	0.5499	0.0061	0.0517	0.1380	0.3440	3.309	37.3	5	0
Sn ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	1.44	88.0	-	NA
Ba ($\mu\text{g L}^{-1}$)	39.86	66.97	0.02	0.99	6.80	51.83	330.23	2.6	500	0
W ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	10.311	86.6	-	NA
Pb ($\mu\text{g L}^{-1}$)	2.10	7.140	0.082	0.267	0.553	1.086	57.957	0	10	4
U ($\mu\text{g L}^{-1}$)	1.182	1.895	0.028	0.216	0.514	1.171	10.454	2.6	30	0
Mg (mg L^{-1})	14.10	9.09	0.03	6.02	12.75	21.51	34.58	1.3	50	0
Si (mg L^{-1})	7.015	3.078	0.06	5.625	7.170	9.225	13.455	9.3	-	NA
Ca (mg L^{-1})	27.70	19.46	1.16	19.96	23.16	38.40	86.23	16.0	200	0
Sr (mg L^{-1})	0.629	2.577	0.004	0.045	0.135	0.255	16.71	10.6	-	NA
Na (mg L^{-1})	25.73	49.17	0.03	11.76	15.63	20.20	312.96	2.6	200	2.6
K (mg L^{-1})	3.789	8.361	0.083	1.125	1.680	2.520	49.915	6.6	5	10.6

Table 6.4. Statistical summary of hydrochemistry data on dug wells sampled in 2014 (n = 29)

Variable	Mean	SD	Min	Q1	Median	Q3	Max	Cen (%)	Limit	% > Limit
Depth (m)	4.936	2.119	1.40	3.55	4.450	6.10	10.14	0	-	NA
Be ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.195	89.6	-	NA
B ($\mu\text{g L}^{-1}$)	23.28	13.42	10.45	13.65	17.63	29.53	63.68	0	1000	0
Al ($\mu\text{g L}^{-1}$)	168.6	386.4	2.1	7.2	36.8	111.1	1731.3	0	200	13.8
Ti ($\mu\text{g L}^{-1}$)	44.33	29.08	5.90	24.39	31.56	72.80	108.75	0	-	NA
V ($\mu\text{g L}^{-1}$)	1.141	1.169	0.412	0.617	0.782	1.139	6.496	0	-	NA
Cr ($\mu\text{g L}^{-1}$)	0.643	0.951	0.189	0.296	0.437	0.595	5.424	0	50	0
Mn ($\mu\text{g L}^{-1}$)	34.1	133.6	0.2	0.7	3.4	11.4	718.9	0	50	6.9
Fe ($\mu\text{g L}^{-1}$)	267	602	6	18	56	122	2239	0	200	17.2
Co ($\mu\text{g L}^{-1}$)	0.1901	0.1937	0.0352	0.1085	0.1280	0.1830	0.9430	17.2	-	NA
Ni ($\mu\text{g L}^{-1}$)	2.142	0.983	0.471	1.441	2.222	2.745	4.946	0	20	0
Cu ($\mu\text{g L}^{-1}$)	45.7	58.9	0.6	1.9	16.7	76.3	206.9	0	2000	0
Zn ($\mu\text{g L}^{-1}$)	228	618	3	11	41	134	3264	0	5000	0
As ($\mu\text{g L}^{-1}$)	0.728	0.759	0.071	0.194	0.514	0.875	3.135	0	10	0
Se ($\mu\text{g L}^{-1}$)	0.5872	0.4408	0.1720	0.3405	0.4780	0.7300	2.5870	0	10	0
Nb ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.089	96.5	-	NA
Mo ($\mu\text{g L}^{-1}$)	0.319	0.667	0.004	0.029	0.090	0.387	3.519	51.7	-	NA
Ag ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	-	100	-	NA
Cd ($\mu\text{g L}^{-1}$)	0.02891	0.02366	0.0054	0.01310	0.02181	0.035	0.122	55.2	5	0
Sb ($\mu\text{g L}^{-1}$)	0.1884	0.4229	0.0002	0.0036	0.0197	0.1410	1.666	72.4	5	0
Sn ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.340	96.6	-	NA
Ba ($\mu\text{g L}^{-1}$)	14.76	11.74	0.98	5.91	8.62	23.04	41.43	0	500	0
W ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.269	96.6	-	NA
Pb ($\mu\text{g L}^{-1}$)	2.040	4.508	0.073	0.308	0.760	2.015	24.199	0	10	3.4
U ($\mu\text{g L}^{-1}$)	0.2853	0.1864	0.0609	0.1330	0.2380	0.3840	0.7650	17.2	30	0
Mg (mg L^{-1})	10.089	4.743	2.250	6.555	10.575	13.118	18.930	0	50	0
Si (mg L^{-1})	5.540	4.207	0.060	0.551	5.685	8.190	14.875	20.6	-	NA
Ca (mg L^{-1})	26.85	19.67	4.14	10.54	19.93	39.71	77.50	31.3	200	0
Sr (mg L^{-1})	0.2098	0.2768	0.0078	0.0375	0.1050	0.2700	1.1400	31.3	-	NA
Na (mg L^{-1})	12.98	10.99	0.03	0.13	12.56	19.73	40.84	13.8	200	0
K (mg L^{-1})	2.77	6.11	0.02	0.08	1.46	2.28	32.01	13.8	5	6.9

Table 6.5. Statistical summary of hydrochemistry data on springs sampled in 2014 (n = 3)

Variable	Mean	SD	Min	Q1	Median	Q3	Max	Cen (%)	Limit	% > Limit
Depth (m)	0.303	0.525	0.0	0.0	0.0	0.910	0.910	0	-	NA
Be ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.158	33.3	-	NA
B ($\mu\text{g L}^{-1}$)	12.01	2.05	10.27	10.27	11.49	14.28	14.28	0	1000	0
Al ($\mu\text{g L}^{-1}$)	87.5	89.6	13.7	13.7	61.6	187.2	187.2	0	200	0
Ti ($\mu\text{g L}^{-1}$)	15.0	11.94	3.92	3.92	13.46	27.64	27/64	0	-	NA
V ($\mu\text{g L}^{-1}$)	0.770	0.486	0.324	0.324	0.697	1.288	1.288	0	-	NA
Cr ($\mu\text{g L}^{-1}$)	0.355	0.1472	0.2120	0.212	0.347	0.506	0.506	0	50	0
Mn ($\mu\text{g L}^{-1}$)	29.1	47.7	0.7	0.7	2.5	84.2	84.2	0	50	33.3
Fe ($\mu\text{g L}^{-1}$)	132.7	159.1	19.6	19.6	63.7	314.6	314.6	0	200	33.3
Co ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.116	33.3	-	NA
Ni ($\mu\text{g L}^{-1}$)	0.855	0.529	0.532	0.532	0.567	1.465	1.465	0	20	0
Cu ($\mu\text{g L}^{-1}$)	0.890	0.308	0.553	0.553	0.958	1.158	1.158	0	2000	0
Zn ($\mu\text{g L}^{-1}$)	3.071	0.873	2.213	2.213	3.043	3.958	3.958	0	5000	0
As ($\mu\text{g L}^{-1}$)	0.259	0.072	0.176	0.176	0.297	0.304	0.304	0	10	0
Se ($\mu\text{g L}^{-1}$)	0.3223	0.1171	0.2300	0.2300	0.2830	0.454	0.454	0	10	0
Nb ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	-	100.0	-	NA
Mo ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.370	66.6	-	NA
Ag ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	-	100.0	-	NA
Cd ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	-	100.0	5	0
Sb ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	-	100.0	5	0
Sn ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	-	100.0	-	NA
Ba ($\mu\text{g L}^{-1}$)	3.89	3.85	1.59	1.59	1.74	8.34	8.34	0	500	0
W ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	-	100.0	-	NA
Pb ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.152	33.3	10	0
U ($\mu\text{g L}^{-1}$)	0.1367	0.0505	0.106	0.106	0.109	0.195	0.195	0	30	0
Mg (mg L ⁻¹)	5.5	3.83	2.52	2.52	4.17	9.83	9.83	0	50	0
Si (mg L ⁻¹)	-	-	-	-	-	-	5.565	33.3	-	NA
Ca (mg L ⁻¹)	-	-	-	-	-	-	42.48	33.3	200	0
Sr (mg L ⁻¹)	-	-	-	-	-	-	0.195	33.3	-	NA
Na (mg L ⁻¹)	-	-	-	-	-	-	31.815	33.3	200	0
K (mg L ⁻¹)	-	-	-	-	-	-	9.135	33.3	5	33.3

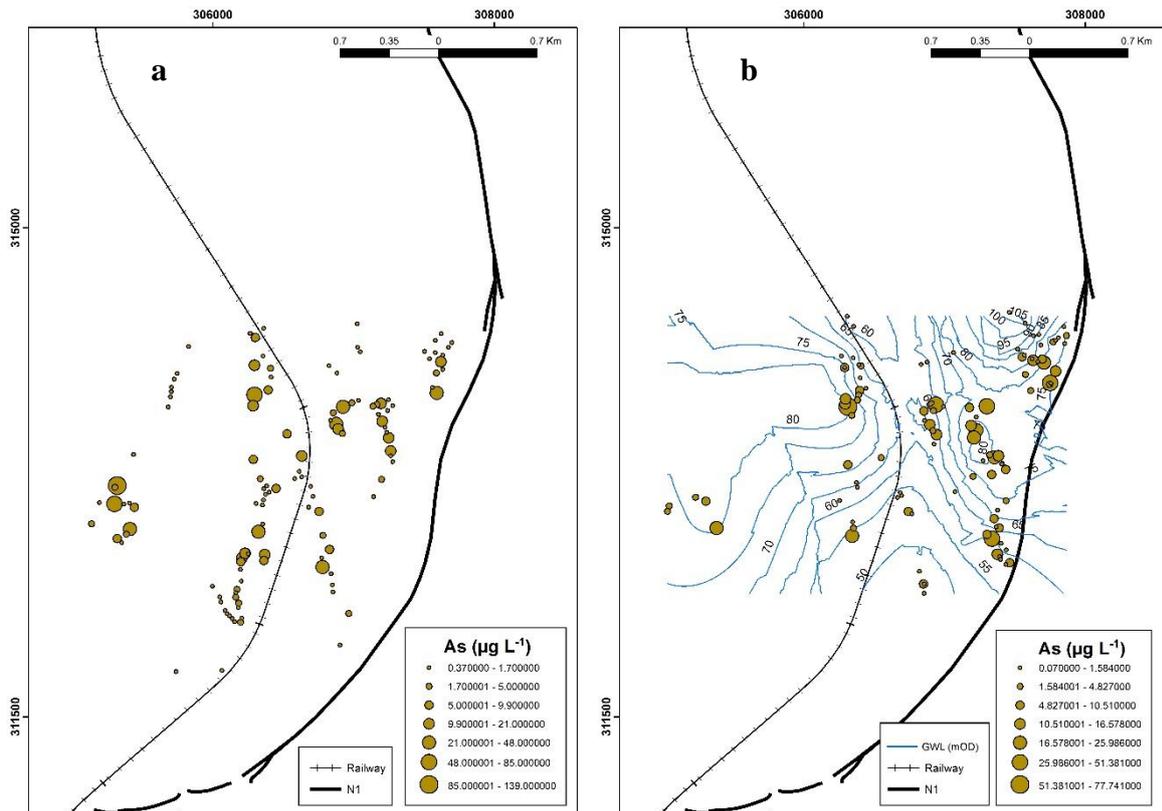


Fig. 6.3. Arsenic concentrations for (a) historic data (2007) and (b) initial characterisation data (2014) showing arsenic ranges and groundwater contours (5m interval).

6.3.3) *Physio-chemical parameters*

Statistical summaries of data measured in 2015 and 2016 are presented in Tables 6.6-6.9 and are separated by groundwater type. Eh values are characteristic 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 reducing conditions were observed in 2016. In 2016 DW-17 and BH-40 (both wells at the same dwelling) had an Eh of -52.1 mV and -121.5 mV with the corresponding pH of 6.7 and 8.04 respectively. Previous studies in Quebec have also demonstrated shallow wells displaying more oxidising conditions compared to bedrock wells (Bondu et al., 2017a). Furthermore, the level of arsenic contamination is generally lower in oxic aquifers compared to anoxic aquifers (Masuda, 2018). Groundwaters from boreholes were acidic to alkaline with pH ranging from 6.33 to 8.57 (mean: 7.54 ± 0.54) with dug wells being acidic ranging from 6.12 to 6.85 (mean: 6.54 ± 0.28). In comparison, pH values in 2016 increased where groundwater in boreholes was slightly acidic to alkaline with pH ranging from 6.87 to 8.33 (mean: 7.71 ± 0.34) with dug wells being acidic to near-neutral ranging from 6.45 to 7.14 (mean: 6.79 ± 0.34). Lower pH values were generally observed in the 15-60 m depth category. Generally, groundwaters were

described as alkaline oxidising (or oxic-alkali) for boreholes and acidic alkaline groundwaters for the shallower dug wells (Fig. 6.4) and while some boreholes were described as acidic oxidising all of these are categorised as low-arsenic wells. The Eh-pH conditions overlap with results obtained for both shallow and deep groundwaters in the Croagh Patrick region in western Ireland (Gilligan et al., 2016). These oxidising conditions are consistent with the concentrations of d-O₂ measured in 2016 (4.17±6.88 mg L⁻¹ for BHs and 5.23±3.06 mg L⁻¹ for DWs). One borehole in 2015 may be considered mildly reducing (BH-66). Only three sites have low d-O₂ measurements (BH-20, 0.22 mg L⁻¹; BH-47 0.12 mg L⁻¹; and BH-25, 0.485 mg L⁻¹) characteristic of a suboxic redox state (McMahon and Chapelle, 2008). As other wells had d-O₂ ≥ 0.5 mg L⁻¹, Mn ≤ 50 µg L⁻¹, and Fe ≤ 100 µg L⁻¹, the redox couple present in these groundwaters is likely O₂ reduction (Thomas, 2007; McMahon and Chapelle, 2008). However, for other wells where Mn ≥ 50 µg L⁻¹ and/or Fe ≥ 100 µg L⁻¹ with d-O₂ ≥ 0.5 mg L⁻¹ this is characteristic for a mixed redox state (Thomas, 2007; McMahon and Chapelle, 2008).

Conductivity was higher in shallow surface dug wells (mean: 2015, 440±320 µS cm⁻¹; 2016, 623±521 µS cm⁻¹) compared to deeper boreholes (mean: 2015, 388.3±220.4 µS cm⁻¹; 2016, 338.3±143.3 µS cm⁻¹). At one site, two wells (DW-11 and BH-23) had high conductivities (>1000 µS cm⁻¹) in 2015 and were slightly lower in 2016. While groundwater temperatures were consistent during monitoring, sometimes a higher temperature than expected was recorded due to solar radiation warming sampling tubing.

Generally, SWLs were <9 m with boreholes in the 60-120m category being 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. When sampling this borehole SWL varied from to a few cm to overflowing. A linear regression showed that GWLs in both years (n = 19) are positively correlated (n = 19, τ = 0.54, p = 0.001) with GWLs from 2016 being approximately 2.9% higher when compared to 2015.

Table 6.6. Statistical summary of hydrochemistry data on bedrock boreholes sampled in 2015 (n = 35)

Variable	Mean	SD	Min	Q1	Median	Q3	Max	Cen (%)	Limit	% > Limit
Depth (m)	76.64	35.83	9.10	49.30	79.40	104.0	148.8	0	-	NA
SWL (m)	6.357	5.75	0.04	2.74	5.22	8.115	32.76	0	-	NA
Temp (°C)	11.3	1.2	9.8	10.3	11.4	11.7	16.3	0	-	NA
C ($\mu\text{S cm}^{-1}$)	388.3	220.4	87.7	239.5	374.0	477.7	1405.0	0	2500	0
TDS (mg L^{-1})	266.8	152.8	60.5	159.9	258.1	329.6	969.4	0	-	NA
pH	7.54	0.54	6.33	7.27	7.65	7.96	8.57	0	≥ 6.5 and ≤ 9.5	5.7
Eh (mV)	463.1	66.3	191.6	442.7	480.8	499.9	538.3	0	-	NA
Cl ⁻ (mg L^{-1})	19.71	8.45	1.44	13.83	18.43	24.73	37.93	0	250	0
SO ₄ ²⁻ (mg L^{-1})	15.73	12.21	8.0	10.0	13.0	17.0	81.0	0	250	0
F ⁻ (mg L^{-1})	0.216	0.397	0.050	0.090	0.140	0.210	2.46	0	1.5	2.8
Alk (mg L^{-1})	119.9	45.8	33.4	76.6	120.1	159.6	203.3	0	-	NA
Be ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.164	97.2	-	NA
B ($\mu\text{g L}^{-1}$)	10.311	4.252	6.305	7.319	8.985	11.782	23.474	0	1000	0
Al ($\mu\text{g L}^{-1}$)	3.57	8.55	0.34	0.67	1.40	2.87	51.30	0	200	0
Ti ($\mu\text{g L}^{-1}$)	0.884	0.915	0.181	0.509	0.830	0.965	5.871	2.8	-	NA
V ($\mu\text{g L}^{-1}$)	1.676	3.358	0.029	0.244	0.483	1.322	15.814	5.7	-	NA
Cr ($\mu\text{g L}^{-1}$)	0.1552	0.5526	0.0001	0.0025	0.0130	0.0723	3.2633	65.7	50	0
Mn ($\mu\text{g L}^{-1}$)	20.6	103.2	0.0	0.2	0.3	1.5	611.0	8.6	50	2.8
Fe ($\mu\text{g L}^{-1}$)	1132	6634	0	0	1	5	39257	45.7	200	5.7
Co ($\mu\text{g L}^{-1}$)	0.0414	0.1291	0.0	0.0002	0.0018	0.0132	0.6857	71.4	-	NA
Ni ($\mu\text{g L}^{-1}$)	1.2347	0.5477	0.4083	0.7799	1.0758	1.6013	2.6218	2.8	20	0
Cu ($\mu\text{g L}^{-1}$)	0.871	0.784	0.112	0.381	0.527	0.996	3.347	5.7	2000	0
Zn ($\mu\text{g L}^{-1}$)	2.911	3.362	0.262	0.978	2.133	2.928	14.134	0	5000	0
As ($\mu\text{g L}^{-1}$)	11.27	12.62	0.11	1.38	7.18	19.43	51.25	8.6	10	45.7
Se ($\mu\text{g L}^{-1}$)	0.480	0.896	0.003	0.030	0.126	0.454	4.029	37.1	10	0
Mo ($\mu\text{g L}^{-1}$)	1.801	1.953	0.059	0.212	1.467	2.394	8.086	17.1	-	NA
Ag ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.1323	97.1	-	NA
Cd ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.049	97.1	5	0
Sb ($\mu\text{g L}^{-1}$)	0.358	0.651	0.005	0.038	0.119	0.321	2.962	40.0	5	0
Ba ($\mu\text{g L}^{-1}$)	43.5	67.7	0.1	0.6	5.2	77.5	285	0	500	0
W ($\mu\text{g L}^{-1}$)	0.275	1.350	0.0	0.001	0.006	0.045	8.021	77.1	-	NA
Pb ($\mu\text{g L}^{-1}$)	0.0676	0.0966	0.0027	0.0137	0.0327	0.0778	0.5123	77.1	10	0
U ($\mu\text{g L}^{-1}$)	1.614	2.407	0.018	0.155	0.635	2.402	9.304	20.0	30	0
Mg (mg L^{-1})	11.78	8.70	0.58	5.14	9.60	17.73	34.44	0	50	0
Si (mg L^{-1})	6.059	1.916	0.984	4.803	5.732	6.884	11.296	0	-	NA
Ca (mg L^{-1})	41.63	19.06	11.78	26.46	39.78	56.71	73.77	0	200	0
Na (mg L^{-1})	13.688	5.724	2.954	9.741	13.092	16.388	35.948	0	200	0
Sr (mg L^{-1})	0.3461	0.3204	0.0260	0.0723	0.2287	0.5183	1.1113	0	-	NA
K (mg L^{-1})	1.946	2.857	0.391	1.10	1.431	1.864	18.084	0	5	2.8

Table 6.7. Statistical summary of hydrochemistry data on dug wells sampled in 2015 (n = 8)

Variable	Mean	SD	Min	Q1	Median	Q3	Max	Cen (%)	Limit	% > Limit
Depth (m)	4.327	1.783	1.960	2.825	3.825	5.985	6.970	0	-	NA
SWL (m)	2.548	1.490	0.500	1.114	2.620	3.230	5.190	0	-	NA
Temp (°C)	10.40	0.922	9.650	9.775	10.025	10.788	12.450	0	-	NA
C ($\mu\text{S cm}^{-1}$)	440	320	134	169	399	619	1044	0	2500	0
TDS (mg L^{-1})	303.6	221.1	92.2	116.5	275.4	427.1	720.0	0	-	0
pH	6.54	0.28	6.12	6.26	6.55	6.83	6.855	0	≥ 6.5 and ≤ 9.5	50.0
Eh (mV)	483.2	24.97	452.85	467.99	478.48	496.11	534.80	0	-	NA
Cl ⁻ (mg L^{-1})	52.5	27.0	76.5	12.2	15.3	17.1	59.9	0	250	0
SO ₄ ²⁻ (mg L^{-1})	12.2	3.4	9.0	10.0	11.0	15.0	19.0	0	250	0
F ⁻ (mg L^{-1})	0.131	0.041	0.06	0.095	0.145	0.157	0.190	0	1.5	0
Alk (mg L^{-1})	101.9	70.5	33.7	38.6	85.6	173.5	216.9	0	-	NA
Be ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	-	100	-	NA
B ($\mu\text{g L}^{-1}$)	13.96	7.93	6.49	7.17	12.65	17.03	30.71	0	1000	0
Al ($\mu\text{g L}^{-1}$)	5.99	6.91	0.74	1.25	2.44	11.86	19.41	0	200	0
Ti ($\mu\text{g L}^{-1}$)	0.717	0.301	0.389	0.492	0.638	0.990	1.229	0	-	NA
V ($\mu\text{g L}^{-1}$)	0.744	0.339	0.445	0.471	0.631	0.938	1.432	0	-	NA
Cr ($\mu\text{g L}^{-1}$)	0.1025	0.0697	0.0283	0.0432	0.0872	0.1502	0.2357	37.5	50	0
Mn ($\mu\text{g L}^{-1}$)	26.4	36.2	0.0	0.4	2.5	60.5	89.5	12.5	50	37.5
Fe ($\mu\text{g L}^{-1}$)	53.1	112.5	0.1	0.4	3.5	66.8	321.9	12.5	200	12.5
Co ($\mu\text{g L}^{-1}$)	0.1538	0.1049	0.0404	0.0625	0.1265	0.2551	0.3290	37.5	-	NA
Ni ($\mu\text{g L}^{-1}$)	1.150	0.875	0.499	0.572	1.708	2.195	2.627	0	20	0
Cu ($\mu\text{g L}^{-1}$)	6.99	14.25	0.34	0.60	1.67	4.79	42.01	0	2000	0
Zn ($\mu\text{g L}^{-1}$)	20.54	27.53	0.58	0.92	2.61	48.77	67.67	0	5000	0
As ($\mu\text{g L}^{-1}$)	0.649	1.262	0.01	0.043	0.204	0.528	3.737	25.0	10	0
Se ($\mu\text{g L}^{-1}$)	0.1194	0.0607	0.0491	0.0665	0.1117	0.1858	0.2103	37.5	10	0
Mo ($\mu\text{g L}^{-1}$)	0.3992	0.0943	0.2779	0.3201	0.3809	0.4947	0.5442	62.5	-	NA
Ag ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.169	87.5	-	NA
Cd ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.0409	87.5	5	0
Sb ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.285	75.0	5	0
Ba ($\mu\text{g L}^{-1}$)	11.22	10.41	3.01	6.40	7.56	12.85	35.78	0	500	0
W ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	-	100	-	NA
Pb ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.312	87.5	10	0
U ($\mu\text{g L}^{-1}$)	0.1837	0.2368	0.0185	0.0412	0.1236	0.1794	0.7508	25.0	30	0
Mg (mg L^{-1})	9.41	7.12	2.07	3.43	7.61	16.52	20.55	0	50	0
Si (mg L^{-1})	5.920	1.653	3.882	4.619	5.741	6.977	9.088	0	-	NA
Ca (mg L^{-1})	52.5	33.9	14.1	18.5	55.5	80.9	94.9	0	200	0
Na (mg L^{-1})	24.6	31.3	8.8	9.8	11.4	27.4	99.8	0	200	0
Sr (mg L^{-1})	0.1464	0.0987	0.0447	0.0580	0.1347	0.2150	0.3123	0	-	NA
K (mg L^{-1})	2.439	2.243	0.720	1.119	1.474	3.231	7.523	0	5	12.5

Table 6.8. Statistical summary of hydrochemistry data on bedrock boreholes sampled in 2016 (n = 17)

Variable	Mean	SD	Min	Q1	Median	Q3	Max	Cen (%)	Limit	% > Limit
Depth (m)	86.9	30.93	17.30	68.5	91.4	110.25	148.8	0	-	NA
SWL (m)	6.48	6.64	1.78	3.31	5.03	5.26	30.15	0	-	NA
Temp (°C)	13.7	2.1	10.9	12.1	13.5	14.7	18.6	0	-	NA
C ($\mu\text{S cm}^{-1}$)	338.3	143.3	88.6	233.2	322.8	415.3	650.0	0	2500	0
TDS (mg L^{-1})	233.5	98.9	61.2	160.9	222.8	286.6	448.5	0	-	NA
pH	7.71	0.34	6.87	7.43	7.75	7.95	8.33	0	≥ 6.5 and ≤ 9.5	0
Eh (mV)	300.6	139.1	-121.5	248.6	300.7	420.5	460.3	0	-	NA
DO (mg L^{-1})	4.17	6.88	0.12	0.65	1.39	5.77	28.47	0	-	NA
Cl ⁻ (mg L^{-1})	17.4	14.2	0.32	11.1	12.1	18.5	62.3	0	250	0
SO ₄ ²⁻ (mg L^{-1})	15.6	6.39	8.0	10.0	13.0	21.5	28.0	0	250	0
F ⁻ (mg L^{-1})	0.1602	0.0609	0.05	0.1050	0.17	0.2117	0.25	0	1.5	0
Alk (mg L^{-1})	118.7	45.4	37.7	80.6	119.8	157.9	226.5	0	-	NA
B ($\mu\text{g L}^{-1}$)	10.29	7.77	5.10	5.96	6.78	11.98	30.29	0	1000	0
Al ($\mu\text{g L}^{-1}$)	1.824	1.847	0.381	0.811	1.099	2.503	8.10	0	200	0
Ti ($\mu\text{g L}^{-1}$)	0.534	0.412	0.094	0.254	0.312	0.909	1.354	5.88	-	NA
V ($\mu\text{g L}^{-1}$)	1.259	1.661	0.030	0.178	0.462	1.830	5.330	11.7	-	NA
Cr ($\mu\text{g L}^{-1}$)	0.2149	0.1864	0.0319	0.0932	0.1573	0.2618	0.7173	5.88	50	0
Mn ($\mu\text{g L}^{-1}$)	4.25	13.81	0.01	0.14	0.37	0.94	57.27	11.7	50	5.88
Fe ($\mu\text{g L}^{-1}$)	4.47	10.38	0.0	0.03	0.37	1.33	32.78	41.1	200	0
Co ($\mu\text{g L}^{-1}$)	0.0794	0.0264	0.0429	0.0591	0.0745	0.0983	0.147	64.7	-	NA
Ni ($\mu\text{g L}^{-1}$)	1.497	0.722	0.583	0.978	1.222	2.053	3.499	0	20	0
Cu ($\mu\text{g L}^{-1}$)	0.877	0.747	0.182	0.374	0.721	1.064	2.881	0	2000	0
Zn ($\mu\text{g L}^{-1}$)	2.456	2.075	0.373	0.904	1.732	3.657	7.463	0	5000	0
As ($\mu\text{g L}^{-1}$)	20.65	19.94	0.13	4.93	15.47	28.75	73.95	0	10	70.5
As ^{III} ($\mu\text{g L}^{-1}$)	0.1724	0.1982	0.008	0.0485	0.0670	0.2765	0.611	0	10	0
As ^V ($\mu\text{g L}^{-1}$)	16.92	16.85	0.10	3.86	11.79	25.27	64.30	0	10	64.7
DMA ($\mu\text{g L}^{-1}$)	0.688	0.543	0.121	0.264	0.532	0.945	2.256	0	10	0
MA ($\mu\text{g L}^{-1}$)	0.0273	0.0287	0.0068	0.0128	0.0182	0.0317	0.128	0	10	0
Se ($\mu\text{g L}^{-1}$)	0.401	1.039	0.001	0.011	0.051	0.298	4.342	58.8	10	0
Mo ($\mu\text{g L}^{-1}$)	2.373	2.323	0.117	0.595	1.855	3.464	8.012	5.8	-	NA
Ag ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	-	100	-	NA
Cd ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.032	94.2	5	0
Sn ($\mu\text{g L}^{-1}$)	0.1102	0.065	0.0361	0.0624	0.0929	0.1515	0.2995	64.7	-	NA
Sb ($\mu\text{g L}^{-1}$)	0.587	0.813	0.028	0.123	0.302	0.589	3.292	11.7	5	0
Ba ($\mu\text{g L}^{-1}$)	64.1	81.9	0.2	0.7	13.7	114.6	284.3	0	500	0
W ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.2057	82.3	-	NA
Pb ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	1.421	82.3	10	0
U ($\mu\text{g L}^{-1}$)	1.610	2.260	0.031	0.204	0.563	2.059	7.579	17.6	30	0
Mg (mg L^{-1})	13.70	10.07	0.16	3.43	15.0	20.76	32.10	0	50	0
Si (mg L^{-1})	6.164	1.872	0.396	5.926	6.258	6.668	10.611	0	-	NA
Ca (mg L^{-1})	30.77	15.74	10.22	21.81	24.90	35.86	81.84	0	200	0
Na (mg L^{-1})	14.20	4.57	3.93	10.97	14.59	17.10	22.65	0	200	0
Sr (mg L^{-1})	0.4158	0.3549	0.009	0.0175	0.4851	0.6030	1.1280	0	-	NA
K (mg L^{-1})	1.497	0.678	0.199	1.117	1.437	1.747	2.965	0	5	0

Table 6.9. Statistical summary of hydrochemistry data on dug wells sampled in 2016 (n = 3)

Variable	Mean	SD	Min	Q1	Median	Q3	Max	Cen (%)	Limit	% > Limit
Depth (m)	3.717	0.293	3.50	3.50	3.60	4.050	4.050	0	-	NA
SWL (m)	2.704	0.914	1.650	1.650	3.203	3.260	3.260	0	-	NA
Temp (°C)	14.7	2.9	12.2	12.2	13.9	18.0	18.0	0	-	NA
C ($\mu\text{S cm}^{-1}$)	623.0	521.0	224.0	224.0	433.0	1213.0	1213.0	0	2500	0
TDS (mg L^{-1})	430.0	360.0	154.0	154.0	299.0	837.0	837.0	0	-	0
pH	6.79	0.34	6.45	6.45	6.78	7.14	7.14	0	≥ 6.5 and ≤ 9.5	33.3
Eh (mV)	247.0	271.0	-52.0	-52.0	316.0	476.0	476.0	0	-	NA
DO (mg L^{-1})	5.23	3.06	2.15	2.15	5.28	8.26	8.26	0	-	NA
Cl ⁻ (mg L^{-1})	118.2	168.3	8.6	8.6	33.9	312	312	0	250	33.3
SO ₄ ²⁻ (mg L^{-1})	14.67	6.03	9.0	9.0	14.0	21.0	21.0	0	250	0
F ⁻ (mg L^{-1})	0.1089	0.0483	0.060	0.060	0.110	0.1567	0.1567	0	1.5	0
Alk (mg L^{-1})	99.6	29.3	73.0	73.0	94.7	131.0	131.0	0	-	NA
B ($\mu\text{g L}^{-1}$)	20.7	14.7	7.08	7.08	18.74	36.28	26.28	0	1000	0
Al ($\mu\text{g L}^{-1}$)	3.12	2.38	1.51	1.51	1.99	5.86	5.86	0	200	0
Ti ($\mu\text{g L}^{-1}$)	0.641	0.523	0.286	0.286	0.396	1.242	1.242	0	-	NA
V ($\mu\text{g L}^{-1}$)	1.4	0.566	0.750	0.750	1.657	1.791	1.791	0	-	NA
Cr ($\mu\text{g L}^{-1}$)	0.3160	0.1455	0.2167	0.2167	0.2483	0.4830	0.4380	0	50	0
Mn ($\mu\text{g L}^{-1}$)	48.0	59.0	6.7	6.7	21.7	115.5	115.5	0	50	33.3
Fe ($\mu\text{g L}^{-1}$)	47.0	57.3	5.5	5.5	23.2	112.3	112.3	0	200	0
Co ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.461	33.3	-	NA
Ni ($\mu\text{g L}^{-1}$)	2.229	1.039	1.220	1.220	2.170	3.296	3.296	0	20	0
Cu ($\mu\text{g L}^{-1}$)	2.85	2.26	0.87	0.87	2.39	5.31	5.31	0	2000	0
Zn ($\mu\text{g L}^{-1}$)	6.68	4.19	2.34	2.34	7.02	10.7	10.7	0	5000	0
As ($\mu\text{g L}^{-1}$)	0.923	0.974	0.307	0.307	0.415	2.046	2.046	0	10	0
As ^{III} ($\mu\text{g L}^{-1}$)	0.208	0.256	0.033	0.033	0.09	0.502	0.502	0	10	0
As ^V ($\mu\text{g L}^{-1}$)	0.695	0.882	0.094	0.094	0.283	1.708	1.708	0	10	0
DMA ($\mu\text{g L}^{-1}$)	0.2077	0.0058	0.2016	0.2016	0.2084	0.2132	0.2132	0	10	0
MA ($\mu\text{g L}^{-1}$)	0.0248	0.0218	0.0116	0.0116	0.0128	0.05	0.05	0	10	0
Se ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	-	100	10	0
Mo ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	1.007	33.3	-	NA
Ag ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.2836	66.6	-	NA
Cd ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.055	66.6	5	0
Sn ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.30	66.6	-	NA
Sb ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	0.164	66.6	5	0
Ba ($\mu\text{g L}^{-1}$)	14.93	15.94	5.32	5.32	6.13	33.33	33.33	0	500	0
W ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	-	100.0	-	NA
Pb ($\mu\text{g L}^{-1}$)	-	-	-	-	-	-	-	100.0	10	0
U ($\mu\text{g L}^{-1}$)	0.328	0.195	0.141	0.141	0.313	0.531	0.531	0	30	0
Mg (mg L^{-1})	9.84	7.94	2.99	2.99	7.99	18.55	18.55	0	50	0
Si (mg L^{-1})	6.258	1.276	5.440	5.440	5.606	7.729	7.729	0	-	NA
Ca (mg L^{-1})	46.8	21.6	25.6	25.6	46.1	68.7	68.7	0	200	0
Na (mg L^{-1})	52.1	54.1	12.5	12.5	30.2	113.7	113.7	0	200	0
Sr (mg L^{-1})	0.176	0.173	0.023	0.023	0.141	0.364	0.364	0	-	NA
K (mg L^{-1})	3.53	3.72	1.10	1.10	1.67	7.81	7.81	0	5	33.3

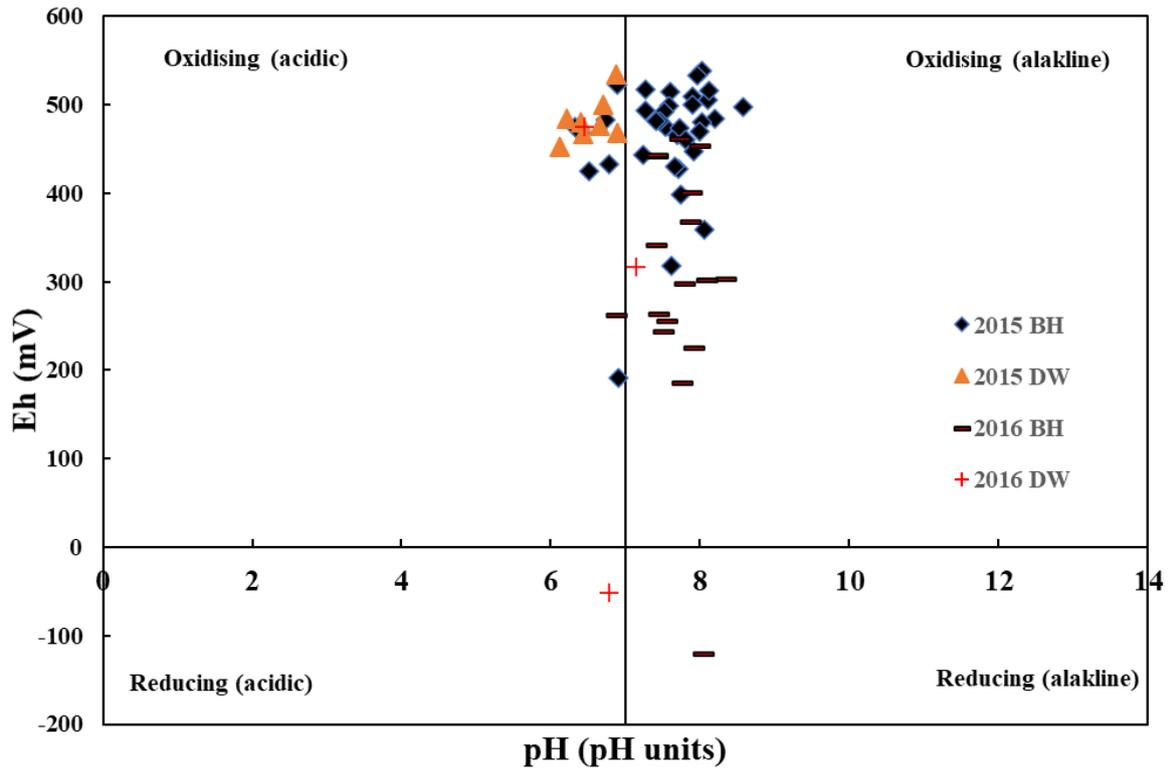


Fig. 6.4. Illustrative representation of oxidising to reducing and acidic to alkaline environments for groundwater data in 2015 and 2016. For reference, both DW-17 and BH-40 are at the bottom of the figure.

6.3.4) Major-ion geochemistry and hydrogeochemical facies

According to the Piper diagram (Fig. 6.5a-b), hydrochemical facies of groundwater mainly consisted of Ca-Mg-HCO₃ indicating mainly recharged groundwater and the predominant water-type of shallow and deep groundwater was Ca-HCO₃ for both 2015 and 2016. This describes the calcareous nature of the Clontail Formation and Dinantian Limestones. The dominant cation was Ca followed by Mg with the dominant anion being HCO₃ followed by Cl. Chloride as a dominant anion was only observed in one well (DW-11) showing a Na-Cl water type. In 2015 Cl was 236 mg L⁻¹, Na was 110.2 mg L⁻¹ and conductivity was 1044 μS cm⁻¹, while in 2016 Cl was 312 mg L⁻¹, Na was 129.1 mg L⁻¹ and conductivity was 1212.5 μS cm⁻¹ at this location. While a deeper borehole in the same location (BH-23, 148.8 m) had a high conductivity it was represented as a Ca-HCO₃ water-type with lower concentrations of Na and Cl.

By understanding the hydrochemical facies of water an overall characterisation of hydrogeochemical processes of natural waters is possible. One method, Chadha's diagram (Chadha, 1999) uses the difference in milliequivalent percentage between alkaline earth metals (Ca²⁺+Mg²⁺) and alkali metals (Na⁺+K⁺), expressed as percentage reacting values and is plotted

on the x-axis while the difference in milliequivalent percentage between weak acid anions (HCO_3^-) and strong acid anions ($\text{Cl}^- + \text{SO}_4^{2-}$) is plotted on the y-axis. The milliequivalent percentage difference between these groups when plotted is placed on four possible subfields of the diagram with the overall rectangle describing the overall characterisation of the water. In both years (Fig. 6.6a-b) most sites fall within the recharging waters (Ca-HCO_3^-) field, i.e. alkaline earths and weak acidic anions exceed both alkali metals and strong acidic anions. 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. Shallow saline groundwaters may be responsible for the elevated concentrations of both Na and Cl in one surface well (DW-11).

In addition, the Gibbs diagram (Gibbs, 1970) can be used and represents the ratio of $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ and $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ (i.e. for cations and anions) as a function of TDS in order to access the functional sources of dissolved chemical constituents such as precipitation dominance, rock dominance, and evaporation dominance in order to find the mechanism controlling groundwater chemistry. For both years (Fig. 6.7a-d) most samples in this locality lie within rock weathering dominance. A small number of samples lie in evaporation dominance and these wells are associated with high Cl^- and Na^+ concentrations (i.e. DW-11). 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 the 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. Fluoride concentrations measured were generally low in boreholes, except for BH-58 which recorded a value of 2.46 mg L^{-1} while K was measured at a few sites above the prescribed value at a maximum concentration of 18.08 mg L^{-1} in BH-06 in 2015. Fluoride does not show many correlations with major anions, but a weak negative correlation exists with K ($\tau = -0.24$) (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-} ($\tau = 0.19^*$), F^- ($\tau = 0.25$), Mg ($\tau = 0.25$), Na ($\tau = 0.23$), and Si ($\tau = 0.22$). Different levels of strength of the monotonic relationship are seen for several ions are shown in Table 6.10. Sr shows a weak positive correlation with pH ($\tau = 0.23$) while K shows a weak negative correlation with depth ($\tau = -0.14^*$). Conductivity shows a strong correlation with Ca

($\tau=0.68$), HCO_3^- ($\tau=0.63$), moderate correlation with SO_4^{2-} ($\tau=0.45$), Cl ($\tau=0.48$), Mg ($\tau=0.46$), Na ($\tau=0.37$), Sr ($\tau=0.40$) and K ($\tau=0.31$), and weak for Si ($\tau=0.26$). The strong correlation with Ca and HCO_3^- ($\tau=0.54$) also indicates that these ions are the major ones resulting from rock 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). 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, 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. $\text{Na/Cl}<1$) while contribution of extra Na may result from silicate weathering given that some samples lie above the equiline of 1:1 (i.e. $\text{Na/Cl}>1$) (Juen et al., 2015; Marghade et al., 2015; Ndoye et al., 2018). 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., 2017a). 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 Section 6.3.9).

Table 6.10. Correlation coefficients of major ions in groundwater

Strong		Moderate		Weak	
Group	τ	Group	T	Group	τ
Sr and Mg	0.65	Ca and Cl	0.44	SO_4^{2-} and K	0.28
		Ca and K	0.39	SO_4^{2-} and Na	0.27
HCO_3^- and Sr	0.57	Cl and Na	0.30	Ca and Sr	0.27
SO_4^{2-} and Mg	0.56	Ca and Na	0.30	Cl and Mg	0.25
HCO_3^- and Sr	0.54	Ca and Si	0.30	Cl and Sr	0.24
HCO_3^- and Mg	0.54	Mg and Ca	0.30	SO_4^{2-} and Ca	0.25
Si and Na	0.51	Si and K	0.30	SO_4^{2-} and Si	0.23
SO_4^{2-} and Mg	0.50	-	-	HCO_3^- and K	0.21
-	-	-	-	Mg and Si	0.17*

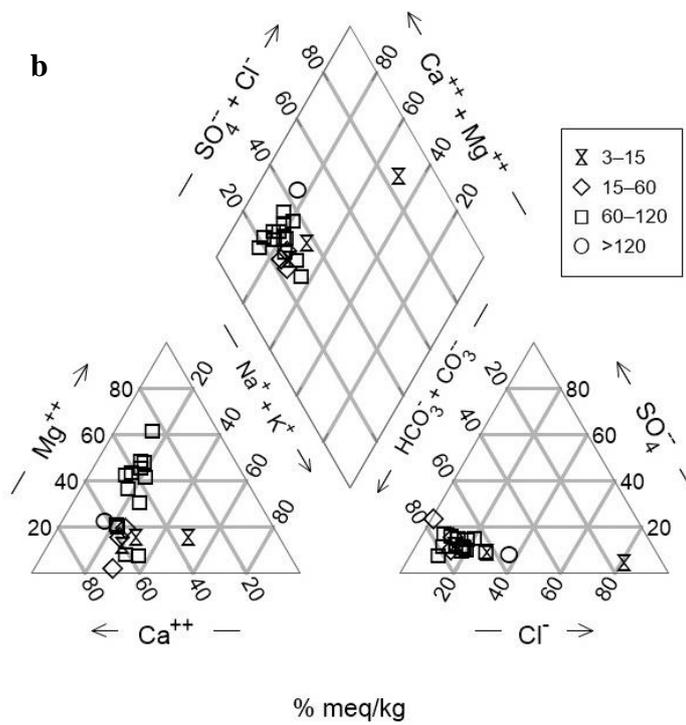
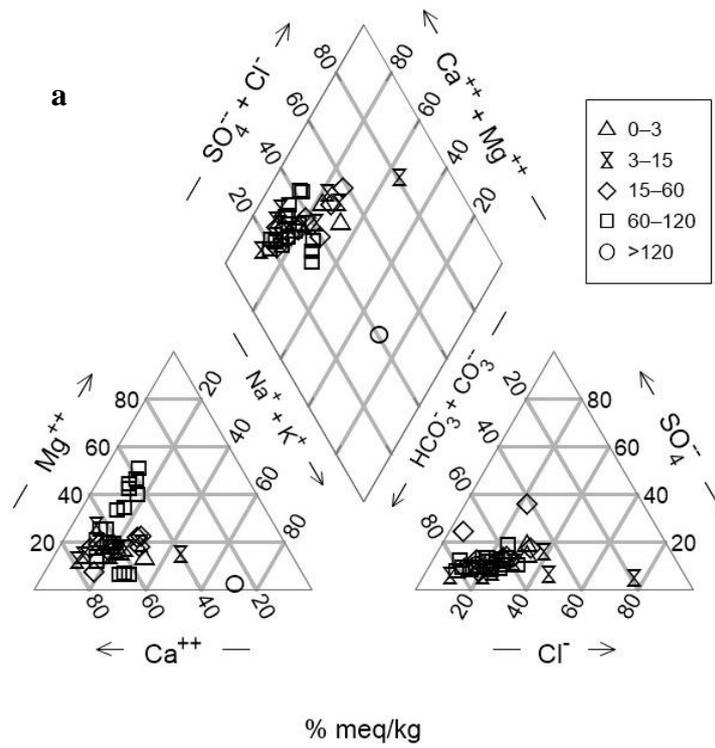


Fig. 6.5. Piper diagram for (a) 2015 and (b) 2016 data. Samples are classified by depth.

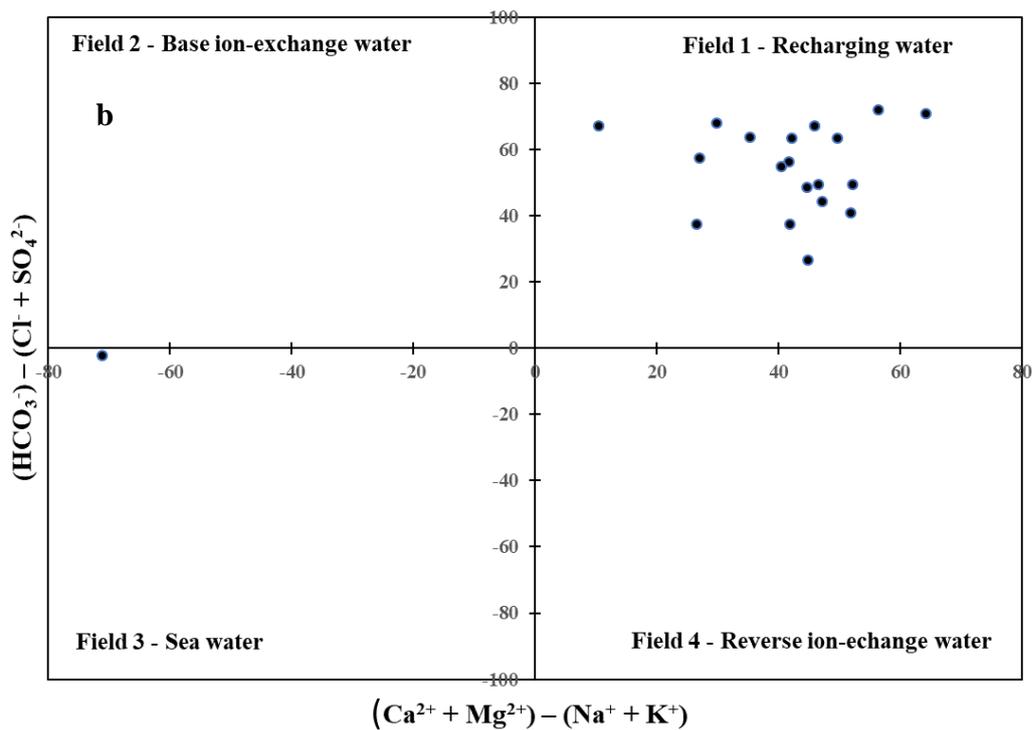
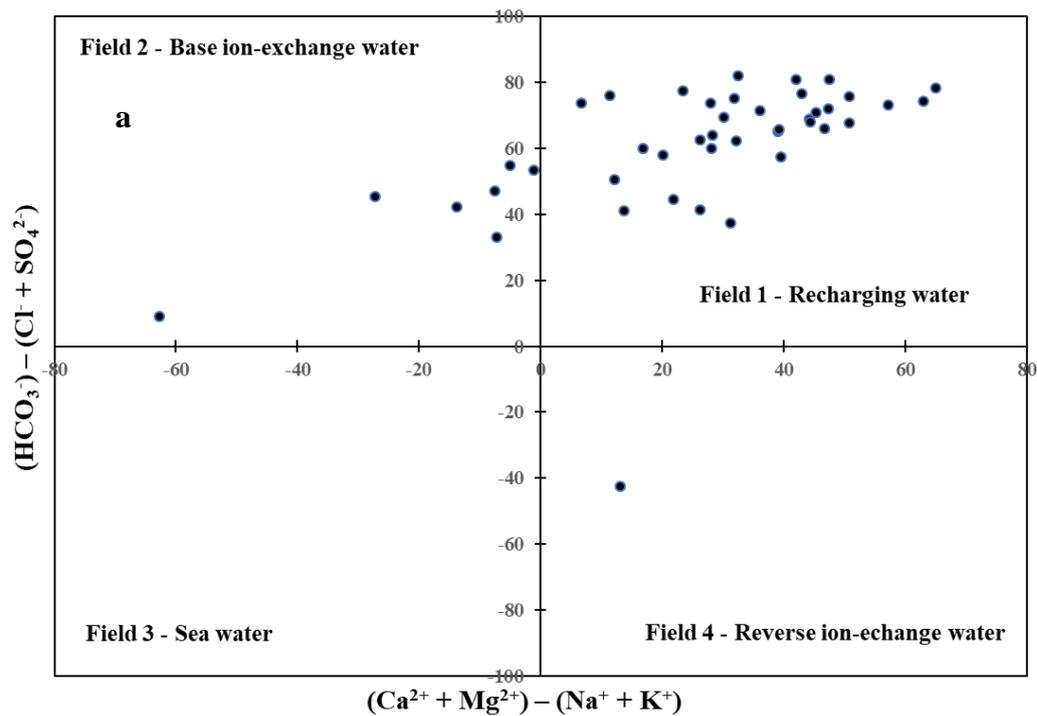


Fig. 6.6. Chadha's diagram for (a) 2015 and (b) 2016 data.

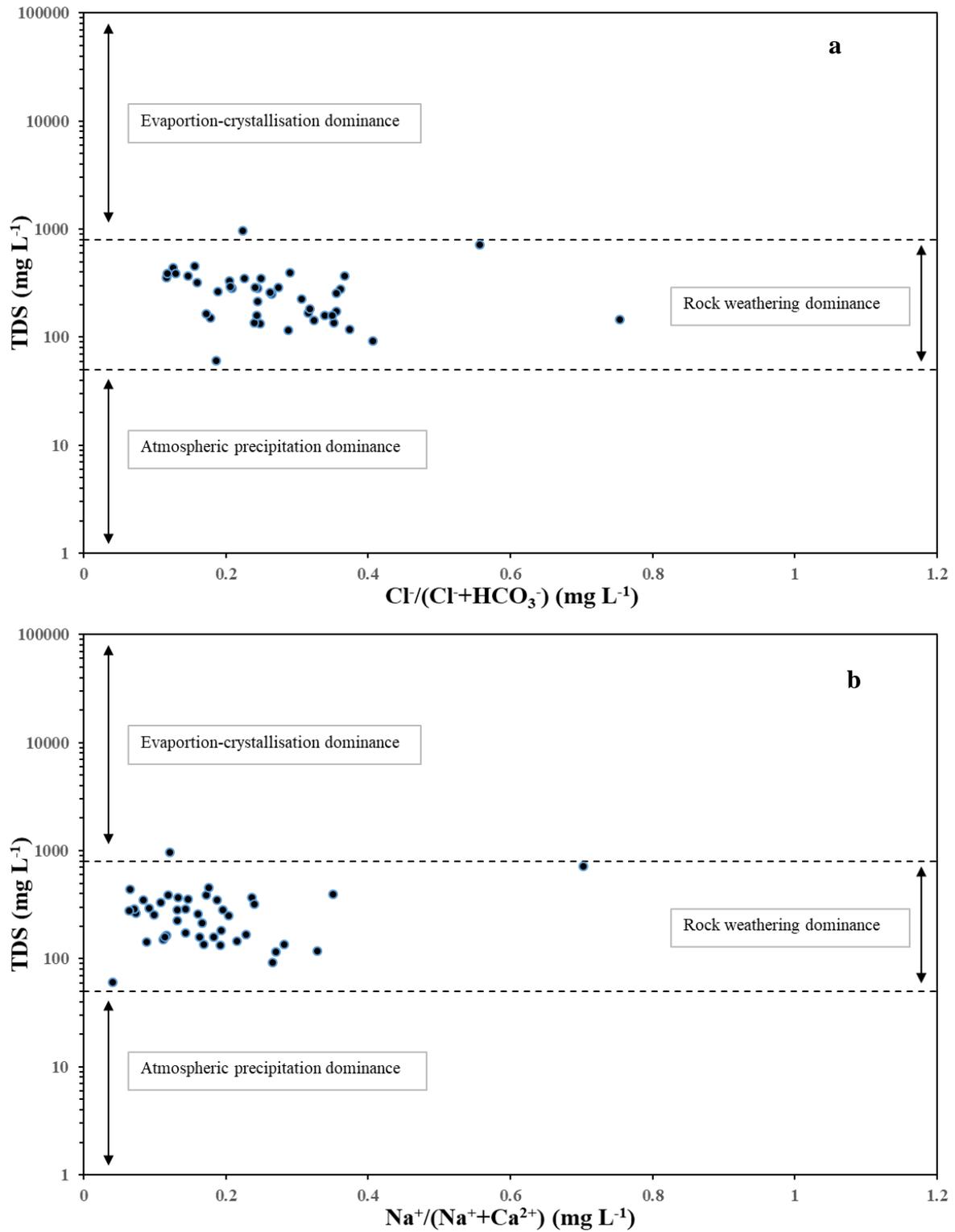


Fig. 6.7. Gibbs diagram illustrating the mechanisms controlling groundwater geochemistry for (a) 2015 anions, (b) 2015 cations, (c) 2016 anions, and (d) 2016 cations.

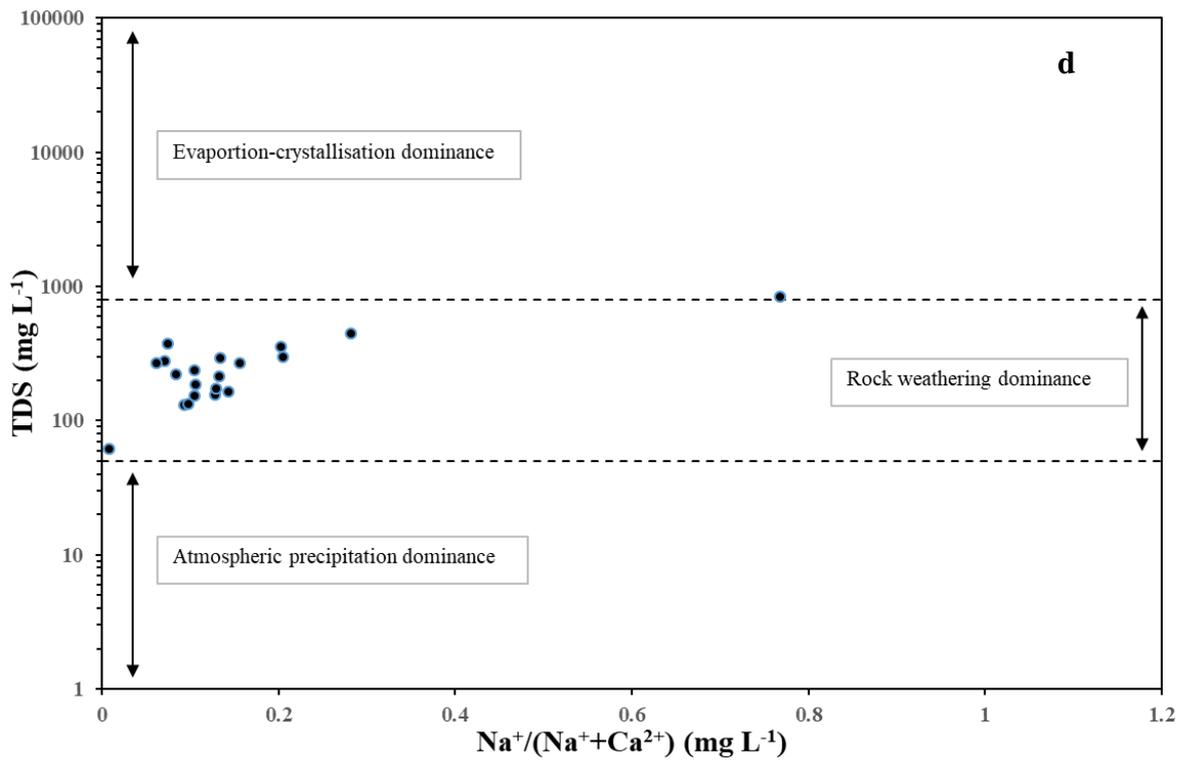
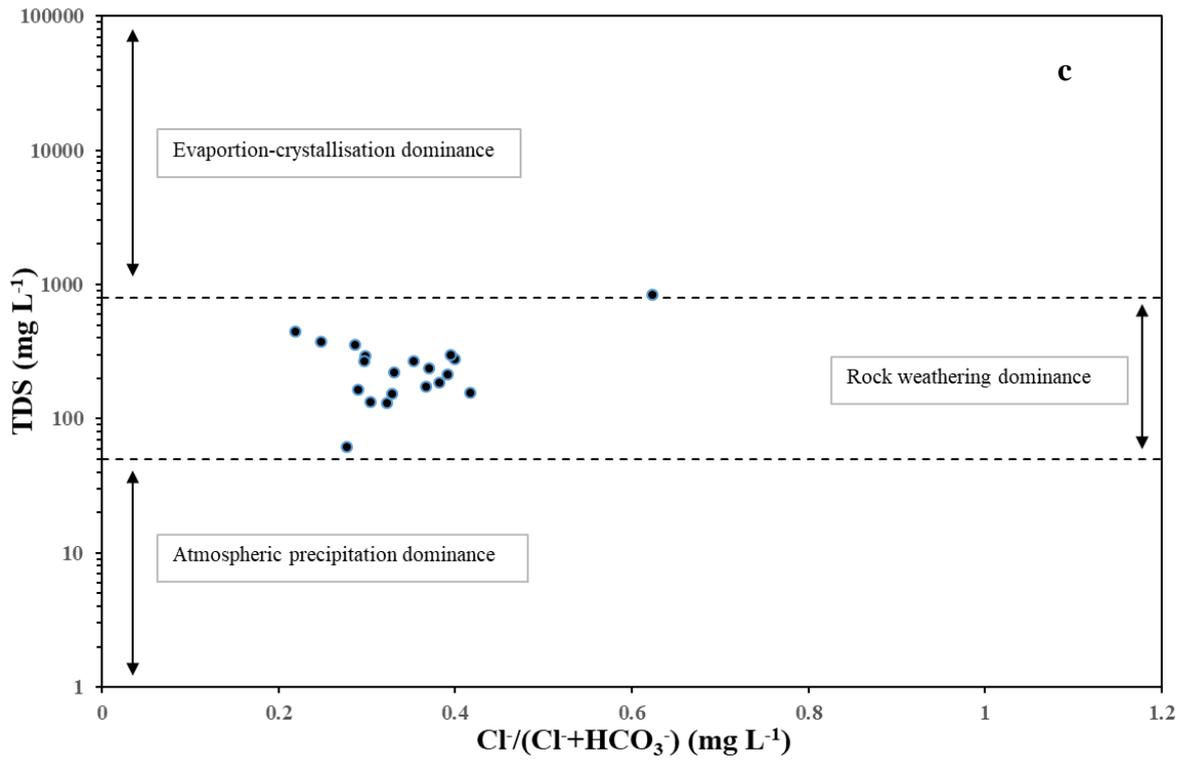


Fig. 6.7. (continued).

6.3.5) 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 (Table 6.11). 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. These linear relationships could not be calculated for some parameters due to high censoring rate, i.e. Be, Ag and Cd. 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 only occurred in bedrock boreholes.

Generally, detected trace elements were observed at low concentrations in groundwater (with lower amounts found in dug wells) with Al, As, Fe, Mn and Ba occurring at higher concentrations (but comparatively still low). 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 elevated concentrations, this is generally a result of an anomaly. Indeed, values are usually low with higher concentrations found in private wells elsewhere (DeSimone et al., 2009; Homoncik et al., 2010). One sampling location in 2015 (BH-66) recorded Mn and Fe concentrations at 611 and 39257 $\mu\text{g L}^{-1}$, 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 as the well is not in active use. This is indicative from the near reducing (191.5 mV) and acidic conditions (pH of 6.9) of the well. When sampling, a strong sulphide smell was noted and elevated sulphate was measured at 81 mg L^{-1} (2015 mean: $15.7 \pm 12.2 \text{ mg L}^{-1}$).

Both Mn and Fe can be derived from the weathering of multiple common bedrock minerals which includes silicates, oxides, carbonates and sulphides (Bondu et al., 2017a). In addition, Fe and Mn are present in higher amounts as total metal concentrations compared to the dissolved aqueous phase. 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). Besides these anomalies of elevated Fe with arsenic, most Fe concentrations are below 100 $\mu\text{g L}^{-1}$.

As previously evident from the 2014 data, several parameters show a positively weak to strong correlation with depth data including pH ($\tau=0.51$), HCO_3^- ($\tau=0.21$), temperature

($\tau=0.34$), F ($\tau=0.25$) and several oxyanions (As ($\tau=0.52$), Mo ($\tau=0.51$), Sb ($\tau=0.31$) and U ($\tau=0.40$)). These oxyanions (except Se) and F are also correlated with pH with no correlation evident for Eh. While Fe and Mn show a strong positive correlation ($\tau=0.63$), 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 geological 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. With the incorporation of d-O₂ in 2016, several of these transition series trace elements were correlated demonstrating a weak to moderate positive correlation with Ti, V, Cr, Ni, Cu, while Ba showed a moderate negative relationship. Different levels of strength of the monotonic relationship are evident for several transition series trace elements: moderate (Cr and V ($\tau=0.37$), Cu and Zn ($\tau=0.31$), Mn and V ($\tau=-0.40^*$), and weak (Cr and Ti ($\tau=0.22$), Co and Mn ($\tau=0.18$), V and Ti ($\tau=0.24$), Ti and Co ($\tau=0.19$), V and Co ($\tau=0.14$), Co and Ni ($\tau=0.29$), Co and Cu ($\tau=0.16$), Ni and Cu ($\tau=0.21$), Pb and Zn ($\tau=0.19$)). While not a transition series trace element, B shows a strong positive correlation with Ni ($\tau=0.50$), Ca ($\tau=0.56$), moderate positive correlation with Na ($\tau=0.31$) and K ($\tau=0.39$) and weak positive correlation with V ($\tau=0.28$), Co ($\tau=0.24$), Cu ($\tau=0.24$), and Si ($\tau=0.26$). Given that the correlations of these transition series trace elements are lower than between Fe and Mn it implies that they have somewhat fractionally comparable source mineralogy. While d-O₂ was only measured in 2016 it shows a moderate to strong correlation with several transition metals including Ti ($\tau=0.34$), V ($\tau=0.39$), Cr ($\tau=0.56$), and Cu ($\tau=0.39$) and has a negative correlation with Ba ($\tau=-0.42$).

Table 6.11. Comparison of filtered and unfiltered trace elements in groundwater (n = 43 for 2015 and n = 20 for 2016).

	2015				2016			
	Tau	p-value	S	Diff (%)	Tau	p-value	S	Diff (%)
B	0.94	≈ 0.000	0.902	9.8	0.80	≈ 0.000	0.925	7.5
Al	0.50	≈ 0.000	0.729	27.1	0.37	0.023	0.108	89.2
Ti	0.29	0.005	0.618	38.2	0.43	0.007	0.525	47.5
V	0.85	≈ 0.000	0.927	7.3	0.96	≈ 0.000	0.974	2.6
Cr	0.47	≈ 0.000	0.870	13.0	0.84	≈ 0.000	0.919	8.1
Mn	0.71	0.000	0.415	58.5	0.70	≈ 0.000	0.688	31.2
Fe	0.51	≈ 0.000	0.124	87.6	0.44	0.008	0.049	95.1
Co	0.36	≈ 0.000	0.998	0.2	0.86	≈ 0.000	0.996	0.4
Ni	0.85	0.000	0.933	6.7	0.77	≈ 0.000	0.710	29.0
Cu	0.81	0.000	0.950	5.0	0.86	≈ 0.000	0.897	10.3
Zn	0.85	0.000	0.898	10.2	0.84	≈ 0.000	0.953	4.7
As	0.93	0.000	0.876	12.4	0.96	0.000	0.978	2.2
Se	0.77	0.000	0.972	2.8	0.83	≈ 0.000	0.962	3.8
Mo	0.98	0.000	0.987	1.3	0.96	≈ 0.000	0.986	1.4
Sn	-	-	-	-	0.55	0.001	0.797	20.3
Sb	0.98	0.000	0.904	9.6	0.95	≈ 0.000	0.963	3.7
Ba	0.96	0.000	0.982	1.8	1.0	0.000	0.970	3.0
W	0.98	0.000	0.919	8.1	-	-	-	-
Pb	0.34	0.004	0.626	37.4	0.33	0.054	0.838	16.2
U	0.97	0.000	0.986	1.4	0.86	0.000	0.914	8.6
Mg	0.96	0.000	0.880	12.0	0.98	0.000	0.952	4.8
Si	0.86	0.000	0.823	17.7	0.77	≈ 0.000	0.884	11.6
Ca	0.86	0.000	0.750	25.0	0.95	0.000	0.934	6.6
Na	0.92	0.000	0.921	7.9	0.90	0.000	0.866	13.4
Sr	0.96	0.000	0.872	12.8	0.90	0.000	0.946	5.4
K	0.86	0.000	0.848	15.2	0.93	0.000	0.873	12.7

6.3.6) Arsenic geochemistry

Arsenic was the most frequently detected parameter above the regulatory limit ($10 \mu\text{g L}^{-1}$) 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 ($73.95 \mu\text{g L}^{-1}$). In comparison, arsenic was detected at lower concentrations in dug wells with the maximum concentration reported at $3.7 \mu\text{g L}^{-1}$ in 2015, comparable to observations noted in a bedrock aquifer in Quebec, Canada where arsenic concentrations in shallow wells did not exceed $4.1 \mu\text{g L}^{-1}$ (Bondu et al., 2017a). In this same area, however, the maximum concentration of arsenic in a dug well was reported as $18 \mu\text{g L}^{-1}$, however, this may have resulted from a misclassification of a well-type (Chapter 5, Section 5.1.4.3). Previous work has identified that arsenic concentrations in this area to the north west of the study site approach $139 \mu\text{g L}^{-1}$ (Chapter 3), however access to this well was not possible during the present study.

Moderate to high concentration of arsenic ($\geq 10 \mu\text{g L}^{-1}$) were usually associated with an Eh of $>390 \text{ mV}$ (lower Eh in 2016 $\sim >120 \text{ mV}$) and near-neutral to alkaline pH, depth $> 70 \text{ m}$ and low concentrations of Fe ($<2 \mu\text{g L}^{-1}$) and Mn ($<1.5 \mu\text{g L}^{-1}$). One borehole (BH-61) had a low arsenic concentration in 2015 ($8.1 \mu\text{g L}^{-1}$), but a moderate one in 2016 ($15.4 \mu\text{g L}^{-1}$) with

Fe and Mn measured at $30.5 \mu\text{g L}^{-1}$ and $0.64 \mu\text{g L}^{-1}$ in 2015 and 2016, respectively. However total concentrations of Fe measured markedly higher at $1588.6 \mu\text{g L}^{-1}$ with Mn at $8.5 \mu\text{g L}^{-1}$ 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 $6.04 \mu\text{g L}^{-1}$ and $8.12 \mu\text{g L}^{-1}$ respectively (2016). This illustrates that even at low concentrations arsenic which 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.

In comparison, elevated arsenic concentrations were mainly distributed between 70-120 m depth (Fig. 6.8a). A small proportion of boreholes with elevated arsenic concentrations occurs at a depth $> 120\text{m}$. For low arsenic concentration boreholes (i.e. $\leq 10 \mu\text{g L}^{-1}$) these occurred within several depth categories. Elevated arsenic is observed at pH $\sim > 7.5$ (occurs up to 8.57 (Fig. 6.8b)) and > 390 mV (Fig. 6.8c). 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. 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). Other trace elements show a pattern with arsenic. Generally, elevated arsenic concentrations show U concentrations below $6 \mu\text{g L}^{-1}$, however, elevated U can be seen in low arsenic wells (Fig. 6.8d). Both Fe and Mn show similar patterns with arsenic (Fig. 6.8e-f) in that elevated arsenic concentrations were observed with low Fe and Mn while elevated Fe and Mn were seen with low arsenic concentrations. 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 showed 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 from 2016 being approximately 8.1% higher when compared to 2015. Similar results have been observed for arsenic in private

bedrock boreholes in New Hampshire (Ayotte et al., 2003). The absolute value of intrawell differences ranged from 0.06-8.1 $\mu\text{g L}^{-1}$, with a median difference of 1.44 $\mu\text{g L}^{-1}$.

Based on results from the correlation matrix, several parameters are associated with arsenic in groundwaters including strong (depth ($\tau=0.52$), Mo($\tau=0.51$)), moderate (pH ($\tau=0.45$), temperature ($\tau=0.37$), HCO_3^- ($\tau=0.37$), SO_4^{2-} ($\tau=0.31$), Sb ($\tau=0.44$), U ($\tau=0.32$), Sr ($\tau=0.47$), and Mg ($\tau=0.36$)), and weak (conductivity ($\tau=0.22$), Se ($\tau=0.20$), Ba ($\tau=0.23$) and F ($\tau=0.15^*$)). The previous correlations with several oxyanions (e.g. Se, Mo and Sb) were reported in previous studies (Section 5.2.3) with the degree of the monotonic relationship being strong in this study. This was possible through lower LOQ values achieved as part of this study. As previously mentioned, both Fe and Mn show a negative relationship with arsenic ($\tau=-0.40$ and $\tau=-0.36$ respectively), this is also obvious for Cu which displays a weak negative relationship ($\tau=-0.27$). While some of these correlations described above were not significant at the 5% significance level in 2016, this is a result of the smaller sample number with the overall trend similar. 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., 2017a).

The small spatial variations in arsenic concentrations observed 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 $\mu\text{g L}^{-1}$ (2016). BH-60 was drilled deeper in 2007 to avoid high arsenic concentrations but had an arsenic concentration of 73.95 $\mu\text{g L}^{-1}$ in 2016 (well only sampled in 2016 detailed survey). These wells are 27.5 m apart which illustrated that arsenic concentrations can vary over small spatial scales. It is widely accepted that the variability of arsenic in groundwater can occur 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; Ahn, 2012; Bondu et al., 2016). Groundwater samples had low Ca/Na ratios with boreholes with elevated arsenic concentrations having lower ratios (Fig. 6.9a-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. 6.8a) (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 6.6a-b) and high arsenic concentrations are associated with low Ca/Na ratios.

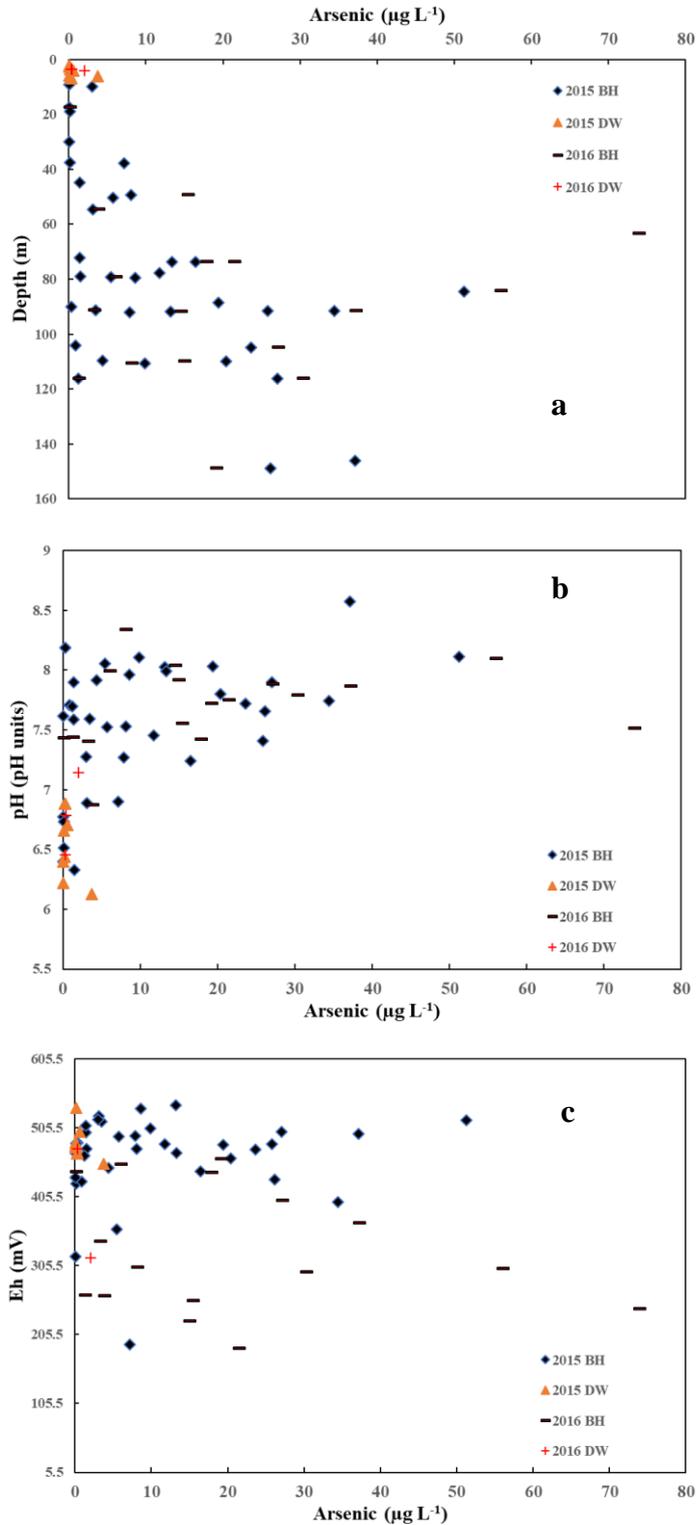


Fig. 6.8. Biplot for arsenic and (a) depth, (b) pH, (c) Eh, (d) uranium, (e) Fe, and (f) Mn. Note for both Fe and Mn that BH-66 was removed from 2015 data.

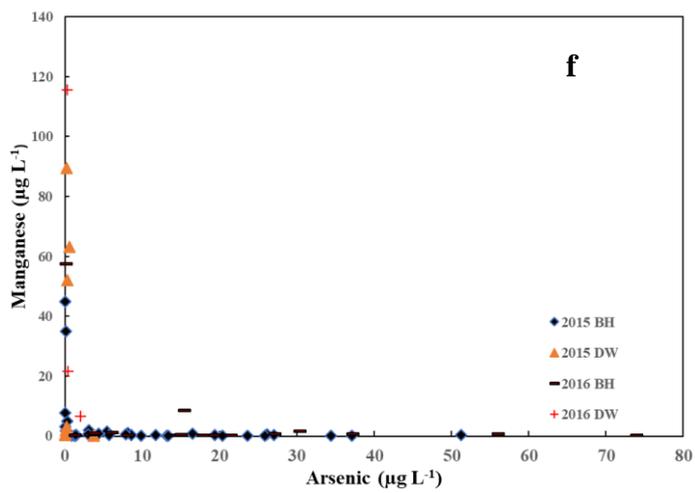
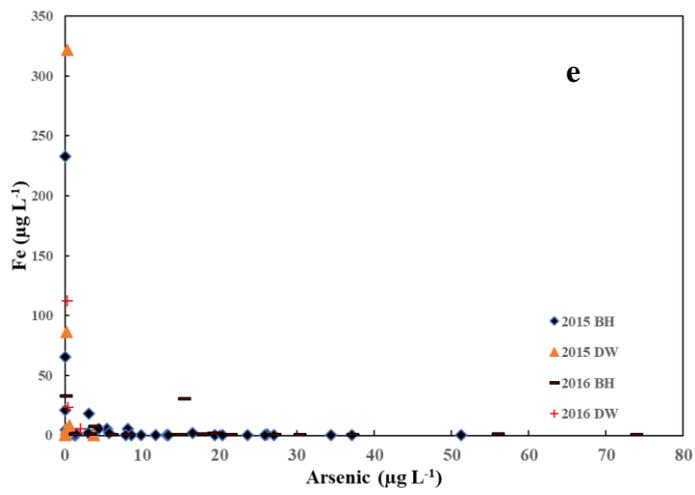
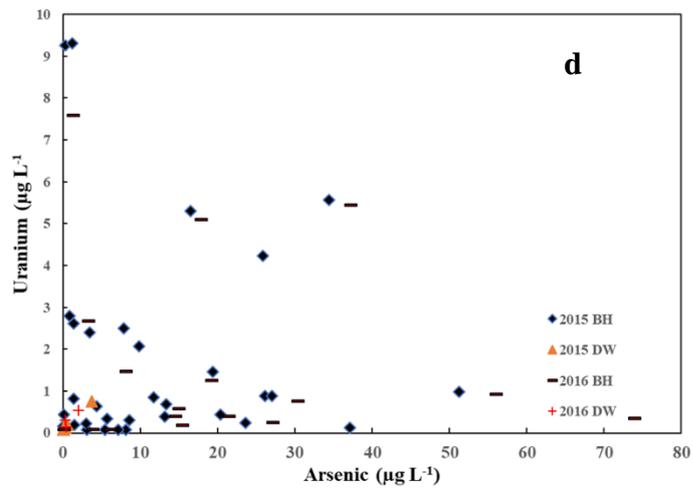


Fig. 6.8. (continued).

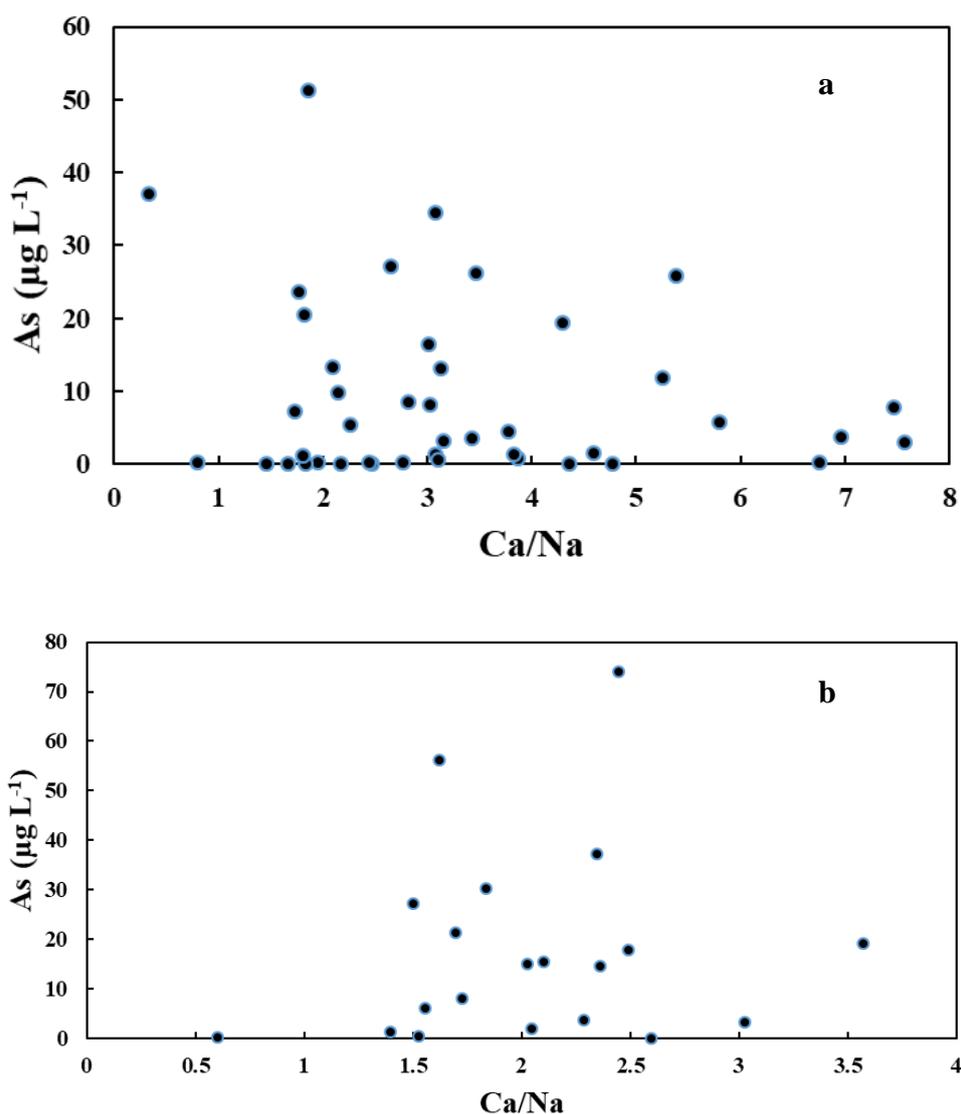


Fig. 6.9. Relationship between arsenic concentrations and Ca/Na ratios in groundwaters for (a) 2015 and (b) 2016.

6.3.7) Arsenic speciation

Arsenic speciation of groundwaters for 2016 data is presented in Table 6.12 with confirmatory analysis by HPLC-ICP-MS showing similar results (data not shown) with good recovery from the SPE technique (O'Reilly et al., 2010; Watts et al., 2010). The dominant arsenic species is the inorganic pentavalent species arsenate (As^{V}) which ranged from 0.09-64.3 $\mu\text{g L}^{-1}$. However, for DW-11 the proportion of As^{V} was minor as most of the arsenic was present as arsenite (As^{III}). Rather than actual dominance of As^{III} in the sample, this originates from analytical sensitivity. When the arsenic concentration in groundwater is low (i.e. $< 0.5 \mu\text{g L}^{-1}$) then the resulting recovery is higher than expected. As noted by Bondu et al. (2017a), the

recovery of arsenic species in low arsenic samples is generally less accurate. This can occur as low arsenic samples can contain concentrations of arsenic species near the LOQ even though they account for a significant proportion of the total dissolved arsenic concentration and the recovery values for low arsenic samples are more susceptible to slight discrepancies for low-arsenic concentrations (Bondu et al., 2017a). The same phenomenon occurred with low metal samples in groundwater with the resulting RSD higher than expected (Section 6.3.1).

While the more toxic inorganic species of arsenite is found in low concentrations ($<1 \mu\text{g L}^{-1}$) the presence of inorganic arsenate can have health implications if consumed as drinking water (see Section 6.3.11). 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. 6.10a-b). Both BH-40 and DW-17 appear to be in the form of $\text{As}(\text{OH})_4$, but are composed of a small amount of As^{III} . Eh-pH diagrams from 2015 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, a finding also noted by Bondu et al. (2017a), however, it can be useful for informative applications. Both MA^{V} and DMA^{V} were detected in groundwaters reaching a maximum concentration of $0.12 \mu\text{g L}^{-1}$ and $2.25 \mu\text{g L}^{-1}$ respectively. The presence of these methylated arsenic species is typical of microbial-mediated 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., 2017a). In addition, strong correlations are evident with total arsenic and As^{V} ($\tau=0.93$), total arsenic and DMA^{V} ($\tau=0.89$), total and moderate correlations with As^{III} and MA^{V} ($\tau=0.49$), As^{V} and DMA^{V} ($\tau=0.91$), and DMA^{V} and MA^{V} ($\tau=0.38$) (correlation coefficients from 2016 used for arsenic species data). These correlations further imply microbial methylation of inorganic arsenic which has been described elsewhere (Maguffin et al., 2015; Bondu et al., 2017a and 2018). Only the methylarsenical DMA^{V} and arsenic were correlated suggesting a biomethylation pathway of inorganic arsenic in water (Maguffin et al., 2015; Bondu et al., 2017a). The absence of the common correlation of DMA^{V} and As^{III} as reported elsewhere (e.g. Maguffin et al., 2015) is not fully understood. The presence of these methylated arsenicals, however, warrants further work as recently the toxicity of these methylated species has been found to be greater than previously considered (Akter et al., 2005; Wang et al., 2014; Mestrot et al., 2013). However, the trivalent counterparts are more toxic than then pentavalent

species detected in this study (Akter et al., 2005; Wang et al., 2014). Given the low concentrations of pentavalent organic species measured in this study, the presence of trivalent species is expected to be negligible.

The redox potential of groundwater and pH are the two critical factors determining the speciation of arsenic and thus mobility (Cullen and Reimer, 1989; Smedley and Kinniburgh, 2013). However, in this study, the dominant aqueous control appears to be pH rather than Eh which is evident from the correlation of As^{III}/As^V with pH ($\tau=0.34$) and lack of correlation with Eh ($\tau=0.07$).

Table 6.12. Dissolved arsenic concentrations and dissolved arsenic species distribution in both boreholes and dug wells using SPE methodology (where $n = 20$) (where As^{III} is arsenite, As^V is arsenate, DMA^V is dimethylarsonic acid, and MA^V is methylarsonic acid).

ID	Dissolved As ($\mu\text{g L}^{-1}$)	As^{III}		As^V		DMA^V		MA^V		Σ As Species ($\mu\text{g L}^{-1}$)	Recovery (%)
		Conc. ($\mu\text{g L}^{-1}$)	%	Conc. ($\mu\text{g L}^{-1}$)	%	Conc. ($\mu\text{g L}^{-1}$)	%	Conc. ($\mu\text{g L}^{-1}$)	%		
DW_11	0.31	0.502	59.2	0.0938	11.1	0.2016	23.8	0.05	5.9	0.85	275.7
BH_23	19.17	0.457	1.7	25.332	94.2	0.964	3.6	0.128	0.5	26.88	140.2
BH_20	37.20	0.067	0.2	29.3658	96.4	0.969	3.2	0.0514	0.2	30.45	81.9
BH_21	17.90	0.092	0.6	14.4912	95.6	0.532	3.5	0.0442	0.3	15.16	84.7
BH_64	27.15	0.058	0.3	20.852	95.9	0.817	3.8	0.0148	0.1	21.74	80.1
BH_47	0.13	0.066	21.6	0.104	34.0	0.1214	39.7	0.0142	4.6	0.31	232.7
BH_46	6.05	0.131	2.5	4.7592	92.6	0.2392	4.7	0.0118	0.2	5.14	85.0
DW_17	0.41	0.09	15.1	0.2834	47.7	0.2084	35.0	0.0128	2.2	0.59	143.4
BH_40	14.56	0.036	0.3	11.794	95.5	0.5048	4.1	0.0194	0.2	12.35	84.8
BH_29	14.99	0.097	0.8	10.8552	94.8	0.488	4.3	0.013	0.1	11.45	76.4
BH_26	21.44	0.186	1.1	16.5518	95.1	0.6508	3.7	0.021	0.1	17.41	81.2
BH_68	1.32	0.051	4.4	0.8626	73.9	0.2414	20.7	0.0126	1.1	1.17	88.2
BH_74	3.30	0.051	2.1	2.1284	85.8	0.2866	11.6	0.014	0.6	2.48	75.2
DW_25	56.09	0.367	0.8	42.4154	95.7	1.5364	3.5	0.0218	0.0	44.34	79.1
DW_28	2.05	0.033	1.7	1.7082	86.9	0.2132	10.8	0.0116	0.6	1.97	96.1
BH_70	8.12	0.008	0.1	6.581	94.4	0.3792	5.4	0.0068	0.1	6.98	85.8
BH_61	15.47	0.611	6.0	9.0092	88.3	0.5446	5.3	0.0394	0.4	10.20	66.0
BH_60	73.95	0.046	0.1	64.3012	96.5	2.2556	3.4	0.0182	0.0	66.62	90.1
BH_67	3.81	0.037	1.1	2.9686	91.4	0.232	7.1	0.0106	0.3	3.25	85.3
BH_39	30.35	0.570	2.1	25.2084	94.3	0.9262	3.5	0.024	0.1	26.73	88.1

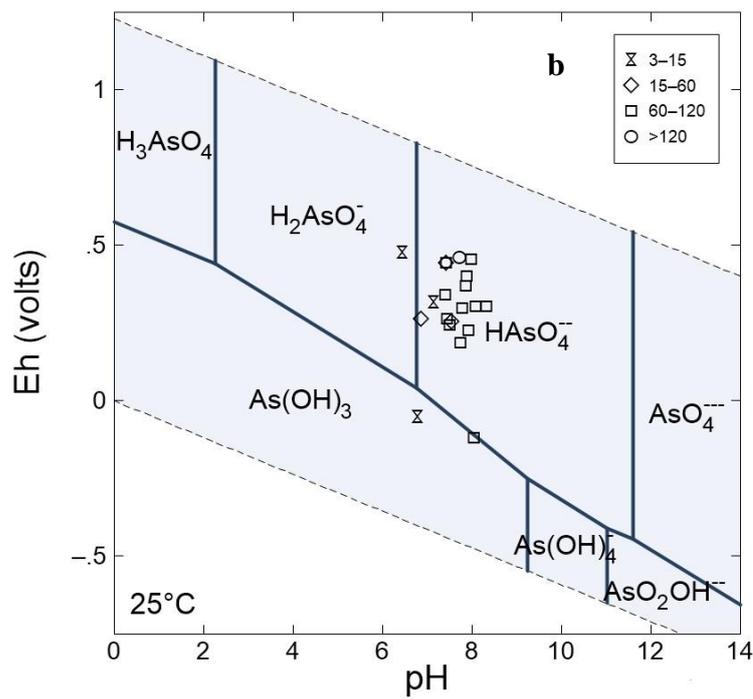
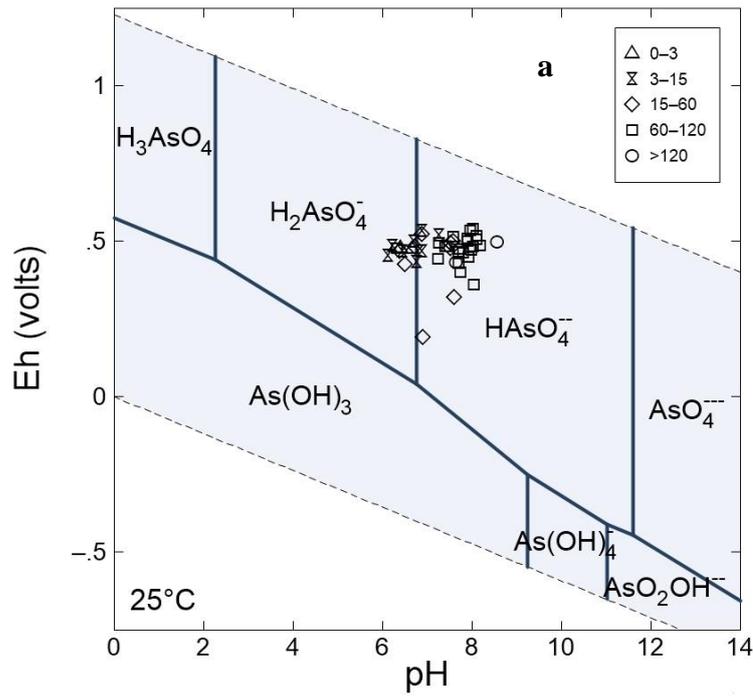


Fig. 6.10. Eh-pH diagrams for (a) 2015 and (b) 2016 as a function of groundwater depth categories.

6.3.8) *Multivariate analysis*

The KMO measure of sampling adequacy was below the recommended minimum value of 0.6 (Kaiser and Rice, 1974) for both years (2015 KMO =0.332 and 2016 KMO = 0.564). However, Bartlett's test of sphericity was satisfied for each dataset, suggesting that there was enough correlation with the variables for PCA to be applicable ($p < 0.001$ for each year) in addition to communalities being high (0.712-0.946 for 2015 and 0.801-0.990 for 2016). No outliers were detected based on Mahalanobis distance (data not shown). As strong similarities existed between both sampling years in addition to speciation being completed in 2016, further interpretation will be discussed in relation to the 2016 season. Multivariate statistical analysis such as the one undertaken here can be used to identify groups where a great deal of parameters and samples have been taken, as shown in other studies (Cloutier et al., 2008; Montcoudiol et al., 2014).

Results from the PCA analysis explained 90.891% of the variance in 10 principal components (PCs) with 25.147% and 20.207% of the variance in both PC1 and PC2 respectively (Table 6.13). The main aspects of controlling groundwater geochemistry in the area can be described in the first two PCs (Fig. 6.11). PC1 is characterised by strong positive PC loadings for conductivity, TDS, Na, Ca, Cl, HCO_3^- , Ni, and moderate positive PC loadings of SO_4^{2-} , Co, Zn, Cd, Sn, MA^V , Mg and Sr. This PC shows that the main groundwater geochemistry is governed by major ions (Mg, Ca, Na, and Sr) and anions (HCO_3^- , SO_4^{2-} , Cl^-) and certain trace elements (B, Ni, Co, Zn, Sn and Cd), which may describe water-rock interactions. On the other hand, 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 in PC2 indicate that with increasing concentrations of arsenic (and other oxyanions) in addition to increased well depth and pH values, a decrease in 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 the depth of groundwater wells, i.e. deeper groundwater at elevated pH (i.e. alkaline conditions) 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, however, it was still negative like Fe and Mn (-0.217) (see Section 6.3.9). Redox conditions do not appear to be a major controlling factor on groundwater geochemistry of arsenic with PC5 having a strong positive loading for Eh, combined with a moderate negative loading with DO and temperature indicating that with a decrease in Eh an increase in DO and temperature was observed. This

describes the general oxic-alkali nature of the groundwaters encountered in this study. 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. Several transition series trace elements contain positive loadings in PC6 showing their common source as described in earlier sections.

Similar results were observed with Q-mode HCA showing 5 clusters in each sampling year (Table 6.14). 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 other transition metals (Al, Ti, V, Cr, Co, Ni) and cations (Si and K). 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. 6.12a-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 Cluster1 and Cluster5 have strong positive loadings for depth, temperature, pH and several oxyanions which are mainly spatially associated near each other. It is worth noting the main difference in these two clusters is that Cluster5 has positive loading 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 DO was associated with this cluster. These clusters associated with Fe and Mn groundwaters show the greatest spatial diversity affecting all of the study area. Interestingly Cluster 4 for 2015 showed a presence of parameters usually associated with arsenic in addition to Eh and is west of the elevated arsenic groundwaters. In general clusters in 2016 broadly showed similar spatial associations, however, the reduction in sample number may have impeded the resolution in the analysis.

Table 6.13. PCA scores for ranked data in 2016

Variable	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8	PC9	PC10
Eigenvalue	10.813	8.689	4.961	3.508	3.272	2.479	1.625	1.403	1.26	1.026
Proportion (%)	25.147	20.207	11.537	8.159	7.609	5.765	3.779	3.262	2.93	2.387
Cumulative (%)	25.147	45.354	56.891	65.05	72.658	78.423	82.202	85.464	88.394	90.981
Depth	0.135	0.471	0.169	0.531	-0.032	-0.22	0.09	-0.193	0.264	0.293
Temp	0.084	-0.171	0.094	0.203	-0.899	-0.036	0.053	-0.147	0.147	0.11
Conductivity	0.912	0.06	0.32	-0.001	0.079	0.047	0.15	0.115	0.084	0.027
TDS	0.912	0.06	0.32	-0.001	0.079	0.047	0.15	0.115	0.084	0.027
pH	-0.197	0.589	0.31	0.288	0.103	-0.499	-0.067	0.009	-0.214	0.249
Eh	0.169	-0.157	0.122	0.158	0.853	0.219	0.111	0.02	0.23	0.027
DO	-0.02	-0.082	-0.703	-0.141	-0.452	-0.167	0.296	0.003	0.167	-0.199
Alk	0.647	0.266	0.562	-0.018	-0.14	-0.1	0.164	-0.153	0.257	-0.044
Sul	0.536	0.238	0.637	-0.015	-0.263	0.155	0.102	0.266	-0.022	0.02
Cl	0.909	0.086	0.06	-0.031	0.181	-0.078	0.063	0.111	-0.214	-0.11
F	0.327	0.183	0.301	0.511	0.445	-0.224	0.283	-0.272	-0.121	-0.096
B	0.533	-0.287	0.083	-0.061	0.606	-0.018	-0.33	0.14	0.12	0.247
Al	-0.253	-0.488	-0.301	0.092	-0.096	-0.212	-0.112	-0.037	0.477	0.379
Ti	0.158	0.076	-0.3	-0.508	-0.066	0.142	0.672	0.004	0.069	0.101
V	0.177	0.063	-0.846	0.282	-0.097	0.137	0.201	0.071	-0.078	0.153
Cr	0.081	-0.154	-0.859	0.127	-0.211	-0.193	0.046	0.083	-0.121	-0.177
Mn	-0.138	-0.506	0.191	-0.533	0.183	0.263	-0.054	0.261	0.132	0.274
Fe	0.049	-0.518	-0.401	-0.372	0.043	0.539	-0.037	0.194	0.243	-0.022
Co	0.631	-0.037	-0.233	-0.26	0.104	0.454	0.271	0.222	-0.11	0.045
Ni	0.753	0.142	-0.353	-0.195	-0.082	0.399	0.105	0.081	0.109	-0.07
Cu	0.207	-0.217	-0.671	-0.452	-0.2	0.292	-0.051	0.135	0.1	-0.12
Zn	0.598	0.003	0.105	-0.211	-0.43	0.113	-0.382	0.006	0.342	0.093
As	-0.015	0.927	0.149	-0.018	-0.026	-0.113	0.156	-0.029	0.068	-0.067
As ^{III}	0.041	0.22	0.341	-0.14	0.071	0.182	0.228	0.687	0.325	0.069
As ^V	0.044	0.947	0.134	-0.006	0.002	-0.094	0.085	-0.096	0.06	-0.013
DMA ^V	0.049	0.934	0.089	0.066	-0.037	-0.031	0.209	-0.048	0.064	0.003
MA ^V	0.352	0.504	0.185	-0.127	0.219	0.394	0.087	0.452	0.15	0.002
Se	0.086	0.669	-0.012	0.312	-0.015	0.078	-0.049	0.042	-0.036	0.53
Mo	0.131	0.586	0.362	0.365	-0.108	-0.265	-0.314	0.115	0.117	-0.251
Ag	0.312	-0.399	-0.063	-0.018	0.236	0.149	0.32	0.602	-0.101	0.033
Cd	0.443	-0.201	-0.088	0.047	0.316	0.183	-0.048	0.565	0.051	-0.447
Sn	0.446	-0.087	-0.259	-0.129	-0.081	0	-0.177	0.674	-0.16	-0.028
Sb	-0.015	0.778	-0.114	0.224	0.06	0.315	-0.279	0.113	0.04	0.123
Ba	0.157	-0.037	0.933	-0.006	-0.124	-0.16	-0.012	0.064	-0.039	-0.02
W	-0.216	0.016	-0.29	0.77	0.024	-0.254	0.021	0.023	-0.04	0.125
Pb	0.363	0.396	0.02	0.001	0.095	0.169	-0.143	0.09	0.743	-0.073
U	0.38	0.357	-0.046	0.768	-0.087	0.221	-0.079	-0.112	0.077	-0.019
Mg	0.466	0.219	0.719	-0.136	-0.165	-0.088	0.303	0.034	-0.021	-0.037
Si	0.253	0.148	0.035	0.175	0.003	0.037	0.849	0.119	-0.109	-0.054
Ca	0.932	0.021	-0.085	0.192	-0.026	0.183	-0.035	0.045	0.045	-0.009
Na	0.817	-0.152	-0.04	0.366	0.081	-0.063	0.097	0.158	0.166	-0.051
Sr	0.408	0.303	0.714	0.248	-0.14	-0.041	-0.009	0.079	-0.041	-0.275
K	0.151	-0.055	0.009	-0.098	0.166	0.92	0.057	0.144	0.006	0.014

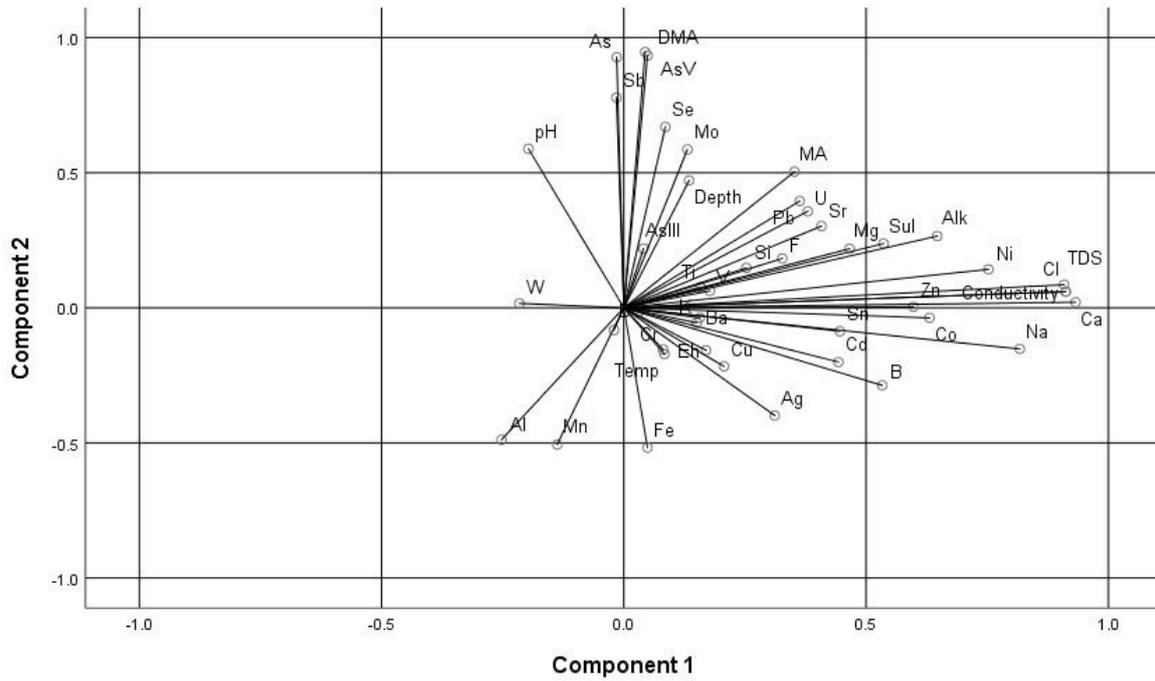


Fig. 6.11. PCA biplot for 2016 data

Table 6.14. HCA parameters (Q-mode)

Cluster	Parameters 2015	2016
1	Depth Temp pH F As Se Mo Sb W U	Depth pH F As As ^V DMA ^V Se Mo SB W U
2	Conductivity TDS Cl B Co Ni Ca	Temp DO Al V Cr
3	Eh Mn Fe Cu Zn Ag Cd Pb K	Conductivity TDS Eh Cl B Zn As ^{III} MA ^V Ag Cd Sn Pb Ca Na
4	HCO ₃ ⁻ , SO ₄ ²⁻ Ba Mg Sr	HCO ₃ ⁻ , SO ₄ ²⁻ Ba Mg Sr
5	Be Al Ti V Cr Si Na	Ti Mn Fe Co Ni Cu Si K

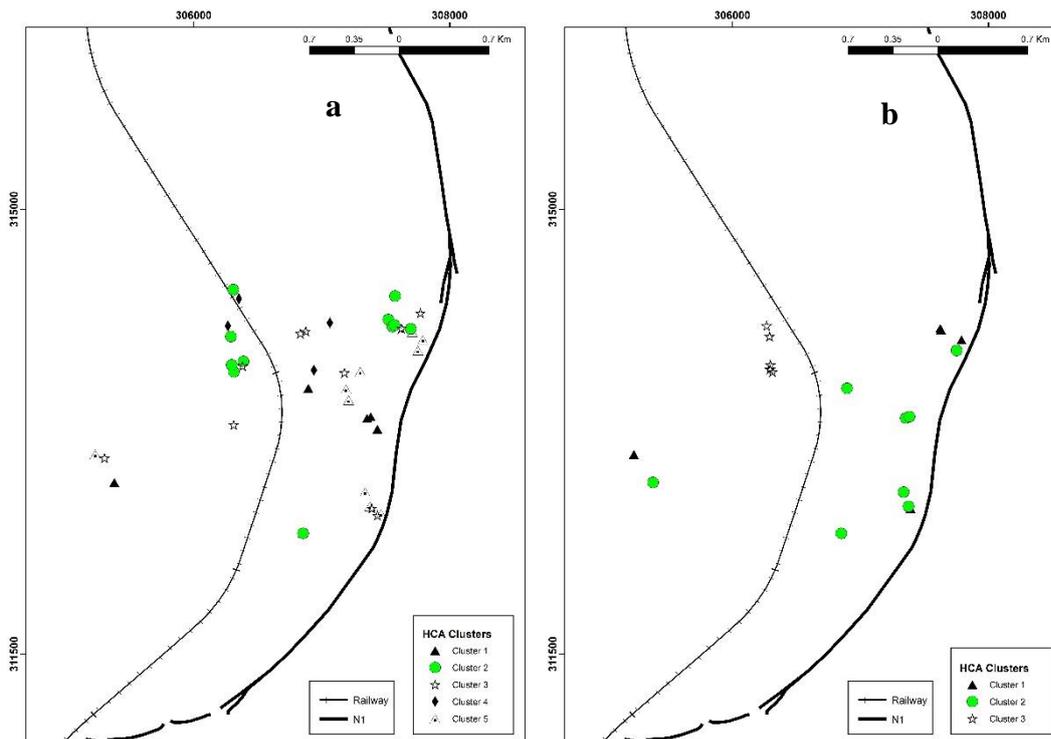


Fig. 6.12. HCA clustering map for monitoring sites in (a) 2015 and (b) 2016 (R-mode)

6.3.9) Thermodynamic calculations

Thermodynamic modelling (Table 6.15) reveals that several Fe, Mn, Cu and Al oxides were supersaturated in groundwater including cupric ferrite, cuprous ferrite, diaspore, $\text{Fe}(\text{OH})_2 \cdot 7\text{Cl} \cdot 3$, $\text{Fe}(\text{OH})_3$ (a), goethite, hematite, maghemite, magnetite, pyrophyllite, K-mica, and adularia. Some minerals were both supersaturated and undersaturated including $\text{Fe}_3(\text{OH})_8$, gibbsite, basaluminite, boehmite, calcite, siderite, kaolinite, dolomite, jarosite-Na, barite, and barium arsenate, while malachite, gypsum, halite, and talc were undersaturated. In addition to several phases above, several minerals were undersaturated, i.e. they could dissolve into solution, and included alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), arsenolite (As_2O_3), fluorite (CaF_2) (data not shown) and specific arsenic bearing minerals including scorodite, $\text{As}_2\text{O}_5(\text{cr})$, 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 could theoretically 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). Several minerals are undersaturated in groundwater samples and contribute to major ion geochemistry of the groundwater including calcite, dolomite, gypsum and halite.

6.3.10) Oxyanion behaviour

Several oxyanion forming elements are present in the groundwater which exhibit a correlation with arsenic, i.e. Se, Mo, Sb and U which is evident in many oxidising aquifers (Rango et al., 2013). Of all the oxyanions in the groundwater system arsenic is the most elevated with lower concentrations of oxyanions being detected in shallow DW when compared to deeper BHs. Based on Eh-pH diagrams most of the selenium is present as the pentavalent selenate ion (SeO_4^{2-}) and smaller amounts of quadrivalent selenium as the species of hydrogen selenite (HSeO_3^-) and selenite (SeO_3^{2-}) (data not shown). The presence of selenate as a predominant species agrees with the redox nature of the groundwaters measured, i.e. oxic-alkali. However, the dominance of selenium species shifts in 2016 to the dominance of selenite which agrees with the lower values of Eh measured in groundwaters in 2016 compared to 2015 (Fig. 6.4). Uranium is present mainly in groundwater as the hexavalent state of the uranyl ion (UO_2^{2+}) in the complex of $\text{UO}_2(\text{CO}_3)_2^{2-}$ groundwater. In comparison, Sb is mainly represented as the pentavalent antimonate ion ($\text{Sb}(\text{OH})_6^-$) while molybdenum is in the heptavalent state of the molybdate ion (MoO_4^{2-}). The main species for each oxyanion encountered are consistent with the redox behaviour of the present groundwater system (i.e. oxic-alkali) (Sappa et al., 2014).

Table 6.15. SIs for several Fe, Mn, Al and Cu minerals (2015 and 2016)

2015						
Name	Formula	Median	Average	SD	Min	Max
Ba ₃ (AsO ₄) ₂	Ba ₃ (AsO ₄) ₂	1.88	3.33	4.81	-4.65	11.41
Basaluminite	Al ₄ (OH)10SO ₄	-4.13	-3.75	3.89	-10.28	6.44
Boehmite	AlOOH	-0.36	-0.24	0.63	-1.41	1.79
Calcite	CaCO ₃	-0.25	-0.59	0.78	-2.47	0.49
Cupric ferrite	CuFe ₂ O ₄	8.81	9.27	1.87	4.68	14.60
Cuprous ferrite	CuFeO ₂	6.19	6.71	1.80	4.19	13.07
Diaspore	AlOOH	1.48	1.59	0.63	0.42	3.61
Dolomite	CaMg(CO ₃) ₂	-1.07	-1.70	1.69	-5.53	0.55
Fe(OH) ₂ .7Cl.3	Fe(OH) ₂ .7Cl0.3	5.35	5.46	0.91	4.03	7.85
Fe(OH) ₃ (a)	Fe(OH) ₃	0.52	0.72	0.86	-1.04	3.01
Fe ₃ (OH) 8	Fe ₃ (OH) 8	-6.65	-5.64	3.37	-9.47	4.89
Gibbsite	Al(OH) ₃	0.33	0.43	0.63	-0.74	2.45
Goethite	FeOOH	5.95	6.10	0.85	4.28	8.39
Gypsum	CaSO ₄ .2H ₂ O	-2.65	-2.61	0.28	-3.11	-1.95
Halite	NaCl	-8.12	-8.11	0.48	-9.87	-6.18
Hematite	Fe ₂ O ₃	13.84	14.14	1.70	10.50	18.72
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	1.68	1.96	1.29	-0.37	6.59
Kmica	KAl ₃ Si ₃ O ₁₀ (OH) ₂	3.89	4.08	1.73	1.15	10.74
Maghemite	Fe ₂ O ₃	4.44	4.85	1.72	1.31	9.41
Magnetite	Fe ₃ O ₄	7.93	9.05	3.34	5.06	19.63
Malachite	Cu ₂ (OH) ₂ CO ₃	-5.49	-5.37	0.84	-7.04	-1.86
Pyrophyllite	Al ₂ Si ₄ O ₁₀ (OH) ₂	2.51	2.61	1.57	0.28	9.84
Scorodite	FeAsO ₄ .2H ₂ O	-8.61	-8.57	0.99	-10.12	-5.57
Siderite	FeCO ₃	-6.59	-6.40	2.15	-10.13	1.17
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	-5.26	-5.84	4.33	-13.90	-0.02
2016						
Name	Formula	Median	Average	SD	Min	Max
Adularia	KAlSi ₃ O ₈	4.93	4.82	0.77	1.94	5.74
Albite	NaAlSi ₃ O ₈	3.33	3.27	0.91	-0.30	4.38
Ba ₃ (AsO ₄) ₂	Ba ₃ (AsO ₄) ₂	12.94	13.05	4.58	2.85	19.01
Barite	BaSO ₄	1.84	1.73	1.09	-0.13	3.25
Basaluminite	Al ₄ (OH)10SO ₄	-4.59	-4.21	2.89	-8.18	0.89
Boehmite	AlOOH	0.34	0.46	0.57	-0.32	1.55
Calcite	CaCO ₃	2.58	2.35	0.49	1.46	2.98
Cupric ferrite	CuFe ₂ O ₄	12.12	11.45	4.67	-2.43	16.51
Cuprous ferrite	CuFeO ₂	10.28	10.40	1.65	7.28	14.16
Diaspore	AlOOH	2.04	2.16	0.57	1.38	3.26
Dolomite	CaMg(CO ₃) ₂	5.04	4.28	1.29	1.42	5.62
Fe(OH) ₂ .7Cl.3	Fe(OH) ₂ .7Cl0.3	6.17	6.04	1.84	1.13	8.80
Fe(OH) ₃ (a)	Fe(OH) ₃	1.11	0.97	1.85	-4.28	3.05
Fe ₃ (OH) 8	Fe ₃ (OH) 8	-1.72	-2.33	3.54	-11.25	4.28
Gibbsite	Al(OH) ₃	0.81	0.93	0.57	0.15	2.03
Goethite	FeOOH	7.00	6.86	1.85	1.61	8.94
Gypsum	CaSO ₄ .2H ₂ O	-0.18	-0.17	0.18	-0.53	0.10
Halite	NaCl	-5.51	-5.49	0.77	-7.67	-3.37
Hematite	Fe ₂ O ₃	16.02	15.74	3.69	5.24	19.89
Jarosite-Na	NaFe ₃ (SO ₄) ₂ (OH) ₆	-6.64	-6.85	5.76	-22.08	3.38
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	6.00	6.17	1.10	4.70	8.36
Kmica	KAl ₃ Si ₃ O ₁₀ (OH) ₂	12.06	12.29	1.41	10.37	15.23
Maghemite	Fe ₂ O ₃	5.63	5.34	3.69	-5.16	9.50
Magnetite	Fe ₃ O ₄	14.83	13.05	5.19	1.84	20.77
Malachite	Cu ₂ (OH) ₂ CO ₃	-2.13	-2.67	2.01	-8.56	-0.58
Pyrophyllite	Al ₂ Si ₄ O ₁₀ (OH) ₂	12.20	12.10	1.33	8.65	14.30
Scorodite	FeAsO ₄ .2H ₂ O	-6.04	-6.56	2.47	-14.19	-3.92
Siderite	FeCO ₃	-1.48	-1.99	1.77	-5.55	0.53
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	8.51	6.77	3.96	-3.35	10.80

6.3.11) Health implications

To assess the effectiveness of removal technologies for arsenic in taps from untreated groundwater several locations were sampled (Table 6.16). While this study uses dissolved arsenic for interpretation, total concentrations were used for these calculations as this would best represent the exposure pathway for consumers. Where censored data were present the removal efficiency of the technology could not be calculated.

Five dwellings used an arsenic filter to remove arsenic with three taps being lower than the WHO limit. For two locations (BH-65 and BH-25) treated drinking water was still $> 10 \mu\text{g L}^{-1}$ with the latter showing high concentrations of arsenate which may pose a health risk. Concentrations in treated water increased in taps with arsenic filters indicating filters may not be routinely changed. These filters are recommended to be changed every year. While tap BH-60(B) had a grossly elevated arsenic concentration of $100.1 \mu\text{g L}^{-1}$ this tap is used for outdoor applications and not drinking water. The kitchen tap for this dwelling (BH-60(A)) had significantly reduced concentrations of arsenic when compared to the borehole. Given the speciation of arsenic other technologies such as reverse osmosis at point of use have been shown to reduce arsenic concentrations (Nicomel et al., 2016).

While several dwellings had no treatment in operation, the arsenic concentration in the tap was reduced (BH-23). The presence of Fe-oxyhydroxides or Mn-oxyhydroxides in groundwater could be sorbing arsenic in the tap thus reducing concentrations for drinking water. In contrast, some wells have increased concentrations of arsenic in taps, i.e. BH-67. The specific scope of how this is occurring was beyond the objectives of this study but provides an overview of arsenic from drinking water taps from wells with elevated arsenic. Given that long-term exposure of arsenic from groundwater as low as $3 \mu\text{g L}^{-1}$ can potentially lead to health conditions (Kozul et al., 2009; Taheri et al. 2017; Dehbandi et al., 2019) more mitigation measures need to be considered. In addition, there may be a misunderstanding of risk perception for end users in this area and other areas highlighted in Chapter 3 and they may benefit from a health messaging approach of contaminants in groundwaters as conducted in other regions (Law et al., 2017; Hooks et al., 2019). However, to fully understand the effects of these elevated arsenic concentrations on public health, an approach using urinary arsenic analysis adopted by Middleton et al. (2016) could be completed as a follow up to this present work. This is critical as there is increasing evidence of association between arsenic concentrations $< 100 \mu\text{g L}^{-1}$ and health outcomes via drinking water (Ander et al., 2016).

Given that arsenite concentrations in all samples are $< 0.7 \mu\text{g L}^{-1}$, it is not expected that these will have a deleterious effect on health. However, while not as toxic as arsenite, arsenate

concentrations are as high as 64.3 $\mu\text{g L}^{-1}$, with 50% of wells having a comparable arsenate concentration above the total arsenic health standard of 10 $\mu\text{g L}^{-1}$. Although a health assessment was not part of this present work, the presence of inorganic arsenic species in drinking water warrants one in future works.

Table 6.16. Removal efficiency of treatment system to remove arsenic from well water (where WS = water softener, ASF = arsenic filter, PF = pre-filter, and NA = where tap sample was higher than arsenic concentration from well). Units for well and tap are $\mu\text{g L}^{-1}$.

ID	Treatment	2015			2016		
		Well	Tap	Removal (%)	Well	Tap	Removal (%)
BH-46	WS	7.170	0.754	89.4	7.459	0.179	97.6
BH-47	N	0.093	5.462	NA	0.196	-	-
BH-06	N	0.191	0.298	NA	-	-	-
BH-07	N	0.976	0.996	NA	-	-	-
DW-03	N	<0.07	0.091	NA	-	-	-
DW-07	N	<0.07	0.343	NA	-	-	-
BH-12	N	0.090	0.074	22.2	-	-	-
BH-58	N	0.504	0.406	19.4	-	-	-
BH-57	WS	1.700	2.312	NA	-	-	-
BH-23	N	30.257	9.126	69.8	20.520	-	-
BH-60	ASF	-	-	-	76.185	5.691	92.5
(A)			3.231				
BH-60	N	-	-	-	76.185	100.10261	NA
(B)			45.685				
BH-60	N	-	-	-	76.185	6.323	91.7
(C)			3.682				
BH-74	N	4.114	3.607	12.2	3.502	5.502	NA
BH-65	WS, ASF	-	18.248	-	-	-	-
BH-39	ASF, WS	31.049	4.279	86.2	31.982	6.916	78.3
BH-70	N	11.295	<0.07	~100%	8.132	8.443	NA
BH-64	ASF	26.473	0.626	97.6	27.512	3.877	85.9
BH-25	PF, ASF	58.068	16.372	71.8	57.059	21.318	62.6
BH-67	N	10.656	-	-	5.3796	12.047	NA

6.3.12) Comparison with historic data

The construction of a motorway 67 boreholes were monitored from 2004 – 2008 (Chapter 5). Some of the sample sites that were within the scope of the previous chapter were also analysed as part of this current study and are a mixture of dug wells and boreholes. Table 6.17 shows the historic monitoring identifiers (IDs) that match up with monitoring wells sampled as part of this current work. As can be seen, the greater analytical sensitivity of this study resulted in much lower detection limits.

Most elevated arsenic concentrations occurred in the calcareous metasedimentary Clontail formation with comparable calcareous metasedimentary aquifers giving rise to elevated arsenic in areas of New England (Peters et al., 1999; Ayotte et al., 2003). The Clontail Formation is contained within the rock type of Sandstone and Shale (Greywacke) which was

found to contain elevated arsenic (Chapter 3). This study illustrates that other fractured bedrock aquifers in Ireland with this rock type may be at risk from elevated arsenic and includes: Clew Bay, Mayo (<5-193 $\mu\text{g L}^{-1}$), Bellewstown, County Meath (<0.37-32 $\mu\text{g L}^{-1}$ and <0.37-242 $\mu\text{g L}^{-1}$), Enniskerry/Kilbride, County Wicklow (<0.5-197 $\mu\text{g L}^{-1}$) Clontibret, County Monaghan (9.7-17.76 $\mu\text{g L}^{-1}$), Faughart/Feede/Aghnaskeagh (<0.37-47 $\mu\text{g L}^{-1}$), and Carrickaneena/Faughart/Feede (0.37-139 $\mu\text{g L}^{-1}$) (Chapter 3). Recent studies in the US have also identified several fractured metasedimentary bedrock aquifers (including calcareous metasedimentary bedrock) as sources of elevated arsenic in groundwater (Ayotte et al., 2003 and 2006; Smedley et al., 2007; Ryan et al., 2013 and 2015b; O'Shea et al., 2015; Andy et al., 2017; Bondu et al., 2017a 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). However, these higher concentrations are reported to be a result of mineralisation or anthropogenic activities. Greywackes can also contain high concentrations of manganese (Homoncik et al., 2010). A recent national database found arsenic in topsoil within this location at between 9.1 – 12 mg kg^{-1} (Fay et al., 2007).

Table 6.17. Comparison of groundwater measured in 2015 and 2016 with data measured in November 2005 with comparison of historic IDs and current sampling IDs. All units in $\mu\text{g L}^{-1}$

Historic IDs	Current IDs	Past study	This study		
		2005	2014	2015	2016
W_7	BH_14	<1	2.1	-	-
W_52	BH_17	<1	21	19.4	-
W_10	BH_18	2	1.7	1.3	-
W_13	BH_21	11	16.6	16.5	17.9
W_11	BH_22	<1	0.83	-	-
W_51	BH_24	25	5.3	0.13	-
W_48	BH_26	13	15.1	13.3	21.4
W_57	BH_30	9	10.5	8.6	-
W_19	BH_31	10	3.5	-	-
W_22	BH_32	15	7.4	-	-
W_46	BH_34	<1	0.31	-	-
W_26	BH_35	9	9.5	-	-
W_53	BH_38	2	8.6	-	-
W_54	BH_39	23	33.2	27.1	30.3
W_30	BH_40	16	16.2	13.2	14.6
W_27	BH_42	<1	0.9	-	-
W_29	BH_43	<1	6.5	-	-
W_23	BH_45	2	1.8	-	-

Table 6.17. (continued).

Historic IDS	Current IDs	Past study	This study		
		2005	2014	2015	2016
W_23	BH_45	2	1.8	-	-
W_59	BH_48	14	2.1	-	-
W_6	DW_04	<1	0.13	-	-
W_8	DW_05	<1	1.1	-	-
W_9	DW_06	<1	0.9	-	-
W_14B	DW_09	<1	0.85	-	-
W_14A	DW_10	3	3.1	-	-
W_21	DW_13	<1	0.56	-	-
W_31	DW_18	<1	0.16	-	-
W_50	DW_19	<1	0.21	0.31	-

6.3.13) Geochemical controls on arsenic mobilisation

Elevated arsenic concentrations reported in this groundwater system in north east Ireland result from a geogenic origin rather than anthropogenic influences. If anthropogenic contamination was the source of arsenic in these groundwaters, then it would be expected that the highest concentrations of arsenic would be in shallow wells (Peters et al., 1999). However, low concentrations of arsenic are seen in these shallow DWs, often less than $\leq 5 \mu\text{g L}^{-1}$ a finding reported elsewhere (Peters et al., 1999; Bondu et al., 2017a). 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 (i.e. NO_3^-) and microbiological contamination from inadequate wastewater treatment facilities (Chapter 5). On the other hand, wells 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). 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 in order 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 $> 500 \text{ mg L}^{-1}$ 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. Both Eh and pH govern the speciation of arsenic in groundwater, but in this study, only pH was the major controlling factor. Redox conditions have been described elsewhere affecting the geochemistry of arsenic in groundwater, particularly south east Asia (Ravenscroft et al., 2009). The groundwater composition of these 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.

6.3.14) 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 sulphide mineralisation in veins and coating fracture surfaces (Ravenscroft et al., 2009). During sampling, it was noted from the homeowner that quartz veins were noted during drilling of the well (BH-60, 73.95 $\mu\text{g L}^{-1}$) which may explain the elevated concentration of arsenic in this well given that a well in the same site (BH-61, 15.46 $\mu\text{g L}^{-1}$) has moderate arsenic concentrations given they are a distance of 27 metres apart. This prior weathering from sulphide oxidation can transfer arsenic from sulphides to secondary phases. It is possible that in this study both sulphide oxidation and alkali desorption could operate simultaneously within the same geological terrain. This geochemical feature occurs when the geology is often granitic which agrees with the geological setting of this study area, i.e. granitoid intrusions into metasedimentary bedrock. This has been seen 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 sulphide 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.

6.4) Conclusions

This study has investigated elevated arsenic occurring in a subset of private water supply boreholes tapping into groundwater flow systems within fractured metasedimentary bedrock in Ireland. Several of the main conclusions from this study are summarised below;

- 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).
- The dominant speciation of arsenic in groundwater is arsenate, with pH rather than both pH and Eh controlling the speciation.
- While arsenic was the most detected oxyanion forming element in these groundwaters the presence of Sb and U above regulated limits warrants further research.

- Source of arsenic is expected to be sulphide minerals within fractures in the bedrock aquifer, with transportation of As and other oxyanion forming elements facilitated mainly by secondary Fe mineral phases.
- Mobilisation of arsenic is through the established process of alkali desorption from Fe oxyhydroxides.
- While some locations had reduced exposure at drinking water taps due to filtration devices, several locations had no such mitigation measures and represent an exposure pathway of inorganic arsenic, particularly arsenate.
- This study confirms past insights from national-scale mapping in arsenic in groundwater with further formations (Clontail Formation in this study) within the group Sandstone and Shale (Greywacke) may contain elevated arsenic concentrations and warrants further research.
- This work highlights that policy may need to be amended for sustainable groundwater use as private drinking water supplies contain elevated arsenic.
- The application of SPE based methodology can be used to overcome many of the limitations of implementing laboratory-based speciation of arsenic.

6.5) Summary

To understand the specific processes controlling arsenic geochemistry in groundwater, a multiyear survey was completed, which was collected using ultra-clean trace element techniques. While alkali desorption was shown to be the major control on arsenic mobilisation, the presence of methylarsenicals indicate that microbial communities may also play a role.

Chapter 7

Overview, key findings and recommendations for future research

7.0) General overview

Using a combination of several methodological and statistical approaches this dissertation investigated the occurrence of arsenic and trace elements in private drinking water sources in several locations in Ireland. This is a critical step towards understanding water quality and the health issue associated with these waters due to trace element mobilisation. This study represents the first detailed overview of geogenic arsenic from national-to-regional-to-local-scale in fractured bedrock aquifers. The research conducted as part of this study succeeded in making original contributions to knowledge around arsenic geochemistry, but also in providing frameworks and a foundation for future work in this area.

7.1) Key findings

Several key findings were discovered during this programme of research and are as follows:

- *Arsenic shows strong spatial associations with bedrock lithology* – As part of this work national-scale data were made available in order to access the spatial distribution of arsenic in groundwater and isolate potential controlling factors. This was completed using developed statistical methodologies to account for censored data. While most sites encountered were below the prescribed legal limit (i.e. $\leq 10 \mu\text{g L}^{-1}$) (EPA, 2014) elevated concentrations of arsenic (i.e. $\geq 10 \mu\text{g L}^{-1}$) were associated with several rock types: Sandstone and Shale (Greywackes), Rhyolite and Impure Limestones. In contrast, elevated concentrations of arsenic are found in Sandstone and Shale (ORS/NRS) in Co Kerry. This is interesting as among the sedimentary rocks globally, sandstones usually have the lowest concentrations of arsenic (Garelick et al., 2009). It has been noted that elevated concentrations of arsenic in groundwater (up to several mg L^{-1}) can be observed with low concentrations of arsenic in host rocks (Smedley and Kinniburgh, 2013). Thus, only a small percentage of solid arsenic is needed in order to desorb or dissolve to give rise to a groundwater arsenic problem.
- *Some geological formations are at risk* – In County Louth elevated arsenic concentrations are persistently observed in the calcareous metasedimentary Clontail Formation. Elsewhere in areas of New England comparable calcareous metasedimentary aquifers give rise to elevated arsenic (Peters et al., 1999; Ayotte et al., 2003). This formation is contained within the rock type of Sandstone and Shale (Greywacke) which this work found to contain elevated arsenic (as above) and highlights that other fractured bedrock aquifers in Ireland with this rock type may be at

risk from elevated arsenic and includes areas in Counties Mayo, Monaghan, Wexford and Meath. This has been observed in regions elsewhere.

- *Poorly productive aquifers are at risk from elevated arsenic* – Both national and regional studies indicate that several aquifer classifications of poorly productive aquifers (PPAs) contain elevated concentrations of arsenic, i.e. Pu (Poor aquifer – bedrock aquifer which are generally unproductive) and Ll (Locally important aquifer - bedrock which is moderately productive only in local zones). Indeed, local investigations in Louth also confirm this. Several of these EPA PPAs have elevated arsenic: Dripsey, Co Cork (up to $156 \mu\text{g L}^{-1}$), Mattock, Co Meath (up to $158.3 \mu\text{g L}^{-1}$), Ryewater, Co Meath (up to $22 \mu\text{g L}^{-1}$) and New Village, Co Galway (up to $15.8 \mu\text{g L}^{-1}$).
- *Arsenic is the most detected trace element above the legal limit* – In several experiments throughout this study arsenic was the most frequently detected trace element above the legal limits. After the trace element arsenic, the frequency of both the indicator parameters of Fe and Mn, and several oxyanions (Sb and U) were observed at elevated levels. Private drinking water supplies are not regulated like public water supplies in Ireland, with responsibility falling to the homeowner. In contrast there is a low number of mitigation strategies in use.
- *Elevated arsenic concentrations are associated with well depth* – Regional investigations in Louth revealed that elevated arsenic concentrations were associated with well depth, mainly distributed between 70-120 m. In addition, for PPA sites the majority of elevated arsenic concentrations were recorded in either deep or transition zone boreholes, which suggested that borehole depth may be an important factor in arsenic mobilisation at these locations.
- *Speciation of arsenic is controlled by pH* – Both pH and the redox potential of groundwater are the two most important factors determining the speciation of arsenic and thus mobility (Cullen and Reimer, 1989; Smedley and Kinniburgh, 2013). However, in this study the dominant aqueous control was governed by pH rather than pH and redox potential.
- *Arsenate is the dominant arsenic species* – Using a solid phase extraction methodology the dominant arsenic species was arsenate (in oxic-alkali waters). Concentrations of the more toxic species of arsenic such as arsenite were detected at lower concentrations.

- *Variations in arsenic concentrations occur over small spatial scales* - The variability of arsenic in groundwater can occur over small spatial scales (Ravenscroft et al., 2009; Smedley and Kinniburgh, 2013). Local investigations in Louth reveals that these scales occur in distances as small as < 30 m. In fractured bedrock aquifers, this large spatial variability is mainly governed by groundwater flow through changes in the dilution process and hydrochemistry. In comparisos, the national-scale approach identified high arsenic wells clustered adjacent to each other.
- *Mobilisation of arsenic through alkali desorption processes* – Local-scale investigations highlight that arsenic and other oxyanions (Sb, Se, Mo and U) are being mobilised in groundwater in Louth through the process of alkali desorption from Fe and Mn oxyhydroxides. These groundwaters are described as oxic-alkali, low Ca/Na ratios, low Fe and Mn, with the co-occurrence of several oxyanions (Mo, Se, Sb and U).
- *Microbially mediated mobilisation is occurring on a smaller scale* – Given the detection of methylarsenicals in groundwater, DMA^V and MA^V, and their correlation to geochemical parameters microbial methylation of arsenic is also occurring. While these methylated arsenic species indicate mobilisation through microbial processes, more detailed microbiological studies would need to be implemented to understand the process of arsenic biomethylation in these fractured bedrock aquifers.
- *Elevated nutrients (NO₃⁻) are a result of inorganic fertilizer/organic waste* – The presence of elevated nitrate concentrations (up to 134.1 mg l⁻¹) potentially results from inorganic fertilizer with less contribution from organic waste (both slurry and septic tank sources).

7.2) Limitations

In this dissertation several limitations were encountered which include:

- *Censored data* – In most environmental datasets, especially natural waters, left-censored data are present. This type of data is reported as non-detects which indicates results are below the reportable detection limit of the analytical technique usually expressed as < x µg L⁻¹ (where x is a numerical value). Approaches employed in this study using a combination of censored-data analysis and spatial techniques were able to overcome these obstacles whilst also avoiding bias by not using substitution methods. For this reason, the methodological framework used in this study can be applied elsewhere for groundwater assessment for a range of parameters.

- *Geological simplification* - To determine statistically significant differences between groundwater hydrochemical parameters and the different geological and hydrogeological, then some simplification of these explanatory variables was required. For example, the 27 rock unit groups of the ‘National Generalised Bedrock Map (Rock Unit Group)’ was reclassified into 11 rock types so that a smaller number of divisions could be achieved to allow an appreciable sample number prior to statistical analysis. Whilst this may have introduced some bias, it ultimately resulted in a better overview and identified several areas in Ireland with elevated arsenic in groundwater.
- *Time series analysis* – Using time series analysis would have resulted in the identification of temporal associations. However, due to several limitations, mainly analytical, in the data, this was not possible for the assessment in Chapter 5.

7.3) Recommendations for further work

Several recommendations for future research were encountered during this research, which included:

- *Detailed investigation of PPA sites*: These hard rock aquifers underlie 60% of the country and provide an important water source for farms, houses, small housing estates, hotels, and small to medium enterprises. Despite not being regarded as sources for large public water supplies, they are important for small private and public group supply schemes, and in terms of delivering water (and associated contaminants) via shallow groundwater pathways. There are several EPA PPA study sites in Ireland with several containing elevated arsenic as outlined in Chapter 3. By using existing PPA data, detailed investigations could be conducted into arsenic mobilisation and geochemistry in differing geological settings. By understanding the mobilisation of arsenic in these aquifers, more appropriate management and mitigation measures could be implemented for more local settings where these PPAs are used as source of drinking water (e.g. Louth).
- *Investigation of metasedimentary formations* – Several of the experiments in this work identified many areas with metasedimentary geological formations which contain elevated arsenic including areas in counties Mayo, Monaghan, Wexford and Meath which warrant further research.
- *Role of microbial influence on the mobilisation of arsenic* – In the study site in Louth, the presence of methylated organic species of arsenic are indicative of microbial

mediated mobilisation processes. However, the spatial extent of this process is not fully understood, and further research would assist in the elucidation of the biomethylation of arsenic in groundwaters. Building upon previous work contained in this dissertation an area in country Mayo was sampled to investigate the microbial community structure and function in groundwaters along an elevated arsenic concentration gradient. Although in development, this work will assist in the understanding of microbial mobilisation and biomethylation of arsenic in addition to the affect that elevated concentrations of arsenic has on the groundwater microbial community and function. This type of study would help in understanding the microbial processes involved in the transformation and remobilization of arsenic at the aquifer-water interface.

- *Arsenic exposure pathways and assessment* – As part of this dissertation the comparison of arsenic in groundwater wells and drinking water taps was assessed. Several locations had elevated arsenic in drinking water taps even with mitigation measures present. To fully understand the effects of these elevated arsenic concentrations on public health, an approach using short-term human biomonitoring (e.g. nails, hair) could be completed as illustrated by Drummer et al. (2015).
- *Follow up to national-scale assessment* – Prior to this research, the understanding of arsenic in groundwater was limited in an Irish context. With the knowledge gained as a result of this work, a follow up to the national-scale study could be implemented by incorporating other hydrochemistry parameters related to arsenic (e.g. Se, Sb, U, pH, well depth, etc) and explanatory variables using machine learning techniques such as logistic regression (i.e. Ayotte et al., 2006) and decision trees. These studies would be able to detect areas with the potential to have elevated arsenic, particularly unsampled locations. Most modelling approaches utilized in the literature have been undertaken with reductive dissolution was the major arsenic mobilisation mechanism (Amini et al., 2008a; Rodríguez-Lado et al., 2008 and 2013; Bretzler et al., 2017a), however this dissertation illustrates multiple arsenic mobilisation mechanisms are occurring in Ireland.

Appendix

(A1)

A1.1) Na

The distributions of sodium concentrations differ across rock type ($p < 0.05$) with pairwise comparisons revealing differences between Pure Limestone and Sandstone ($p = 0.020$), between Pure Limestone and Sandstone (ORS/NRS) ($p < 0.05$), and between Pure Limestone and Sandstone/Shale ($p = 0.017$). Looking at rock groupings, there are differences in sodium ($p < 0.05$) with pairwise comparisons showing significant differences between BJ and GH ($p < 0.05$), BJ and SHG ($p < 0.05$), BJ and VIS ($p < 0.05$), BJ and WA ($p = 0.003$), GC and SHG ($p = 0.006$), GC and VIS ($p = 0.020$), GH and NAM ($p = 0.020$), NAM and SHG ($p < 0.05$), NAM and VIS ($p = 0.011$), and between NAM and WA ($p = 0.040$). The data also suggest differences across quaternary groupings ($p = 0.020$) with pairwise comparisons highlighting the comparison of TNSSs and TDSs in particular ($p = 0.011$).

Aquifer groupings display significant differences in sodium ($p < 0.05$) with pairwise comparisons showing differences between Rkd and L1 ($p < 0.05$) and between Rkd and P1 ($p = 0.001$). Regarding groundwater vulnerability groupings, there is evidence that the distributions of sodium concentration differ ($p < 0.05$), pairwise comparisons show differences between L and E ($p = 0.000$), L and H ($p = 0.007$), L and M ($p = 0.002$), and between L and X ($p = 0.008$).

The distribution of sodium concentrations differ across the CORINE (L1) groupings ($p = 0.017$), with pairwise comparisons showing one pair having significant difference, Artificial Surfaces and Wetlands ($p = 0.048$). CORINE (L2) groupings display differences in the global test ($p = 0.006$) however no differences existed between the groups applying pairwise testing. CORINE (L3) groupings also show statistical significance in the global test ($p = 0.011$) but no statistical significance between any pair when applying pairwise comparisons with correction for multiple testing.

A1.2) K

Potassium concentrations display significant differences across rock types ($p < 0.05$) with pairwise comparisons indicating differences between Pure Limestone and Sandstone ($p = 0.013$), Pure Limestone and Sandstone (ORS/NRS) ($p < 0.05$), Pure Limestone and Sandstone/Shale ($p = 0.008$), and between Sandstone/Shale and Sandstone (ORS/NRS) ($p < 0.05$). The distributions of potassium differs across the rock groupings ($p < 0.05$) with pairwise comparisons specifying differences between the groups of BJ and GH ($p < 0.05$), BJ and SHG ($p = 0.001$), BJ and VIS ($p < 0.05$), BJ and WA ($p < 0.05$), BM and GH ($p = 0.012$), BM and VIS ($p = 0.004$), BM and WA ($p = 0.020$), CA and GH ($p = 0.002$), CA and VIS ($p < 0.05$), CA and WA ($p = 0.002$), CH and GN ($p < 0.05$), CH and VIS ($p < 0.05$), CH and WA ($p <$

0.05), FS and GH ($p = 0.004$), FS and VIS ($p = 0.030$), GC and GH ($p = 0.001$), GC and SHG ($p = 0.022$), GC and VIS ($p = 0.003$), GC and WA ($p = 0.002$), GH and NAM ($p = 0.036$), GH and SF ($p = 0.004$), GH and VS ($p = 0.003$), NAM and VIS ($p = 0.018$), SF and VIS ($p = 0.002$), SF and WA ($p = 0.024$), VIS and VS ($p = 0.002$), and VS and WA ($p = 0.040$). For quaternary groupings the distributions of potassium concentrations differ ($p < 0.05$) with pairwise comparisons indicating differences between the groups of TNSSs and Rck ($p = 0.040$) and between TNSSs and TDSs ($p < 0.05$).

The observations provide evidence that the distribution of potassium concentrations differ across aquifer groupings ($p < 0.05$) with pairwise comparisons showing differences between Rkd and LI ($p < 0.05$) and between Rkd and PI ($p < 0.05$). The distributions of potassium differs across groundwater vulnerability groupings ($p = 0.005$) with pairwise comparisons revealing differences between E and X ($p = 0.040$), between L and X ($p = 0.008$), and between M and X ($p = 0.008$).

Each of three CORINE groupings show statistically significant differences in potassium concentrations. Pairwise comparisons within CORINE (L1) categorisation show differences between the groups Artificial Surfaces and Wetlands ($p < 0.05$) and between Agricultural Areas and Wetlands ($p = 0.020$). Pairwise comparisons within CORINE (L2) groupings also show differences between the groups Urban Fabric and Heterogeneous Agricultural Areas ($p = 0.0030$), Urban Fabric and Inland Wetlands ($p < 0.05$), Pastures and Heterogeneous Agricultural Areas ($p = 0.002$), and between Pastures and Inland Wetlands ($p = 0.002$). For CORINE (L3) categorisation pairwise comparisons specified differences between the groups Discontinuous Urban Fabric and Land Principally Occupied by Agriculture ($p = 0.004$), Discontinuous Urban Fabric and Peat Bogs ($p < 0.05$), Pastures and Land Principally Occupied by Agriculture ($p = 0.003$), and between Pastures and Peat Bogs ($p = 0.002$).

A1.3) Ca

The distributions of calcium concentration differ across rock type ($p < 0.05$) with pairwise comparisons indicating differences between Pure Limestone and Sandstone ($p < 0.05$), Pure Limestone and Sandstone (ORS/NRS) ($p < 0.05$), and between Pure Limestone and Sandstone/Shale ($p \approx 0.000$). For rock type grouping the calcium concentration distributions differ ($p < 0.05$) with pairwise comparisons showing differences between groups BJ and VIS ($p < 0.05$), BJ and WA ($p < 0.05$), CH and VIS ($p = 0.041$), CH and WA ($p = 0.044$), GC and VIS ($p = 0.006$), GC and WA ($p = 0.023$), GH and NAM ($p < 0.05$), NAM and SHG ($p = 0.005$), NAM and VIS ($p = 0.002$), NAM and WA ($p = 0.003$), SF and VIS ($p = 0.015$), VIS

and VS ($p = 0.007$), and between VS and WA ($p = 0.006$). The observations provide no evidence that the distributions of calcium concentration differ across quaternary groupings.

The distributions of calcium concentration differ across aquifer groupings ($p < 0.05$) with pairwise comparisons showing differences between Rkd and L1 ($p < 0.05$) and between Rkd and P1 ($p < 0.05$). Groundwater vulnerability groupings also display differences in calcium concentrations ($p = 0.006$) with pairwise comparisons showing a difference exists between E and M ($p = 0.034$).

No differences in the distribution of calcium concentration across CORINE (L1), CORINE (L2), and CORINE (L3) groupings were observed.

A1.4) Mg

The distribution of magnesium concentrations differ across rock type ($p < 0.05$) with pairwise comparisons indicating differences between Sandstone (ORS/NRS) and Sandstone/Shale ($p \approx 0.000$). Considering rock groupings, there is evidence of differences ($p < 0.05$) with pairwise comparisons showing differences between the groups CCG and SF ($p = 0.011$), CCG and VS ($p = 0.038$), CF and SF ($p < 0.05$), CF and VS ($p = 0.002$), SF and SHG ($p = 0.010$), and between SHG and VS ($p = 0.002$). Quaternary groupings display significant differences ($p < 0.05$) with pairwise comparisons showing differences between TNSSs and Rck ($p = 0.041$) and between TNSSs and TDSs ($p < 0.05$).

The observations provide no evidence of a difference in the distribution of magnesium concentrations in relation to aquifer groupings but suggest a difference across groundwater vulnerability groupings ($p = 0.009$). Pairwise comparisons found differences between X and H ($p = 0.032$), and between X and M ($p = 0.044$).

The distribution of magnesium concentrations did not differ across the CORINE groupings.

A1.5) Total Hardness

Distributions of hardness concentration across rock type were significantly different ($p = 0.003$) and pairwise comparisons indicated differences in particular between Sandstone (ORS/NRS) and Sandstone/Shale ($p = 0.049$). Looking across the categories of there is evidence of a difference in hardness concentration ($p < 0.05$) with pairwise comparisons showing differences between the groups BJ and SHG ($p = 0.025$), FS and SHG ($p = 0.041$), and between SHG and VS ($p = 0.049$). The observations give no evidence to suggest the distribution of hardness concentrations differ in quaternary groupings.

For aquifer groupings the distributions of hardness concentrations differ ($p = 0.040$) with pairwise comparisons showing differences between groups Rkd and L1 ($p = 0.046$). The observations provided no evidence of differences in the distribution of hardness concentration across groundwater vulnerability groupings.

The distribution of hardness concentrations did not differ across the CORINE groupings, however pairwise comparisons indicated differences between CORINE (L1) groups Artificial Surfaces and Agricultural Areas ($p = 0.013$), Artificial Surfaces and Forests and Seminatural Areas ($p = 0.006$), and between Artificial Surfaces and Wetlands ($p = 0.042$).

Appendix

(A2)

Table A2.1. Sampling point of groundwater wells season (where RS = reservoir; GDT = tank below ground; BH = borehole; DW = dug well; T = tap; W = well and ND = not determined).

Well-ID	Depth (m)	Type	Sampling Location
W-1A/1B	60.7	BH	RS
W-1C	70	BH	RS
W-2	ND	BH	T
W-3	ND	BH	W
W-5	<2	DW	W
W-6	4	DW	W
W-7	54.8	BH	W
W-8	2,8	DW	W
W-9	4	DW	W
W-10	91.4	BH	W
W-11	ND	BH	W
W-12	27.4	BH	W
W-13	4	DW	W
W-14A	38	DW	W
W-14B	3.25	DW	W
W-15A	4.3	DW	W
W-15B	60.9	BH	W
W-16	3.6	DW	W
W-17	3.6	DW	W
W-18	<5	DW	W
W-19	ND	BH	T
W-21	ND	BH	W
W-22	ND	BH	T
W-23	85.3	BH	W
W-24	3.25	DW	W
W-25	5	DW	T
W-26	85.3	BH	W
W-27	ND	BH	T
W-28	5	DW	W
W-29	ND	BH	W
W-30	ND	BH	W
W-31	ND	DW	W
W-32	3.5	DW	W
W-33	4.3	DW	T
W-34	3.6	DW	W
W-35	2.8	DW	W
W-36	ND	BH	W
W-37	ND	BH	W
W-38	ND	BH	W
W-39	ND	BH	T
W-40	5.9	BH	W
W-41	60	BH	W
W-42	ND	BH	W
W-43	60	BH	W
W-44	5.37	DW	W
W-45	<6	DW	W
W-46	15.2	BH	W
W-47	ND	BH	W
W-48	ND	BH	W
W-49	150	BH	W
W-50	6.6	BH	W

Table A2.1. (continued).

Well-ID	Depth (m)	Type	Sampling Location
W-51	ND	BH	W
W-52	ND	BH	W
W-53	ND	BH	W
W-54	>50	BH	T
W-55	ND	BH	T
W-56	ND	BH	W
W-57	ND	BH	W
W-58	5	DW	W
W-59	ND	BH	GDT
W-60	ND	BH	W
W-61	ND	BH	T
W-62	79.2	BH	W
W-63	ND	BH	W
W-64	ND	BH	W
W-65	<3	DW	W
W-66	3.5	DW	W

A2.1) Chemical analysis

A2.1.1) Field parameters

pH, temperature and conductivity were measured in-situ.

A2.1.2) Microbiological parameters

The presence of faecal indicator bacteria (FIB), including faecal coliforms, total coliforms and faecal Streptococci (enterococcus) have been used to assess the presence of faecal pollution in water and possible association with enteric pathogens (Savichtcheva and Okabe, 2006). However, their application is associated with certain limitations (Savichtcheva and Okabe, 2006). While the presence of FIB can be determined in water, precise information in relation to the original of this contamination is not known (Smith et al., 2014). An alternative indicator of faecal pollution is with the detection of *Clostridium perfringens* (Savichtcheva and Okabe, 2006). *C. perfringens*, Faecal Coliforms, Faecal Streptococci and Total Coliforms were determined using the filtration method. The detection limit was < 1 colony forming unit (CFU) 100 ml⁻¹ for each parameter.

A2.1.3) Trace elements

Trace elements were analysed by inductively coupled plasma – mass spectrometry (ICP-MS). Detection limits for trace elements were 1 µg L⁻¹ (Cr, Mn, Ni, Cu, As, Se, Cd, Sb, and Pb), 2 µg L⁻¹ (Al and Fe) or 3 µg L⁻¹ (B). Mercury was determined by cold vapour atomic absorption spectrometry (CV-AAS) with a detection limit of <0.05 µg L⁻¹.

A2.1.4) Anions and nutrients

Sodium was analysed using a flame photometer with a method detection limit of $< 0.2 \text{ mg L}^{-1}$. TOC was determined using infra-red (IR) spectrometry with a detection limit of $< 2 \text{ mg L}^{-1}$. Turbidity, as nephelometric turbidity units (NTUs), was determined using a turbidity meter with a detection limit of 0.1 NTU. Bromate was determined using ion chromatography (IC) with a detection limit of 0.0007 mg L^{-1} . Colour was determined by spectrophotometry and had a detection limit of 0 Hazen units. Chloride, fluoride, nitrate, nitrite and sulphate were analysed using a photometric analyser and had a detection limit of $<1 \text{ mg L}^{-1}$, $<0.1 \text{ mg L}^{-1}$, $<0.3 \text{ mg L}^{-1}$, $<0.05 \text{ mg L}^{-1}$ and $<3 \text{ mg L}^{-1}$, respectively.

A2.1.5) Organic geochemistry

Within this study, several classes of organic geochemical parameters were determined including polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs) and pesticides. Individual PAHs were summed in two totals based on environmental legislation: sum of 4 USEPA PAHs (benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(123cd)pyrene and benzo(ghi)perylene) and sum of 16 USEPA PAHs (naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoroanthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluorathene, benzo(k)fluorathene, benzo(a)pyrene, indeno(123cd)pyrene, dibenzo(ah)anthracene) and benzo(ghi)perylene). While the sum of 16 USEPA PAHs does not have a regulatory limit, it is often used as an environmental indicator of organic contamination. Under the Irish Drinking Water Regulations, the maximum concentration of the sum of 4 PAHs is 100 ng L^{-1} . Benzo(a)pyrene is the only individual PAH to have its own limit which is 10 ng L^{-1} (EC, 2014). All PAHs were analysed by gas chromatography – mass spectrometry (GC-MS) with a detection limit for each PAH of 10 ng L^{-1} .

Volatiles were analysed by GS-MS with a detection limit of 1 ng L^{-1} for each VOC and were corrected using a water blank based on USEPA method 624/8260 (USEPA, 1984 and 2006). VOCs (61) measured included dichlorodifluoromethane, dichloromethane, vinyl chloride, bromomethane, dichloroethane, trichlorofluoromethane, trans-1,2-dichloroethene, dichloromethane, carbon disulphide, 1,1-dichloroethene, 1,1-dichloroethane, tert-butyl methyl ether, cis-1,2-dichloroethene, bromochloromethane, chloroform, 2,2-dichloropropane, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1-dichloropropene, benzene, carbontetrachloride, dibromomethane, 1,2-dichloropropane, bromodichloromethane, trichloroethene, cis-1,3-dichloropropene, trans-1,3-dichloropropene, 1,1,2-trichloroethane, toluene, 1,3-

dichloropropane, dibromochloromethane, 1,2-dibromoethane, tetrachloroethene, 1,1,1,2-tetrachloroethane, chlorobenzene, ethylbenzene, p/m-xylene, bromoform, styrene, 1,1,2,2-tetrachloroethane, o-xylene, 1,2,3-trichloropropane, isopropylbenzene, bromobenzene, 2-chlorotoluene, propylbenzene, 4-chlorotoluene, 1,2,4, trimethylbenzene, 4-isopropyltoluene, 1,3,5-trimethylbenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, sec-butylbenzene, tert-butylbenzene, 1,2-dichlorobenzene, n-butylbenzene, 1,2-dibromo-3-chloropropane, 1,2,4-trichlorobenzene, 1,2,3-trichlorobenzene, and hexachlorobutadiene. The limits in waters for tetrachloroethane and trichloroethane is 10 ug L^{-1} (sum of concentrations of both parameters), 3 ug L^{-1} for 1,2-dichloroethane, 0.5 ug L^{-1} for vinyl chloride and 100 ug L^{-1} for total trihalomethanes (TTHMs) (EC, 2014). TTHMs include chloroform (CHCl_3), bromoform (CHBr_3), dibromochloromethane (CHBr_2Cl) and bromodichloromethane (CHBrCl_2).

Lastly, organochlorine and organophosphorus pesticides (23) were analysed by GC-MS with a detection limit of $0.01 \text{ } \mu\text{g L}^{-1}$ which included dichlorvos, mevinphos, α -hexachlorocyclohexane (BHC), β -BHC, lindane (γ -BHC), diazinon, methyl parathion, heptachlor, fenitrothion, malathion, aldrin, parathion, heptachlor epoxide, endosulfan 1, p,p'-DDE, dieldrin, endrin, endosulfan 2, p,p'-DDD, ethion, p,p'-DDT, endosulfan sulphate, p,p'-methoxychlor, and azinphos methyl.

Appendix

(A3)

A3.1) Instrumental analysis

A3.1.1) Trace element determination

Trace element determination was performed with an inductively coupled plasma – mass spectrometry (ICP-MS) (Elan DRCe, Perkin Elmer, Waltham, USA) (Table A3.1).

Because of 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 $^{40}\text{Ar}^{35}\text{Cl}^+$ (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). Any concentrations that was above the linear dynamic range of the analyte being analysed was diluted with Milli-Q and reanalysed until it fell within the specified range. Full information on linear-working range and LODs of each analyte are documented in Table A3.2.

Triplicate samples taken at each monitoring location were averaged.

Table. A3.1. Operating conditions for ICP-MS and HPLC for total metal and speciation analysis

	Settings	
Analytical system	Total/dissolved trace elements	Speciation analysis
HPLC (<i>Perkin-Elmer series 200</i>)		
Guard column		
Analytical column		Hamilton PRP-X100 (4.1 x 250 mm, 5 μm)
Mobile phase		4 mM NH_4NO_3 and 60 mM NH_4NO_3 (pH 8.67)
Flow rate (1 $\text{cm}^3 \text{min}^{-1}$)		1
Injection volume (μL)		100
Acquisition time (min)		15
<i>ICP-MS (PE Elan DRC-e)</i>		
RF Power (W)	1200	1200
Lens voltage (V)	8.25	8.25
Plasma gas flow (L min^{-1})	15.00	15.00
Auxiliary gas flow (L min^{-1})	1.00	1.00
Nebuliser gas flow (L min^{-1})	0.93-0.97	0.93-0.97
Nebuliser type	Cyclonic spray chamber	Cyclonic spray chamber
Sampling cone	Nickel	Nickel
Skimmer cone	Nickel	Nickel
Dwell time (ms)	50	50
Scan mode	Peak hopping	Peak hopping
Internal standard (100 $\mu\text{g L}^{-1}$)	^{115}In	^{115}In
DRC reaction gas	CH_4/O_2	O_2
Units	Counts per second	Counts per second
Carrier gas	Ar (99.999%)	Ar (99.999%)
Reaction gas	O_2 (99.9995%), CH_4 (99.99%)	O_2 (99.9995%),

Table A3.2. ICP-MS analytical figures of merit

Analyte	Units	LOD	LOQ	ICP-MS mode	Calibration range
⁹ Be	µg L ⁻¹	0.05	0.12	Standard	0.1-200
¹¹ B	µg L ⁻¹	0.35	0.68	Standard	0.1-200
²³ Na	mg L ⁻¹	0.01	0.02	Standard	0.1-200
				(Majors)	
²⁴ Mg	mg L ⁻¹	0.01	0.02	Standard	0.1-200
				(Majors)	
²⁷ Al	µg L ⁻¹	0.05	0.12	Standard	0.1-200
²⁸ Si	mg L ⁻¹	0.01	0.06	Standard	0.025-50
				(Majors)	
³⁹ K	mg L ⁻¹	0.01	0.02	Standard	0.025-50
				(Majors)	
⁴³ Ca	mg L ⁻¹	0.01	0.09	Standard	0.1-200
				(Majors)	
⁴⁷ Ti	µg L ⁻¹	0.01	0.16	Standard	0.01-20
⁵¹ V	µg L ⁻¹	0.06	0.12	Standard	0.1-200
⁵² Cr	µg L ⁻¹	0.02	0.06	DRC (CH ₄)	0.1-200
⁵⁵ Mn	µg L ⁻¹	0.05	0.10	Standard	0.1-200
⁵⁶ Fe	µg L ⁻¹	0.02	0.33	DRC (CH ₄)	0.1-200
⁵⁹ Co	µg L ⁻¹	0.03	0.09	Standard	0.1-200
⁶⁰ Ni	µg L ⁻¹	0.19	0.41	Standard	0.1-200
⁶³ Cu	µg L ⁻¹	0.08	0.17	Standard	0.1-200
⁶⁶ Zn	µg L ⁻¹	0.04	0.17	DRC (CH ₄)	0.1-200
⁷⁵ As	µg L ⁻¹	0.03	0.07	DRC (O ₂)	0.1-200
⁸² Se	µg L ⁻¹	0.01	0.09	DRC (CH ₄)	0.1-200
⁸⁸ Sr	mg L ⁻¹	0.002	0.004	Standard	0.025-50
				(Majors)	
⁹³ Nb	µg L ⁻¹	0.03	0.07	Standard	0.01-20
⁹⁸ Mo	µg L ⁻¹	0.06	0.14	Standard	0.01-20
¹⁰⁷ Ag	µg L ⁻¹	0.05	0.09	Standard	0.1-200
¹¹¹ Cd	µg L ⁻¹	0.01	0.03	Standard	0.1-200
¹¹⁸ Sn	µg L ⁻¹	0.03	0.10	Standard	0.01-20
¹²¹ Sb	µg L ⁻¹	0.05	0.10	Standard	0.01-20
¹³⁰ Te	µg L ⁻¹	0.004	0.05	Standard	0.01-20
¹³⁸ Ba	µg L ⁻¹	0.05	0.10	Standard	0.1-200
¹⁸⁴ W	µg L ⁻¹	0.03	0.07	Standard	0.01-20
²⁰⁵ Tl	µg L ⁻¹	0.03	0.06	Standard	0.1-200
²⁰⁸ Pb	µg L ⁻¹	0.03	0.07	Standard	0.1-200
²⁰⁹ Bi	µg L ⁻¹	0.07	0.10	Standard	0.1-200
²³⁸ U	µg L ⁻¹	0.03	0.07	Standard	0.1-200

A3.1.2) Arsenic speciation analysis

High performance liquid chromatography – inductively coupled plasma – mass spectrometry (HPLC-ICP-MS) is the most commonly used technique for arsenic speciation analysis (Ali and Jain, 2004; Gong et al., 2002; Grotti et al., 2014; Michalke, 2009; Sharma and Sohn, 2009) because of its high levels of sensitivity (Gong et al., 2002). A Perkin Elmer Series 200 HPLC system (Perkin Elmer, Waltham, USA) equipped with a quaternary pump, autosampler, vacuum degasser and column oven in addition to an ICP-MS which was used for chromatographic determination for arsenic speciation. The on-line injector contained in the pump was a metal Rhenodyne® 9725 injector with a 100 µL polyether ether ketone (PEEK)

sample loop. Separation was achieved using the Hamilton® PRP-X100 (4.1 x 250 mm, 5 µm) with NH₄NO₃ as the eluting phase (Xie et al., 2002; Gault et al., 2003; Ammann, 2010). The use of the polymeric anion-exchange column, Hamilton PRP X100 (polystyrene divinylbenzene (PS-DVB) as the packing material in sizes of 3, 5 and 10 µm), has been used extensively for the separation of arsenic species (Gong et al., 2002).

Separation was achieved using a gradient elution method developed by Watts et al. (2007 and 2008), which was adapted from Martínez-Bravo et al. (2001). This is 4 mM NH₄NO₃ (solvent A) and 60 mM NH₄NO₃ (solvent B) (99.999% Trace Metal Basis, Sigma-Aldrich, Dublin) both adjusted to pH 8.7 (InoLab pH7110) with NH₄ (Ammonia Solution SpA, Romil, Ireland). An injection volume of 100 µL with a flow rate of 1 mL min⁻¹ (25°C) was used. Column equilibration was achieved using solvent A. The gradient profile of the method is shown in Table A3.3. The inorganic arsenic species arsenate (As^V) and arsenite (As^{III}) calibration standards were prepared from 1000 mg L⁻¹ standards (Apex Scientific, Maynooth, Ireland), while organoarsenicals standards were prepared from powders of dimethylarsinic acid ((CH₃)₂As(O)OH) and disodium methyl arsenate hexahydrate (CH₃AsNa₂O₃•6H₂O) (Supelco, Sigma-Aldrich, Ireland) with a calibration range of 12.5 – 100 µg L⁻¹. Groundwater samples were prepared into HPLC vials which had a PTFE/Silicone pre-slit septum (Perkin Elmer, Dublin, Ireland). The instrumentation was arranged to minimise tubing length from effluent of column to the inlet of the nebuliser of the ICP-MS and controlled using Chromera® speciation software (Perkin Elmer, Waltham, USA). Standards were reanalysed during each analytical batch to ensure quality and precision. The maximum holding time of samples from sample collection before analysis was five days.

Table A3.3. HPLC programme using 4 mM NH₄NO₃ (A) and 60 mM NH₄NO₃ (B) (between each step between 0.25 and 1 minute was allowed to change from 100% of one solvent to another. The last step of the programme was extended to allow for adequate column equilibration prior to subsequent injection).

Mobile phase	Time (minutes)				
	0-2	3-6.5	7.5-10.75	11-13	13.25-17
A (%)	100	0	100	0	100
B (%)	0	100	0	100	0

A3.1.3) Anion Analysis

Protocols adopted from the Standard Methods for the Examination of Water and Wastewater using a Hach DR 3900™ spectrophotometer (Colarado, USA) were utilised for sulphate (SO₄²⁻) determination using the turbidity method (SulfaVer4, 2-70 mg L⁻¹ SO₄²⁻), fluoride (F⁻) using

the SPADNS method (ACCUVAC, 0.02-2.00 mg L⁻¹ F⁻), chloride (Cl⁻) using the iron(III)-thiocyanate method (LCK311 1-70 mg L⁻¹ and 70-1000 mg L⁻¹ Cl⁻), and sulphide (S²⁻) using the *N,N*-dimethylbenzene-1,4-diamine (dimethyl-*p*-phenylenediamine) method (LCK653, 0.1-2.0 mg L⁻¹ S²⁻). Additionally, chloride, fluoride and sulphate were checked against ADDISTA quality assurance solutions (LCA 703) and standard solutions.

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