

Assessing and Developing Natural Background Levels for Chemical Parameters in Irish Groundwater

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ENVIRONMENTAL PROTECTION AGENCY

The Environmental Protection Agency (EPA) is responsible for protecting and improving the environment as a valuable asset for the people of Ireland. We are committed to protecting people and the environment from the harmful effects of radiation and pollution.

The work of the EPA can be divided into three main areas:

Regulation: *We implement effective regulation and environmental compliance systems to deliver good environmental outcomes and target those who don't comply.*

Knowledge: *We provide high quality, targeted and timely environmental data, information and assessment to inform decision making at all levels.*

Advocacy: *We work with others to advocate for a clean, productive and well protected environment and for sustainable environmental behaviour.*

Our Responsibilities

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We regulate the following activities so that they do not endanger human health or harm the environment:

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- large scale industrial activities (*e.g. pharmaceutical, cement manufacturing, power plants*);
- intensive agriculture (*e.g. pigs, poultry*);
- the contained use and controlled release of Genetically Modified Organisms (*GMOs*);
- sources of ionising radiation (*e.g. x-ray and radiotherapy equipment, industrial sources*);
- large petrol storage facilities;
- waste water discharges;
- dumping at sea activities.

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- Monitoring and reporting on Bathing Water Quality.

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- Preparing Ireland's greenhouse gas inventories and projections.
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- Funding environmental research to identify pressures, inform policy and provide solutions in the areas of climate, water and sustainability.

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- Assessing the impact of proposed plans and programmes on the Irish environment (*e.g. major development plans*).

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- Monitoring radiation levels, assessing exposure of people in Ireland to ionising radiation.
- Assisting in developing national plans for emergencies arising from nuclear accidents.
- Monitoring developments abroad relating to nuclear installations and radiological safety.
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- Providing advice and guidance to industry and the public on environmental and radiological protection topics.
- Providing timely and easily accessible environmental information to encourage public participation in environmental decision-making (*e.g. My Local Environment, Radon Maps*).
- Advising Government on matters relating to radiological safety and emergency response.
- Developing a National Hazardous Waste Management Plan to prevent and manage hazardous waste.

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- Generating greater environmental awareness and influencing positive behavioural change by supporting businesses, communities and householders to become more resource efficient.
- Promoting radon testing in homes and workplaces and encouraging remediation where necessary.

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The EPA is managed by a full time Board, consisting of a Director General and five Directors. The work is carried out across five Offices:

- Office of Environmental Sustainability
- Office of Environmental Enforcement
- Office of Evidence and Assessment
- Office of Radiation Protection and Environmental Monitoring
- Office of Communications and Corporate Services

The EPA is assisted by an Advisory Committee of twelve members who meet regularly to discuss issues of concern and provide advice to the Board.

EPA RESEARCH PROGRAMME 2014–2020

Assessing and Developing Natural Background Levels for Chemical Parameters in Irish Groundwater

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EPA Research Report

Prepared for the Environmental Protection Agency

by

Trinity College Dublin

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The EPA Research Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

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Executive Summary

The natural background levels established in this report are the range in concentration of chemical parameters in Irish groundwater arising from natural processes. They are important for understanding pollution and for setting regulatory limits. The EU Water Framework Directive (2000/60/EC) and Groundwater Daughter Directive (2006/118/EC) require Member States to consider natural background levels when establishing threshold values that are used to assess the chemical status of groundwater bodies.

In 2007, O'Callaghan Moran and Associates, on behalf of the South Eastern River Basin District, established natural background levels for 22 parameters in Irish groundwater. This report updates that work by establishing natural background levels for 39 parameters in Irish groundwater comprising major ions, nutrients, minor ions and trace elements.

The natural background levels were established using Environmental Protection Agency (EPA) groundwater quality monitoring data. As in the EU BRIDGE project (which developed a methodology to derive threshold values and included natural background levels), this study used pre-selected datasets to establish the natural background levels. The natural background levels of parameters such as barium, radon and arsenic, the concentrations of which are unlikely to be affected by anthropogenic activities, were established using data from more than 97% of the EPA's monitoring network. In contrast, natural background levels for parameters such as nitrate, phosphorus and chloride, the concentrations of which are likely

to be affected by anthropogenic activities, were established by data from less than 10% of the EPA's monitoring network. This reflects the extensive nature of anthropogenic activities in Ireland and their potential to alter groundwater chemistry.

The most likely hydrogeological/hydrochemical controlling processes for each parameter were considered and the natural background levels were defined accordingly. For example, the natural background levels for (1) parameters that are influenced by lithology (e.g. pH, electrical conductivity, calcium and alkalinity) were defined for simplified lithological groupings; (2) parameters that are influenced by degree of confinement (e.g. nitrate, ammonium, iron and manganese) were defined for unconfined conditions with a note on the likely impact of confined conditions; and (3) parameters that show little spatial variation, sometimes because of a high percentage of samples with concentrations below the limit of detection, were defined nationally.

The methodology used to establish natural background levels for Irish groundwater followed international best practice and made best use of available data. The results are comparable to natural background levels established for other countries or regions. However, the natural background levels were established at a national or regional scale and, as such, the results average out spatial variabilities. Therefore, when applying the results at different scales, particularly local scale studies, caution should be exercised and there should be an emphasis on understanding the local hydrogeological/hydrochemical conditions.

1 Introduction

Knowledge of the natural background levels of parameters in groundwater is a prerequisite for understanding pollution and for imposing regulatory limits (Edmunds *et al.*, 2003). In Ireland, the status of groundwater is assessed via the EU Water Framework Directive (WFD) (EC, 2000), which stipulates that groundwater status must be assessed and that good chemical and quantitative status must be achieved in order to protect human health and that of associated dependent ecosystems. Article 17 of the WFD stresses the need for Member States to identify significant and sustained upward trends of contamination concentrations to determine the starting points for reversing these trends. The Groundwater Daughter Directive (GWDD) (EC, 2006) explicitly asks Member States to consider background levels when establishing threshold values for groundwater pollutants. The 2014 amendments of the GWDD Annexes placed much greater emphasis on natural background levels. The upper limits of natural background levels can exceed environmental

quality or drinking water standards, as these are usually based on ecotoxicological or human health grounds. This may have important implications for regulatory bodies.

Determining natural background levels is not straightforward due to the ubiquitous nature of anthropogenic influences on the groundwater chemistry. Humans have had a long-term impact on the environment, including land use changes spanning several thousand years, alteration of rainfall chemistry due to emissions from burning fossil fuels, diffuse pollution from agricultural activities and urban point source pollution (Figure 1.1) (Shand *et al.*, 2007). The presence of purely anthropogenic substances (such as pesticides) indicates an obvious departure from “natural” groundwater chemistry, though for most parameters, which have natural and anthropogenic sources, the distinction is more difficult.

There are, however, a limited number of ways to determine natural background levels. Kelly and Panno

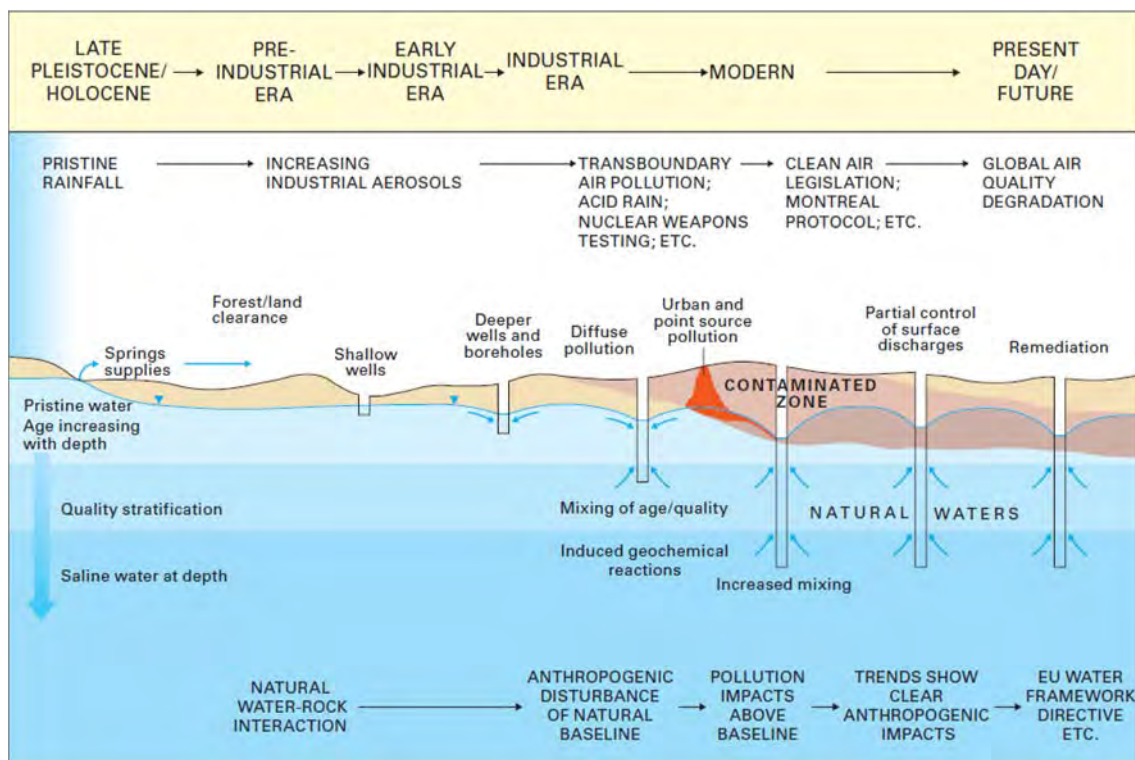


Figure 1.1. Conceptual model highlighting temporal changes from pristine conditions to the modern day (from Shand *et al.*, 2007). Reproduced with permission from the British Geological Survey. © NERC.

(2008) describe the options as (1) temporal, where groundwater data prior to human activity are reviewed; (2) spatial, where current groundwater data from areas unaffected by human activities are collected; or (3) a combination of these. The temporal option uses historical data, which are assumed to represent conditions prior to considerable human influence and are likely to be the best estimate of background levels. The primary limitation of this method is that historical datasets are scarce. It is also possible that historical datasets were collected using methods considered unacceptable by modern standards. For these reasons, the spatial option is more commonly used, primarily by collecting groundwater samples from “pristine” areas. However, caution should be exercised when applying values calculated for pristine areas to potentially impacted areas, as the two may have substantially different physical, chemical and biological characteristics. For example, the natural geochemistry of deep or confined groundwater, which is likely to be protected from pollution, is inherently different to shallow, unconfined, aerobic groundwater in the same aquifer due to differences in residence times and/or redox conditions. In addition, in many parts of the world, locating an appropriate pristine area can be problematic. The third method, which may incorporate both spatial and temporal aspects, is to evaluate large datasets using descriptive statistics. This method is the most useful for regional or national scale studies, but it often relies on datasets which are not designed for establishing natural background levels and the required statistical techniques may be difficult to apply.

The natural background levels established in this report use descriptive statistics of spatial datasets. However, even if the “local” impacts of agriculture can be screened out using pre-selection of monitoring points (MPs), the results will still reflect the national scale alteration of groundwater chemistry due to the changing rainfall chemistry. Care should be taken when applying the results of this study, particularly for nutrients and for parameters which are potentially impacted by anthropogenic activities.

Different countries have used variations of the methodology options outlined above in order to fulfil their obligations to establish natural background levels in groundwater. Selected approaches are summarised in the following section.

1.1 Summary of International Approaches

1.1.1 European Union BaSeLiNe project

The EU project “Natural Baseline Quality in European Aquifers: A Basis for Aquifer Management” (BaSeLiNe, 2000) was established in 2000 and involved research groups from 12 European countries (Nieto *et al.*, 2005). As outlined on the BaSeLiNe website, the objective of the BaSeLiNe project was to establish criteria for defining natural water quality baselines and to develop a standardised Europe-wide approach for use in the emerging WFD. Such standards, based on geochemical principles, were needed to scientifically assess the natural variations in groundwater quality, since these may breach existing health limits. These criteria were also needed as a reference to assess quantitatively whether anthropogenic pollution is taking place.

The project focused on timescales influencing the natural processes and the rates at which these occurred, and appropriate dating tools [including radioisotopes and chlorofluorocarbons (CFCs)] were used. The extent to which pristine waters were being infiltrated by contaminated waters moving into aquifers was also assessed. As well as establishing a scientific framework, this project provided a forum for discussion between policy-makers and end users, including the utility companies and the general public.

The work was conducted in a number of representative aquifer cross sections in both carbonate and non-carbonate terrain in groundwater catchments within several European countries (Estonia, Poland, Denmark, Belgium, France, the UK, Spain and Portugal).

The BaSeLiNe project recommends a deductive geochemically-based approach aided by simple statistical tools (Edmunds *et al.*, 2003). The approach treats aquifers (or groundwater bodies) as individual entities and therefore relies on there being sufficient high-quality data within each unit without reference to other similar units. Pre-selection of monitoring data was limited to excluding water sources that showed obvious signs of point-source pollution (Shand *et al.*, 2007). Median concentrations for most elements were regarded as representative of the average unpolluted

groundwater composition, as it was assumed that non-natural effects are likely to be found in the upper 50% (Edmunds *et al.*, 2003). The exception is nitrate and it was estimated that 80% of groundwater in unconfined aquifers has significant contributions from agricultural sources (Edmunds *et al.*, 2003). Either the 95th (Edmunds *et al.*, 2003) or 97.7th (Shand *et al.*, 2007) percentiles of the concentration distributions were regarded as the upper threshold of baseline concentrations.

1.1.2 Baseline projects in the UK

Between 1999 and 2005, the British Geological Survey and the Environment Agency undertook a collaborative project called “The Natural (Baseline) Quality of Groundwaters in England and Wales” (the Baseline project) (Shand *et al.*, 2007). Between 2005 and 2011, the British Geological Survey and the Scottish Environment Protection Agency ran the equivalent project “Baseline Scotland” (MacDonald and Ó Dochartaigh, 2005; Smedley *et al.*, 2009). These projects aimed to define the natural baseline chemistry of groundwater from a number of defined aquifers or aquifer regions in England, Wales and Scotland and adopted similar methodologies to those established in the EU BaSeLiNe project.

The term “baseline” is sometimes used in an equivalent way to “ambient background” to describe “the immeasurably perturbed and no longer pristine natural background” (Reimann and Garrett, 2005). This is used in the context of measuring levels “now” so that future change may be quantified (Reimann and Garrett, 2005). However, the Baseline project defines the baseline concentration as “the concentration of a given element, species or chemical substance present in solution, which is derived from natural geological, biological or atmospheric sources” (Edmunds *et al.*, 2003).

The Baseline project involved the characterisation of spatial and temporal variations in groundwater chemistry and the interpretation of the dominant controlling processes within a given study area (Shand *et al.*, 2007). A Baseline study has been carried out for the Palaeogene lavas in Northern Ireland (P. Wilson, Geological Survey Northern Ireland, March 2015, personal communication). For further details on the Baseline projects in the UK, the reader is referred to

Shand *et al.* (2007); the Baseline chemistry report series is available on the UK Government website (<http://www.bgs.ac.uk/research/groundwater/quality/BaselineUK/baselineEngWales.html>; MacDonald and Ó Dochartaigh, 2005) and the Baseline Scotland reports are available on the British Geological Survey website (<http://www.bgs.ac.uk/research/groundwater/quality/baselineScotland/home.html>).

1.1.3 German approach

The Working Group of the Federal States of Germany on Water Problems (LAWA) commissioned a project to develop a procedure to define natural groundwater conditions from groundwater monitoring data. Wendland *et al.* (2003) estimate that 99% of Germany is influenced by anthropogenic activities; therefore, they used Schenk’s definition of natural groundwater concentrations to be “the concentration of the most important cations and anion originating from not significantly anthropogenically influenced soils and rocks of a watershed including groundwater areas under agricultural use or from areas where land cover change occurred over the last centuries” (Schenk, 2001). The approach developed was statistical and relied on the availability of large amounts of data. In this approach, the natural groundwater quality of a chemical species was assumed to be defined by log normal distributions of concentrations, while the anthropogenic impact was assumed to be defined by a normal distribution. For each chemical dataset, these two functions were separated, and 10th and 90th percentiles of the natural distribution were reported as the range of natural concentrations.

1.1.4 ESI ERDTI report

In 2004, the Environmental Protection Agency (EPA) commissioned ESI Ltd and TMS Environmental Ltd to develop a methodology for characterising the natural background level in groundwater bodies in Ireland (Buss *et al.*, 2004). The methodology involved:

- assessing data availability;
- characterising the hydrochemistry of the groundwater bodies;
- deriving natural background levels using one of the suggested techniques (in order of preference):
 - examination of historical data (pre-1973);

- analysis of filtered recent groundwater quality data;
- examination of surface water/rainfall quality data; and
- checking outputs are reasonable in comparison to nearby or similar aquifers.

Natural background levels were calculated and reported for a pilot study of individual groundwater bodies or groundwater body groups.

1.1.5 The BRIDGE project

An EU-specific targeted research project, BRIDGE (Background cRiteria for the Identification of Groundwater thrEsholds) was initiated in 2005, involving 27 partners from 19 countries, to develop a methodology for the derivation of groundwater threshold values based on scientific principles (Hinsby *et al.*, 2008; Wendland *et al.*, 2008; Quevauiller, 2008). The methodology proposed by BRIDGE was a tiered approach and focused on understanding the receptor at risk. The first tier took account of the natural background levels and referred to existing standards or reference values. Further tiers took into account dilution and attenuation processes (Hinsby *et al.*, 2008). The proposed methodology was tested on 14 case studies representing most of the major European aquifer typologies defined within the project and most of the ecoregions defined in the WFD (Hinsby *et al.*, 2008; Wendland *et al.*, 2008).

The BRIDGE project recommended deriving natural background levels from a pre-selected dataset, using pollutant indicators and aquifer typology, to approximate the natural groundwater composition of a given aquifer type. The definition of natural background levels within the BRIDGE project was “the concentration of a given element, species or chemical substance present in solution which is derived by natural processes from geological, biological or atmospheric sources” (BRIDGE project, 2006). The procedure proposed by BRIDGE may be applied if no national methodology exists or if data does not allow the derivation of natural background levels by more advanced methods using environmental tracers, oxidation capacity or other pollution indicators. Hinsby *et al.* (2008) and Wendland *et al.* (2008) outline the pre-selection criteria used in the BRIDGE case study evaluations:

- Samples with incorrect ion balance (exceeding 10%), unknown depth and unknown aquifer type are excluded.
- Data from hydrothermal and brackish or saline $[(Na) + (Cl)] > 1000 \text{ mg/l}$ aquifers are excluded (salinised aquifers are evaluated separately).
- Time series at each monitoring point are converted to median values (in order to assure that long time series do not bias results and that all sampling sites contribute equally to the natural background level derivation).
- Appropriate pollution indicators are applied, such as:
 - data from monitoring points that contain purely anthropogenic substances (such as polycyclic aromatic compounds or pesticides) are considered to be polluted and are excluded;
 - data from monitoring points representing an aerobic environment with median nitrate concentrations above 10 mg/l are considered to be polluted and are excluded; and
 - data from monitoring points representing an anaerobic environment with median ammonium $> 0.5 \text{ mg/l}$ are considered to be polluted and are excluded. Alternative pollution indicators for anaerobic environments include sulphide, oxidation capacity, potassium concentration, sum of anions and N_2 gas pressure.

It was suggested that the 90th or 97.7th percentiles of the remaining data per aquifer typology should be used as the upper limit of the natural background level, depending on the amount and quality of data (Hinsby and Condesso de Melo, 2006; Muller *et al.*, 2006). The 97.7th percentile may be used with large amounts of data (more than 60 data points) from groundwater bodies where all data points represent groundwater with a natural composition. The 90th percentile has been suggested for small datasets (less than 60 data points) or datasets where human impact cannot be excluded (Muller *et al.*, 2006). For further details, the reader is referred to Pauwels *et al.* (2006), Hinsby *et al.* (2008) and Wendland *et al.* (2008).

1.1.6 The O’Callaghan Moran & Associates report

In 2007, the South Eastern River Basin District (SERBD) Project Team commissioned O’Callaghan

Moran & Associates (OCM) to derive natural background levels using national data and the methodology developed by Buss *et al.* (2004). The brief also included updating the methodology to include the risk assessments on groundwater bodies developed by the Working Group on Groundwater, namely the impact potential maps, which combine aquifer type, vulnerability and pressure magnitude (Working Group on Groundwater, 2004a). OCM pre-selected 30 monitoring points from the EPA national groundwater quality monitoring network using the impact potential maps to exclude monitoring points likely to be affected by anthropogenic activities. They grouped the national geology into four lithological groups: (1) Lower Palaeozoics and Precambrian; (2) Devonian; (3) karst and (4) mixed (OCM, 2007).

OCM used two techniques to define the upper (or lower) limit of natural background levels, both of which were developed in Buss *et al.* (2004):

1. If there was sufficient data available, the “cumulative frequency plot technique” was used. A cumulative frequency plot was used to identify the natural distribution; the upper and lower limits were obtained by extrapolating that distribution up or down to the 90th or 5th percentiles. The 90th percentile was used because of the relatively limited datasets and the inherent level of uncertainty in terms of variation in analytical techniques used to derive values during laboratory analysis (OCM, 2007).
2. If data was limited (less than 50 records) the “statistical technique” was used, which determines the mean plus or minus two standard deviations (approximately the 95th and 5th percentiles, respectively) of the log concentration (Buss *et al.*, 2004; OCM, 2007). In the review process with the Groundwater Working Group (GWWG), it was thought that the statistical approach was over-estimating the threshold levels, particularly with small datasets. The results produced using the statistical method were omitted from the final results table (OCM, 2007).

OCM established natural background levels for 24 parameters (see Table 1.1). Sixteen of these parameters were termed “global parameters”, which

are not significantly influenced by lithology and of which natural background levels were reported at a national scale. For the remaining eight parameters, natural background levels were established and reported for each of the four lithological groups. Natural background levels were not established for 19 of the 43 parameters originally identified by the EPA due to lack of data.

1.1.7 Other regional and national studies

A number of studies aiming to establish natural background levels across Europe have been carried out since the EU BaSeLiNe and BRIDGE projects. These studies have varied in scope and scale. Coetsiers *et al.* (2009) tested the BRIDGE methodology on four Belgian aquifers. Preziosi *et al.* (2010) emphasised the importance of understanding hydrogeological settings and hydrogeochemical features when establishing natural background levels for arsenic and fluoride in central Italy. Gemtzi (2012) used an adjusted BRIDGE methodology and compared natural background levels from pristine and cultivated areas in Greece. Urresti *et al.* (2013) presented an isotopic technique for determining natural background levels for sulphate in Spain. Rotiroti *et al.* (2015) presented a component separation methodology for determining natural background levels in different hydrogeological settings in northern Italy.

Reimann and Birke (2010) compiled a comprehensive study of European groundwater quality by sampling bottled water samples. While this study was not a natural background levels study, bottled water quality can partly be considered to be representative of European groundwater quality. The results have been included in Table 1.1 as they are comprehensive both spatially and in the range of chemical parameters included.

A comparison of natural background levels from selected studies are included in Table 1.1. It should be noted that different methods were used to establish natural background levels (or natural baseline quality) for differing aquifer systems. Therefore, the values in Table 1.1 are not directly comparable to one another but they nonetheless provide a useful reference.

Table 1.1. A comparison of natural background levels or natural baseline quality from selected international studies

Parameter	Units	Ireland (OCM, 2007)	England and Wales (Shand, 2007)	GEOHINT National approach, Austria (Schramm <i>et al.</i> , 2006)	European bottled water (Reimann and Birk, 2010)	Glacial sediments, Germany (Wendland <i>et al.</i> , 2003)	Upper Rhine Valley, Germany (Wendland <i>et al.</i> , 2008)	Berkshire chalk, England unconfined (Edmund <i>et al.</i> , 2002)	Berkshire chalk, England unconfined (Edmund <i>et al.</i> , 2002)	Jurassic limestones, Germany (Wendland <i>et al.</i> , 2003)
pH	pH units	6.7–7.8	8.17		8.20	7.80		7.36	7.79	7.70
Electrical conductivity	uS/cm	115–731	3055	910	3582		951	887	1410	702
Turbidity	NTU									
Dissolved oxygen	mg/l O ₂		10.7			4.6		10.5	9.2	
Calcium	mg/l Ca	33–132	235	134	377	143		150	114	126
Sodium	mg/l Na	18–26	406	22	620	24	41	22	122	6.3
Magnesium	mg/l Mg	12997	76.5	41	92	30	25	8.2	29	37
Total hardness	mg/l CaCO ₃	95–419								
Potassium	mg/l K	2–3.8	27	7.7	33	4.0	7.2	4.3	10	1.9
Alkalinity	mg/l CaCO ₃	92–407			1466			330	324	
Chloride	mg/l Cl	24	667	32	378	43	84	41	151	37
Sulphate	mg/l SO ₄	37	326	80	809	68	173	125	56	32
Silica	mg/l SiO ₂		12		25			11	11	
Fluoride	mg/l F	0.21	1.79		1.61			0.33	2.4	
Ammonia	mg/l N		1.12	0.09	0.89	0.50	0.39	0.07	0.75	<0.01
Nitrate	mg/l NO ₃	9.2			15	0.1	8.2	7.5	6.7	
Nitrite	mg/l NO ₂		0.1	0.08			0.04			
Molybdate reactive phosphorus	µg/l P	20					55	6.5	13	
Total phosphorus	µg/l P			50	150					
Total organic carbon	mg/l C	3.0	7							
Aluminium	µg/l Al		559	31	30			2.8	<7	
Antimony	µg/l Sb		1.75							
Arsenic	µg/l As		23	4.1	5.2		4.0	3.5	4.0	
Barium	µg/l Ba	162	438		390			100	124	
Beryllium	µg/l Be		0.51		0.51					
Boron	µg/l B		448	0.04	1618		0.1	87	1180	
Cadmium	µg/l Cd		2.50	0.20	0.04			<2	<2	
Chromium	µg/l Cr	8.0	5.00		1.47					
Cobalt	µg/l Co		5.14		0.36			1.9	<1.33	
Copper	µg/l Cu	23	93	4.1	5			6.0	13	
Iron	µg/l Fe	130	5073	470	43	5000	3600	834	719	150
Lead	µg/l Pb		28	3.0	0.32			<2.8	<6.4	
Manganese	µg/l Mn	32	910	44	249	640	820	82	35	<10
Mercury	µg/l Hg		0.20							
Molybdenum	µg/l Mo		3.50		4.0			<7	<7	
Nickel	µg/l Ni	8	15	3.7	4.3			7.5	<3	
Radon	Bq/l									
Strontium	µg/l Sr		5144		6906			1400	6190	
Uranium	µg/l U		6.87		4.3			1.37	0.23	
Zinc	µg/l Zn	55	373		19			30	207	

Table 1.1. Continued

Parameter	Units	Triassic limestones, Germany (Wendland et al., 2003)	Lower Palaeozoic mudstone, Wales (Shand and Frengstad, 2001)	Devonian sandstone, Scotland (Shand and Frengstad, 2001)	Carboniferous sedimentary aquifers, Scotland (Ó Dochartaigh et al., 2011)	Triassic sandstones, Germany (Wendland et al., 2003)	Volcanic rocks, Germany (Kundel et al., 2004)	Carmenellis granite, SW England (Shand and Frengstad, 2001)	Egersund anorthosit, Norway (Shand and Frengstad, 2001)	Lower Palaeozoic metasediment, Norway (Shand and Frengstad, 2001)
pH	pH units	7.50	7.30	6.58	7.85	7.70	7.70	8.10	9.49	8.70
Electrical conductivity	uS/cm	939	575	468	1380	256		673	524	
Turbidity	NTU									
Dissolved oxygen	mg/l O ₂		10.7		7.6			8.1		
Calcium	mg/l Ca	154	61	31	123	29	54	69	40	70
Sodium	mg/l Na	9.2	23	26	182	16	9.3	22	97	114
Magnesium	mg/l Mg	50	14	6.3	48	23	22	45	17	17
Total hardness	mg/l CaCO ₃									
Potassium	mg/l K	2.1	8.9	19	12	3.6	1.4	5.4	7.6	8.0
Alkalinity	mg/l CaCO ₃		154	47	508			282	216	
Chloride	mg/l Cl	49	44	48	123	17	22	45	71	56
Sulphate	mg/l SO ₄	147	27	35	115	58	26	54	36	58
Silica	mg/l SiO ₂		6.0	4.8	8.2			6	10	9.2
Fluoride	mg/l F		0.18		0.53			0.09	75	1.97
Ammonia	mg/l N	<0.01	0.70		0.74	<0.01	0.02	0.02		
Nitrate	mg/l NO ₃		18.5	13.9			13.0			
Nitrite	mg/l NO ₂						0.0004		<0.05	<0.05
Molybdate reactive phosphorus	µg/l P									
Total phosphorus	µg/l P									
Total organic carbon	mg/l C									
Aluminium	µg/l Al		338	0.8	18		12	<50	151	183
Antimony	µg/l Sb		0.3						0.10	0.2
Arsenic	µg/l As		2.2		1.4				0.77	7.8
Barium	µg/l Ba		29	28	2.1			416	19	119
Beryllium	µg/l Be				0.02				0.004	0.1
Boron	µg/l B		40	50	329		36	54	135	182
Cadmium	µg/l Cd		0.1		0.09		0.04	<8	0.05	0.7
Chromium	µg/l Cr									
Cobalt	µg/l Co				2.1				0.37	2.5
Copper	µg/l Cu		37	80	4.4			37	98	121
Iron	µg/l Fe	100	670	173	3940	100		29	90	763
Lead	µg/l Pb		3		0.30		0.07	<60	1.7	1.8
Manganese	µg/l Mn	10	370	164	465	<10		6	151	441
Mercury	µg/l Hg				1.00		0.03		0.03	0.1
Molybdenum	µg/l Mo		1.2		1.00			<40	0.51	15
Nickel	µg/l Ni		6		5.3		0.13	<20	1.96	15
Radon	Bq/l									
Strontium	µg/l Sr		214	147	4.0			466	337	1977
Uranium	µg/l U		0.47		3.6				0.31	27
Zinc	µg/l Zn		62		80			32	120	

NTU, Nephelometric Turbidity Units.

2 Approach for Determining Natural Background Levels

2.1 Parameters

A list of 40 parameters was defined by the EPA for this study for which natural background levels should be established. This list comprises field parameters, major ions, minor ions, nutrients and trace elements. Buss *et al.* (2004) outlined the reasons for the inclusion of the majority of the parameters in their study (Table 2.1).

Additional parameters were included in the OCM study (OCM, 2007). All parameters are included in Table 2.2.

To aid the pre-selection of monitoring points, the 40 parameters were divided into two groups based on whether or not the concentration of the substance in groundwater has the potential to be affected by anthropogenic activities. The parameters which were

Table 2.1. Indicator species (from Buss *et al.*, 2004)

WFD Annex V core indicators	
Ammonium	Primarily from sewage and farm wastes, also in artificial fertilisers
Dissolved oxygen	Absence indicates reducing groundwaters
Electrical conductivity	Primarily used as an indicator of saline intrusion, but also increases with contamination by most ionic species
pH	Indicator of many types of pollution in non-buffered aquifers. Controls the toxicity of ammonium to fish
Nitrate	From artificial fertilisers and animal waste, but can also arise from transformation of ammonium in aerobic groundwaters. Controlled under the Nitrates Directive (91/676/EEC)
Groundwater Directive Annex III groundwater pollutants	
Ammonium	Primarily from sewage and farm wastes, also in artificial fertilisers
Arsenic	Present in fertilisers, wood preservatives and acid mine drainage, but high in some rock types. Soluble in reducing conditions and at high pH
Cadmium	Present at trace concentrations in phosphate fertilisers
Chloride	From sewage and farm wastes, but also where road salts have been applied and where saline intrusion is occurring
Lead	Present in acid mine drainage, adjacent to roads and shooting ranges. Usually tightly sorbed to soil so leaching is moderate
Mercury	Present in acid mine drainage, also in low concentrations from septic wastes
Sulphate	Leaching of construction rubble, slag heaps and acid mine drainage, also an indicator of acid rain. Very low sulphates indicate reducing conditions
Other species recommended by Buss <i>et al.</i> , 2004	
Alkalinity	Depletion of alkalinity leads to risk of acidification of aquifers
Barium	Mainly from natural sources, but a nationwide survey should be made
Boron	Indicative of urban pollution
Chromium	Used in wood preservation processes
Copper	Used in wood preservation processes and some pesticide mixtures. Indicates urban (industrial) sewer leakage
Fluoride	Indicative of pollution by urban sewer leakage
Iron and manganese	High concentrations are indicative of reducing conditions (and are more sensitive indicators than dissolved oxygen measurements) and also released on drainage of peat bogs and in acid mine drainage
Phosphate	From artificial fertilisers, sewage and farm wastes. Phosphate is not normally considered a risk to groundwater but can lead to eutrophication of surface waters at low concentrations
Radon	From natural sources, but a nationwide survey should be made
Uranium	From natural sources, but a nationwide survey should be made
Zinc	Present on galvanised steel and in acid mine drainage, it is liberated at low pH. Can be an indicator of elevated cadmium concentrations. Harmful to aquatic organisms at low concentrations

Table 2.2. Parameters whose concentrations are potentially affected by anthropogenic activities

Parameter	Macronutrient in fertiliser	Micronutrient in fertiliser	Sewage/slurry	Insecticides	Lime	Other agriculture	Concentration potentially affected by anthropogenic activities
Ammonia (NH ₃)	Y		Y				Y
Nitrate (NO ₃)	Y		Y				Y
Nitrite (NO ₂)	Y		Y				Y
Molybdate reactive phosphorus (P)	Y		Y				Y
Total phosphorus (P)	Y		Y				Y
Sodium (Na)	Y		Y				Y
Sulphate (SO ₄)	Y			Y			Y
Calcium (Ca)	Y				Y		Y
Magnesium (Mg)	Y				Y		Y
Potassium (K)	Y						Y
Total organic carbon (C)	Y						Y
Boron (B)		Y		Y			Y
Chloride (Cl)		Y					Y
Copper (Cu)		Y					Y
Fluoride (F ⁻)		Y					Y
Iron (Fe)		Y					Y
Manganese (Mn)		Y					Y
Molybdenum (Mo)		Y					Y
Nickel (Ni)		Y					Y
Zinc (Zn)		Y					Y
Cadmium (Cd)				Y			Y
Alkalinity					Y		Y
Hardness					Y		Y
pH					Y		Y
Dissolved oxygen						Y	Y
Electrical conductivity						Y	Y
Turbidity						Y	Y
Aluminium (Al)							N
Antimony (Sb)							N
Arsenic (As)							N
Barium (Ba)							N
Beryllium (Be)							N
Chromium (Cr)							N
Cobalt (Co)							N
Lead (Pb)							N
Mercury (Hg)							N
Radon (Rn)							N
Silica (SiO ₂)							N
Strontium (Sr)							N
Uranium (U)							N

N, no; Y, yes.

classed as potentially being affected by anthropogenic activities included substances contained in macro- or micronutrients in inorganic fertilisers (Scherer *et al.*, 2009), slurry, insecticides and those affected by liming (see Table 2.2 for details). This distinction was made to maximise the number of monitoring points used to establish natural background levels for the parameters where concentrations are not potentially affected by anthropogenic activities. More than two-thirds of Ireland's land surface is used for agriculture (EPA, 2003). Therefore the number of monitoring points with groundwater chemistry that is not affected by anthropogenic activities is likely to be low. However, the natural background levels of parameters whose concentrations are not potentially impacted by anthropogenic activities (Al, Sb, As, Ba, Be, Cr, Co, Pb, Hg, Si, Sr and U; see Table 2.2 for further details) may be established using data from a much larger number of monitoring points. For the purposes of pre-selecting monitoring points, nitrogen and phosphorus species were considered separately to the other parameters that are potentially affected by anthropogenic activities.

2.2 Groundwater Quality Monitoring in Ireland

Groundwater quality data have been collected in Ireland since the 1960s. Typically these data were collected by the Geological Survey of Ireland (GSI) or local authorities for specific projects such as the protection of drinking water supplies and investigating the impacts of pollution events. These data have not been used in this report for reasons including different limits of detection, unknown analytical techniques and lack of knowledge about borehole construction or zone of contribution (ZOC).

The EPA has been collecting groundwater quality data since the 1990s. The current groundwater quality monitoring network was established in 2006 in accordance with Article 8 of the WFD. This involved a review of all existing monitoring points and an assessment of their suitability. The EPA's groundwater quality monitoring programme is required to:

- supplement and validate the risk assessment described in Article 5 of the WFD;
- help determine the chemical status of groundwater bodies;

- establish the presence of significant upward trends in pollutant concentrations and the reversal of such trends when measures are introduced; and
- support the design and evaluation of programmes of measures.

Surveillance monitoring is required in groundwater bodies that are both "at risk" and "not at risk" of failing the WFD groundwater quality objectives. Generally, this network focuses on validating the Article 5 risk assessment, particularly at locations where the degree of uncertainty is greatest. Surveillance monitoring will also be used to detect both natural and anthropogenic trends in water quality.

Operational monitoring is required in groundwater bodies that are "at risk" of failing the WFD groundwater quality objectives. Generally this network focuses on assessing anthropogenically-induced upward trends in pollutants and will be used to support the design and provide feedback on the effectiveness of programmes of measures that are introduced to improve water quality in groundwater bodies.

A standard suite of 40 determinants, including field parameters, nutrients, major ions and certain minor and trace elements are analysed at each monitoring location within the surveillance and operational monitoring networks three to four times a year. Currently, the groundwater monitoring network comprises 223 monitoring points, of which 76 are springs. For further details, the reader is referred to www.epa.ie.

Figure 2.1 shows the locations of the EPA's 223 groundwater quality monitoring points. The EPA's monitoring points are mostly located within "productive" aquifers as defined by the GSI (DELG, EPA and GSI, 1999) and which are regionally or locally important as sources of groundwater for public or private supply schemes. With the exception of wells that are located within higher yielding fault zones, the monitoring network does not include wells or springs located within "poorly productive" aquifers, i.e. aquifers that are considered to have low well yields (EPA and CDM, 2010). Poorly productive aquifers, as defined by the GSI, include the following categories: (1) bedrock aquifers that are generally unproductive (Pu); (2) bedrock aquifers that are generally unproductive except for local zones (PI); and (3) bedrock aquifers

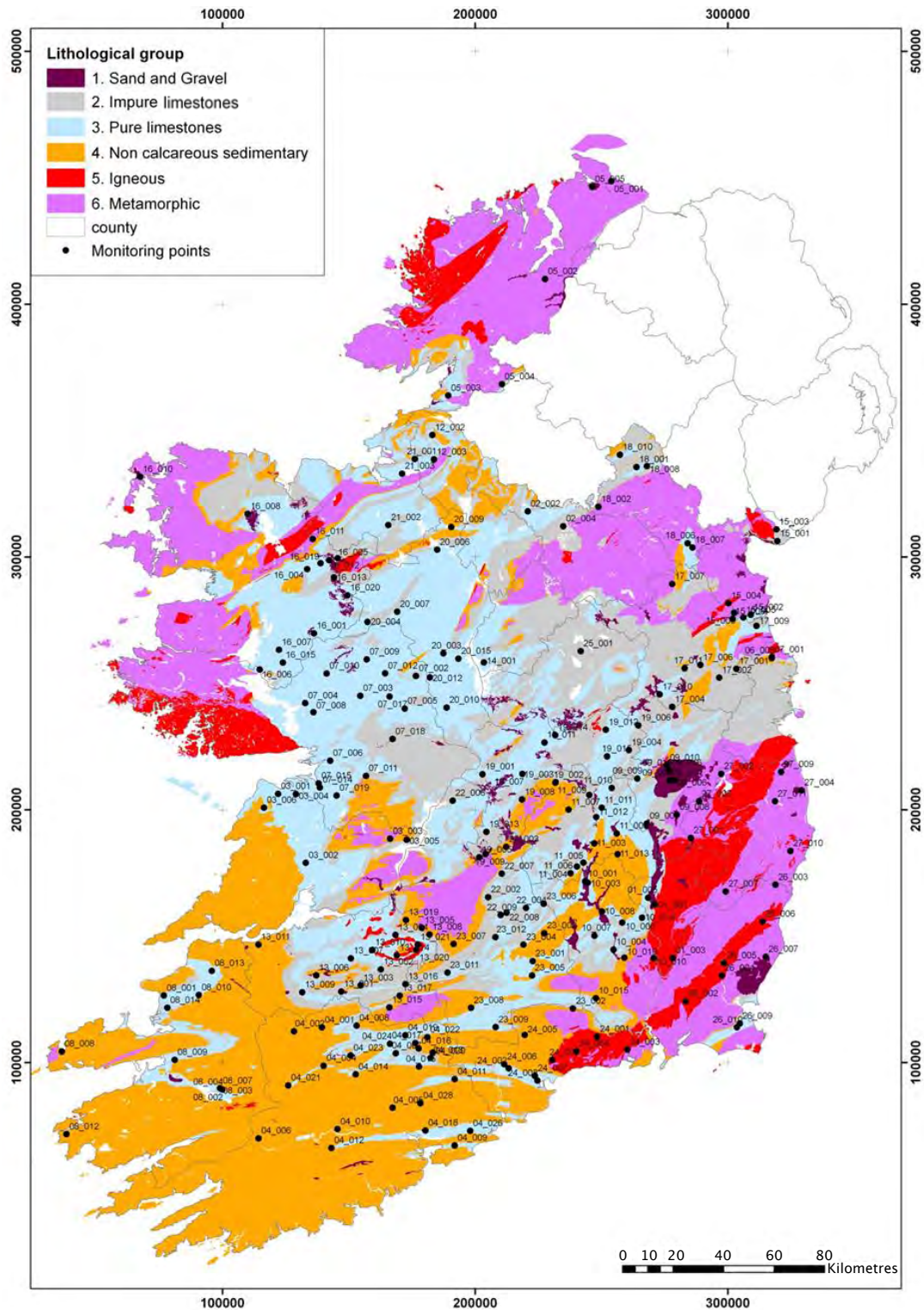


Figure 2.1. Locations of the EPA's groundwater quality monitoring network's monitoring points used to establish natural background levels.

that are moderately productive only in local zones (LI) (DELG, EPA and GSI, 1999). Poorly productive aquifers have been mapped by the GSI to cover nearly two-thirds of the total land area of Ireland. Therefore, the bias of the monitoring network towards productive

aquifers exists and will have implications for the natural background levels established. The EPA have supplemented the 223 monitoring points with six sets of monitoring wells in poorly productive aquifers, which were drilled between 2007 and 2009 [further details

may be found in EPA and CDM (2010)]. Data from these monitoring wells are not included in this study, but a recommendation of this report is that they should be included in any further work on natural background levels.

It should be noted that, with the exception of monitoring points in sand and gravel aquifers, the majority of the monitoring point installations are open hole. This means that the groundwater abstracted will be a mixture of deep and shallow (and therefore old and young groundwater). This has implications for the natural background levels calculated.

2.2.1 Confined monitoring points

The Swan (11_013) and Tydavnet (18_010) monitoring points abstract water from confined aquifers, so their geochemistry differs from that of many of the other monitoring points. For a number of parameters, the concentrations observed in these boreholes represent outliers and are included as a note, but are not used to calculate natural background levels for “normal” aerobic settings. Their hydrogeological settings are outlined below.

The Swan (13_010) monitoring point is located on the Castlecomer Plateau in County Laois. The geological succession comprises Westphalian sandstones, shales and thin coal seams. The Swan borehole taps the confined Swan Sandstone (which is about 10 metres thick). The aquifer is classified as a bedrock aquifer which is generally unproductive (Pu). The sandstone is recharged at its outcrop some 1.0–1.5 km to the north and north-east. The borehole is artesian. The geochemistry of the monitoring point indicates that the groundwater has undergone the process of ion exchange. For further information, the reader is referred to Daly and Misstear (1976), Misstear *et al.* (1980), Daly *et al.* (1980) and Wright (2000).

The Tydavnet (18_010) monitoring point is located in the locally important (LI) Knockatallon bedrock aquifer near Tydavnet in County Monaghan. Test pumping indicates a low storativity, which is consistent with a confined, secondary porosity aquifer. The geochemistry indicates that ion exchange has occurred along the groundwater flow path in the aquifer. For further information, the reader is referred to Misstear *et al.* (2008).

2.3 Groundwater Quality Data Processing

The groundwater quality data from the monitoring points were uploaded to a Microsoft Access database for assessment along with pathway data and pressure data for each monitoring point's ZOC. Further details of the pathway and pressure parameters are outlined in section 2.4.

The following steps were undertaken to improve the reliability of the groundwater quality data:

- removal of duplicate data;
- limits of detection/limits of quantification replaced by half the limit of detection/limit of quantification;
- removal of data points where limits of detections/limits of quantification were an order of magnitude higher than detected values;
- data of metals before 2007 have been removed as it is (a) unlikely that the samples were filtered prior to analysis or (b) not possible to know whether the samples were filtered. Samples taken after 2007 are filtered through 0.45 µm filter paper prior to analysis. Summary statistics were calculated for the metals first by using all data and then by using data taken after 2007. The 95th percentiles calculated using all the data were higher than those calculated using data collected since 2007;
- natural background levels were calculated for total phosphorus and molybdate reactive phosphorus using post-2010 data; and
- box and whisker plots for each parameter were plotted for each monitoring point and anomalous ranges were investigated and data/monitoring points removed from calculations if necessary.

It should be noted that individual outliers have not been removed as it was deemed too time-consuming to check time series plots for each monitoring point for each parameter.

2.4 Pathways and Pressure Datasets

The pathway data (including information on soils, subsoils, bedrock geology, aquifer type, nitrate susceptibility and molybdate reactive phosphorus susceptibility) and pressure data [impact potential, pressure magnitude and Land Parcel Identification System (LPIS)] formed an important part of the

pre-selection process. The pressure and pathway data were collated, using ESRI ArcMap 10.0, from a number of sources including the EPA, the GSI, Teagasc and the Department of Agriculture, Food and the Marine. Table 2.3 outlines details of the pathway and pressure datasets used. The bedrock and aquifer types that were recorded are the units from which water is being abstracted, where the information is available, which is not necessarily the same as the levels present at surface. Details of these units were sourced from EPA records, source protection reports (available on GSI website: www.gsi.ie); GSI groundwater body descriptions (available on GSI website: www.gsi.ie) and published literature.

The pathway and pressure data were recorded for each monitoring point's ZOC. A ZOC is defined, by the US Environmental Protection Agency's guidelines for delineation of wellhead protection areas, as "the area surrounding a pumping well that encompasses all areas or features that supply groundwater recharge to the well" (US EPA, 1987). Recording the pressure and pathway parameters within the ZOC, rather than at the monitoring point itself or for a fixed radius around the monitoring point, allows examination of the pressure and pathway parameters in the zone that

influences the concentration of dissolved substances in groundwater. ZOCs have been delineated for the monitoring points used in this study using a hydrogeologically robust methodology, using recharge, abstraction rates and the groundwater flow direction, outlined by DELG, EPA and GSI (1999) and Kelly (2010). 75% of the ZOCs in this study have an area of less than 5 km².

2.5 Lithological Groups

Ireland is underlain by heterogeneous bedrock strata, principally of Early Palaeozoic, Devonian and Carboniferous age, which are overlain by extensive and spatially variable, subsoil deposits. The regionally important aquifers in Ireland are found in the Carboniferous limestones and sandstones, Devonian Kiltorcan-type sandstones and Ordovician volcanics, as well as Quaternary sand and gravel deposits. Alteration, cementation and intensive structural deformation mean that groundwater flow within the bedrock aquifers is through secondary porosity and is dominated by fracture flow.

The chemistry of groundwater is affected by numerous interacting processes, which are often difficult to

Table 2.3. Details of the pathway and pressure datasets used in this study

Dataset	Data source	Reference
<i>Pathway</i>		
Groundwater recharge	Groundwater recharge map	GSI (2013)
Soil type	Indicative soils map	EPA/Teagasc (2006)
Subsoil type	Subsoil map	GSI/Teagasc/EPA (2006)
Subsoil permeability	Subsoil permeability map	GSI (2011a)
Groundwater vulnerability	Groundwater vulnerability map	GSI (2011b)
Bedrock geology	Grouped rock unit map	GSI (2005)
Bedrock aquifer type	National draft bedrock aquifer map	GSI (2006)
Gravel aquifer type	National draft gravel aquifer map	GSI (2008)
Aquifer flow regime	Aquifer flow regime data	Working Group on Groundwater (2003)
N susceptibility	N susceptibility map	EPA (2013)
P susceptibility	P susceptibility map	EPA (2013)
Denitrifying potential of the bedrock	Denitrifying potential of bedrock map	GSI (2012)
<i>Pressure</i>		
Land cover categories	CORINE 2000 land cover	EPA (2003)
Fertiliser application rates	Inorganic fertiliser purchases at district electoral division (DED) scale	CSO (2002); Teagasc (2010)
Livestock units	Agricultural census data	CSO (2002)
	LPIS	DAFM (2013)
Percentage of tillage	Agricultural census data	CSO (2002)

distinguish and quantify. However, the ultimate source of most dissolved ions is the mineral assemblages in rocks near the land surface (Hem, 1985). Therefore, in order to best reflect groundwater chemistry, the monitoring points were initially grouped based on lithology. Details of the lithological groups used, based on the GSI's Groundwater Rock Units (GSI, 2005), are shown in Table 2.4 and Figure 2.1.

To allow a representative number of monitoring points in each group, natural background levels have been calculated and reported using the general lithological groups. The detailed lithological groups and information, such as the potential impact of calcareous subsoil overlying non-calcareous bedrock and degree of confinement, have been used to check anomalies.

2.5.1 Other groupings

For some parameters it is possible that there is a more appropriate grouping than lithology, e.g. flow regime

rather than lithology may be important for phosphorus transfer. Therefore, a number of other groupings were explored. These include:

- The Working Group on Groundwater's flow regime, i.e. poorly productive, productive fissured, karstic and intergranular (Working Group on Groundwater, 2003). This grouping was used to improve the pre-selection criteria for the natural background levels of phosphorus.
- Redox reactions can have a significant impact on groundwater chemistry as they affect the concentrations and speciation of a number of important constituents including dissolved oxygen, organic carbon, sulphur, nitrogen, iron and manganese as well as a number of trace elements (Appelo and Postma, 2005). Therefore, monitoring points were also grouped based on confinement. Information on confinement was obtained from source reports (available on the GSI website), groundwater body descriptions (available on the

Table 2.4. Number of monitoring points in the lithological groups and detailed lithological groups

Lithological group	No of MPs	Detailed Lithological Group – GSI rock unit	No of MPs
1. Sand and gravel	30	1.1. Sand and gravel (limestone origin)	18
		1.2. Sand and gravel (other origin)	12
2. Impure limestones	30	2.1. Dinantian (early) sandstones, shales and limestones	3
		2.1. Dinantian lower impure limestones	6
		2.1. Dinantian mixed sandstones, shales and limestones	4
		2.1. Dinantian shales and limestones	1
		2.1. Dinantian upper impure limestones	16
3. Pure limestones	96	3.1. Dinantian pure bedded limestones	65
		3.1. Dinantian pure unbedded limestones	26
		3.2. Dinantian dolomitised limestones	5
4. Non-calcareous sedimentary	32	4.1. Devonian Kiltorcan-type sandstones	9
		4.2. Devonian Old Red sandstones	18
		4.3. Namurian sandstones	2
		4.3. Namurian undifferentiated	1
		4.3. Westphalian sandstones	2
5. Igneous	13	5.1. Basalts and other volcanic rocks	3
		5.2. Granites and other igneous intrusive rocks	2
		5.2. Ordovician volcanics	8
6. Metamorphic	16	6.1. Cambrian metasediments	1
		6.1. Ordovician metasediments	4
		6.1. Precambrian quartzites, gneisses and schists	4
		6.1. Silurian metasediments and volcanics	6
		6.2. Precambrian marble	1
Total No. of MPs	217		217

GSI website), published literature, e.g. Daly *et al.* (1980), Misstear *et al.* (2008) and Tedd *et al.* (2014), and groundwater chemistry data. It should be noted that this information is not complete (currently not all monitoring points have a source report) and is on occasion qualitative (comments include “some degree of confinement” or “aquifer is probably confined”). As a general rule, where there was no evidence to the contrary, it was assumed that groundwater was unconfined.

- Monitoring points were grouped based on groundwater vulnerability type (GSI, 2011b).
- The impact of saline deposition (i.e. the natural influence of the sea on rainfall composition as opposed to saline intrusion which involves anthropogenic groundwater abstraction) was considered and based on: (1) distance from the coast; and (2) Jordan’s 1995 mean annual concentration of Na⁺ and Cl⁻ ions in rainwater (Jordan, 1995).

2.6 Pre-selection of Monitoring Points

As in the EU BRIDGE project, this study has derived natural background levels using a pre-selected dataset. The criteria used for selecting monitoring points to define natural background levels for each of the different groups of parameters (outlined in section 2.1) are detailed in the following sections.

2.6.1 For nitrogen species assessment

The criteria for pre-selecting the dataset for establishing the natural background level for nitrogen species (nitrate, ammonium and nitrite) are as follows:

Pressure is low [defined as less than one livestock unit per hectare OR less than 3% of tillage within the ZOC using the Central Statistics Office datasets (CSO, 2002)]

AND

nitrate susceptibility is low (defined as 90% or more of the ZOC having low nitrate susceptibility).

The ZOCs of the selected monitoring points were checked against the LPIS (supplied by the Department of Agriculture, Forestry and the Marine), CORINE

(EPA, 2003) and aerial photography [supplied by Ordnance Survey Ireland (OSI)] data. A further four monitoring points were removed from the selection as these extra data sources indicated a higher intensity of agriculture than the Central Statistics Office (CSO) data suggested.

These criteria select 12 monitoring points (see Table 2.5 for details of the monitoring points and Figure 2.2 for their location). The statistical confidence in natural background levels based on data from only 12 monitoring points is low. The criteria were selected after iterations of investigating low pressure or low susceptibility scenarios. However, these scenarios selected a number of monitoring points with high nitrate values that are likely to represent scenarios where (1) even though the pressure is low, the pathway susceptibility is sufficiently high that nitrate is being lost to groundwater or (2) even though 90% of the ZOC is low nitrate susceptibility, the pressure or pathway in the remaining 10% of the ZOC is sufficiently high or susceptible respectively that nitrate is being lost to the groundwater.

2.6.2 For phosphorus species assessment

The criteria for pre-selecting the dataset for establishing the natural background level for phosphorus species (molybdate reactive phosphorus and total phosphorus) are as follows:

Pressure is low [defined as less than one livestock unit per hectare OR less than 3% of tillage within the ZOC using the CSO datasets (CSO, 2002)]

AND

molybdate reactive phosphorus susceptibility is low (defined as 90% or more of the ZOC having low molybdate reactive phosphorus susceptibility)

AND

sampling date is after 2010.

The ZOCs of the selected monitoring points were checked against data from the LPIS (supplied by the Department of Agriculture, Forestry and the Marine), CORINE (EPA, 2003), aerial photography

Table 2.5. Details of monitoring points selected to define natural background levels for nitrogen species

MP code	MP name	County	Lithological group	Mean ammonium (mg/l N)	Mean nitrite (mg/l NO ₂)	Mean nitrate (mg/l NO ₃)	% Tillage	Livestock density (LU/area)
16_013	Kilkelly	Mayo	2. Impure limestone	0.019	0.007	6.050	0.0	0.49
18_010	Tydavnet (PW-A)	Monaghan	2. Impure limestone	0.209	0.043	0.620	0.0	0.55
21_001	Calry	Sligo	2. Impure limestone	0.019	0.013	2.110	0.0	0.00
02_002	Bawnboy	Cavan	3. Pure limestone	0.017	0.009	3.160	0.0	0.97
07_002	Ballygar	Galway	3. Pure limestone	0.063	0.013	6.310	0.0	0.93
12_002	Kinlough/Tullaghan	Leitrim	3. Pure limestone	0.021	0.013	1.350	0.0	0.00
15_002	Ballymakenny	Louth	3. Pure limestone	0.020	0.011	3.900	0.0	0.52
03_005	Whitegate	Clare	4. Non-calcareous sedimentary	0.023	0.018	3.550	0.0	0.37
08_012	Portmagee (Lateeve)	Kerry	4. Non-calcareous sedimentary	0.021	0.010	6.700	0.0	0.13
11_013	Swan WS	Laois	4. Non-calcareous sedimentary	0.325	0.009	0.460	0.0	0.53
23_008	Kilcoran	Tipperary	4. Non-calcareous sedimentary	0.016	0.006	2.540	0.0	0.00
01_003	Glynn/St. Mullins	Carlow	5. Igneous	0.042	0.013	0.730	0.0	0.08

LU, livestock unit.

(supplied by OSI), flow regime (WGGW, 2003), the GSI's karst features database (GSI, 2007) and the EPA's microbiological data (EPA, 2011). A further six monitoring points were removed from the selection as these additional data sources indicated either (1) a higher intensity of agriculture than the CSO data; (2) a high percentage of urban land use; (3) the presences of karst features associated with a spring monitoring point or (4) previous local contamination incidents.

These criteria selected 18 monitoring points (see Table 2.6 for details of the monitoring points and Figure 2.2 for their location). The statistical confidence in natural background levels based on data from only 18 monitoring points is low. As with the selection of monitoring points for nitrogen species, the selection criteria for phosphorus were chosen after iterations of investigating low pressure or low susceptibility scenarios.

2.6.3 *When assessing parameters whose concentrations are potentially impacted by anthropogenic activities*

The criteria for pre-selecting the dataset for establishing the natural background level for parameters whose concentrations are potentially impacted by anthropogenic activities (alkalinity, B, Cd, Ca, Cl, electrical conductivity, Cu, dissolved oxygen, F, Fe, Mg, Mn, Mo, Ni, pH, K, Na, SO₄, total hardness, turbidity and Zn; see Table 2.2 for details) are as follows:

Maximum nitrate (as NO₃) is less than 10 mg/l

AND

pressure is low [defined as less than one livestock unit per hectare OR less than 3% of tillage within the ZOC using the CSO datasets (CSO, 2002)].



Figure 2.2. Location of the monitoring points used to define natural background levels for each of the different groups of parameters. (a) Nitrogen species, (b) phosphorus species, (c) parameters potentially impacted by anthropogenic activities and (d) parameters not potentially impacted by anthropogenic activities.

Table 2.6. Details of monitoring points selected to define natural background levels for phosphorus species

MP code	MP name	County	Lithological Group	Mean MRP (mg/l P)	Mean TP (mg/l P)	% Tillage	Livestock density (LU/area)
09_005	Curragh Camp	Kildare	1. Sand and gravel	0.008	0.005	0.0	0.39
09_006	Curragh Camp	Kildare	1. Sand and gravel	0.008	0.009	0.0	0.13
11_007	Knocks	Laois	1. Sand and gravel	0.008	0.004	0.0	0.90
16_012	Kilaturley	Mayo	1. Sand and gravel	0.008	0.004	0.0	0.63
11_009	Mountmellick WS (Derrygile)	Laois	2. Impure limestone	0.008	0.004	2.7	0.03
16_013	Kilkelly	Mayo	2. Impure limestone	0.008	0.005	0.0	0.49
18_010	Tydavnet (PW-A)	Monaghan	2. Impure limestone	0.008	0.004	0.0	0.55
22_002	Bouladuff/Borrisoleigh	Tipperary	2. Impure limestone	0.008	0.006	0.0	0.98
02_002	Bawnboy	Cavan	3. Pure limestone	0.017	0.018	0.0	0.97
07_002	Ballygar	Galway	3. Pure limestone	0.010	0.009	0.0	0.93
07_010	Kilbannon	Galway	3. Pure limestone	0.009	0.002	0.0	0.91
16_004	Bohola	Mayo	3. Pure limestone	0.008	0.020	0.0	0.79
16_005	Charlestown	Mayo	3. Pure limestone	0.008	0.004	0.0	0.62
16_019	Swinford	Mayo	3. Pure limestone	0.008	0.012	0.0	0.63
19_001	Banagher BH	Offaly	3. Pure limestone	0.008	0.004	0.3	0.84
23_011	Tipperary Co-op Ltd	Tipperary	3. Pure limestone	0.008	0.011	0.0	0.38
04_028	Waterglasshill PWS	Cork	4. Non-calcareous sedimentary	0.008	0.011	0.0	0.25
16_011	Killasser	Mayo	6. Metamorphic	0.008	0.008	0.0	0.15

LU, livestock unit; MRP, molybdate reactive phosphorus; TP, total phosphorus.

The ZOCs of the selected monitoring points were checked against data from the LPIS (supplied by the Department of Agriculture, Forestry and the Marine), CORINE (EPA, 2003), aerial photography (OSI, 2010), flow regime (WGGW, 2003) and the GSI's karst features database (GSI, 2008). A further three monitoring points were removed from the selection as these additional data sources indicated a higher intensity of agriculture than the CSO data or a high percentage of urban land use.

These criteria selected 21 monitoring points (see Table 2.7 for details of the monitoring points and Figure 2.2 for their location). The statistical confidence in natural background levels based on data from only 21 monitoring points is low. As with the selection of monitoring points for nitrogen and phosphorus species, the selection criteria for the parameters which are potentially impacted by anthropogenic activities were chosen after iterations of investigating a number of screening criteria. These iterations involved using the pressure, vulnerability, susceptibility and groundwater quality data sources as well as grouping the parameters based on their mobility.

Summary statistics (minimum, 5th percentile, 25th percentile, median, 75th percentile and 95th percentile) were calculated for the parameters potentially impacted by anthropogenic activities using (1) the monitoring points selected by this criteria and (2) all monitoring points. The summary statistics calculated using all of the monitoring points were higher than the summary statistics calculated using the selected monitoring points, providing support to the selection of parameters which may be impacted by anthropogenic activities.

2.6.4 When assessing parameters whose concentrations are not potentially impacted by anthropogenic activities

A total of 217 of the EPA's 223 monitoring points were used to establish the natural background levels for parameters in this group (Al, Sb, As, Ba, Be, Cr, Co, Pb, Hg, Si, Sr and U). See Table 2.8 for details of the monitoring points and Figure 2.2 for their location. This is based on the assumption that none of the EPA monitoring points are affected by point sources of pollution.

Table 2.7. Details of monitoring points selected to define natural background levels for the parameters potentially impacted by anthropogenic activities

MP code	MP name	County	Lithological Group	% Tillage	Livestock density (LU/area)
16_012	Kilaturley	Mayo	1. Sand and gravel	0.0	0.63
16_013	Kilkelly	Mayo	2. Impure limestone	0.0	0.49
18_010	Tydavnet (PW-A)	Monaghan	2. Impure limestone	0.0	0.55
21_001	Calry	Sligo	2. Impure limestone	0.0	0.00
02_002	Bawnboy	Cavan	3. Pure limestone	0.0	0.97
03_006	Killeany	Clare	3. Pure limestone	0.0	0.22
07_019	Poldeelin Spring	Galway	3. Pure limestone	0.0	0.45
08_007	FBH9 - Flesk River study catchment	Kerry	3. Pure limestone	0.0	0.00
12_002	Kinlough/Tullaghan	Leitrim	3. Pure limestone	0.0	0.00
12_003	Manorhamilton	Leitrim	3. Pure limestone	0.0	0.39
16_004	Bohola	Mayo	3. Pure limestone	0.0	0.79
16_019	Swinford	Mayo	3. Pure limestone	0.0	0.63
20_009	Keadew	Roscommon	3. Pure limestone	0.0	0.20
21_002	Culfadda	Sligo	3. Pure limestone	0.0	0.62
03_005	Whitegate	Clare	4. Non-calcareous sedimentary	0.0	0.37
04_028	Waterglasshill PWS	Cork	4. Non-calcareous sedimentary	0.0	0.25
11_013	Swan WS	Laois	4. Non-calcareous sedimentary	0.0	0.63
23_008	Kilcoran	Tipperary	4. Non-calcareous sedimentary	0.0	0.00
01_003	Glynn/St. Mullins (GWS)	Carlow	5. Igneous	0.0	0.08
03_003	Scarriff	Clare	6. Metamorphic	0.0	0.62
16_011	Killasser	Mayo	6. Metamorphic	0.0	0.15

LU, livestock unit.

2.7 Method of Establishing Natural Background Levels

This study utilises pre-selected datasets to establish natural background levels of chemical parameters in Irish groundwater. For each pre-selected dataset, i.e. data from monitoring points and/or time periods that best represent the parameters, a number of outputs were produced including:

1. descriptive statistics for each dataset and for each lithological, or other, group;
2. box and whisker plots for each monitoring point;
3. cumulative frequency plots for each lithological, or other, group; and
4. bubble plots for each parameter showing the spatial variation in concentration across the country.

These outputs are shown in Chapter 3 and in Appendices A and B. The groundwater monitoring data are included in Appendix C.

Natural background levels are a range rather than a single value. In this study, the upper limits of the ranges of natural background levels are defined as the 95th percentile. Other studies have used the 90th or 99.7th percentile (see section 1.1). In some cases, it is more reasonable to specify a lower limit to the range of natural background levels, for example in the case of dissolved oxygen. The lower limits of natural background levels were defined as the 5th percentile. Complications involving the limits of detection are discussed further in section 3.3. Unless otherwise stated, the upper or lower limits to the range of natural background levels have been calculated for unconfined conditions.

The hydrogeological and hydrochemical settings were considered for each parameter and the natural background levels were defined accordingly. Natural background levels were established either nationally or for each lithological, or other group. One-way analyses of variance (ANOVA) tests were used to distinguish whether the differences between lithological groups

Table 2.8. Details of monitoring points selected to define natural background levels for the parameters not potentially impacted by anthropogenic activities. Lithological groups comprise: 1. sand and gravel; 2. impure limestone; 3. pure limestone; 4. non-calcareous sedimentary; 5. igneous; and 6. metamorphic

MP code	Lithological Group	MP code	Lithological Group	MP code	Lithological Group	MP code	Lithological Group
01_001	1. S&G	21_001	2. Imp Lmst	13_007	3. P Lmst	04_010	4. Non calc
04_012	1. S&G	22_002	2. Imp Lmst	13_009	3. P Lmst	04_014	4. Non calc
04_018	1. S&G	22_004	2. Imp Lmst	13_010	3. P Lmst	04_015	4. Non calc
05_005	1. S&G	22_006	2. Imp Lmst	13_016	3. P Lmst	04_016	4. Non calc
07_018	1. S&G	22_007	2. Imp Lmst	13_021	3. P Lmst	04_020	4. Non calc
08_014	1. S&G	25_001	2. Imp Lmst	14_001	3. P Lmst	04_021	4. Non calc
09_005	1. S&G	01_005	3. P Lmst	15_002	3. P Lmst	04_022	4. Non calc
09_006	1. S&G	02_002	3. P Lmst	15_005	3. P Lmst	04_028	4. Non calc
09_008	1. S&G	03_001	3. P Lmst	16_001	3. P Lmst	07_011	4. Non calc
09_010	1. S&G	03_002	3. P Lmst	16_004	3. P Lmst	08_008	4. Non calc
10_003	1. S&G	03_004	3. P Lmst	16_005	3. P Lmst	08_012	4. Non calc
10_008	1. S&G	03_006	3. P Lmst	16_006	3. P Lmst	10_015	4. Non calc
11_003	1. S&G	04_009	3. P Lmst	16_007	3. P Lmst	10_019	4. Non calc
11_007	1. S&G	04_011	3. P Lmst	16_015	3. P Lmst	11_013	4. Non calc
11_008	1. S&G	04_013	3. P Lmst	16_019	3. P Lmst	13_001	4. Non calc
11_012	1. S&G	04_017	3. P Lmst	16_020	3. P Lmst	13_003	4. Non calc
13_008	1. S&G	04_019	3. P Lmst	18_006	3. P Lmst	13_005	4. Non calc
13_011	1. S&G	04_023	3. P Lmst	18_007	3. P Lmst	13_015	4. Non calc
13_019	1. S&G	04_024	3. P Lmst	19_001	3. P Lmst	13_017	4. Non calc
15_004	1. S&G	04_026	3. P Lmst	19_007	3. P Lmst	19_002	4. Non calc
16_012	1. S&G	05_003	3. P Lmst	19_011	3. P Lmst	19_008	4. Non calc
17_010	1. S&G	07_002	3. P Lmst	19_012	3. P Lmst	22_003	4. Non calc
19_005	1. S&G	07_003	3. P Lmst	19_013	3. P Lmst	23_003	4. Non calc
19_009	1. S&G	07_004	3. P Lmst	19_015	3. P Lmst	23_008	4. Non calc
19_014	1. S&G	07_005	3. P Lmst	20_003	3. P Lmst	24_005	4. Non calc
23_002	1. S&G	07_006	3. P Lmst	20_004	3. P Lmst	24_006	4. Non calc
23_007	1. S&G	07_008	3. P Lmst	20_006	3. P Lmst	01_003	5. Ig
27_004	1. S&G	07_009	3. P Lmst	20_007	3. P Lmst	10_010	5. Ig
27_006	1. S&G	07_010	3. P Lmst	20_009	3. P Lmst	13_014	5. Ig
27_009	1. S&G	07_012	3. P Lmst	20_010	3. P Lmst	13_020	5. Ig
02_004	2. Imp Lmst	07_015	3. P Lmst	20_012	3. P Lmst	19_006	5. Ig
04_004	2. Imp Lmst	07_017	3. P Lmst	20_015	3. P Lmst	24_001	5. Ig
04_007	2. Imp Lmst	07_019	3. P Lmst	21_002	3. P Lmst	24_003	5. Ig
06_008	2. Imp Lmst	08_001	3. P Lmst	21_003	3. P Lmst	24_004	5. Ig
08_002	2. Imp Lmst	08_003	3. P Lmst	22_008	3. P Lmst	24_009	5. Ig
08_004	2. Imp Lmst	08_007	3. P Lmst	22_009	3. P Lmst	26_002	5. Ig
11_009	2. Imp Lmst	08_009	3. P Lmst	23_001	3. P Lmst	26_004	5. Ig
13_002	2. Imp Lmst	08_010	3. P Lmst	23_004	3. P Lmst	26_005	5. Ig
13_006	2. Imp Lmst	08_013	3. P Lmst	23_005	3. P Lmst	26_006	5. Ig
15_001	2. Imp Lmst	09_001	3. P Lmst	23_006	3. P Lmst	03_003	6. Meta
15_003	2. Imp Lmst	09_009	3. P Lmst	23_009	3. P Lmst	05_001	6. Meta
16_008	2. Imp Lmst	10_001	3. P Lmst	23_011	3. P Lmst	05_002	6. Meta
16_013	2. Imp Lmst	10_004	3. P Lmst	23_012	3. P Lmst	05_004	6. Meta
17_001	2. Imp Lmst	10_006	3. P Lmst	24_002	3. P Lmst	15_008	6. Meta
17_002	2. Imp Lmst	10_007	3. P Lmst	24_007	3. P Lmst	15_009	6. Meta

Table 2.8. Continued

MP code	Lithological Group	MP code	Lithological Group	MP code	Lithological Group	MP code	Lithological Group
17_004	2. Imp Lmst	10_014	3. P Lmst	24_008	3. P Lmst	16_010	6. Meta
17_006	2. Imp Lmst	11_004	3. P Lmst	26_009	3. P Lmst	16_011	6. Meta
17_009	2. Imp Lmst	11_005	3. P Lmst	26_010	3. P Lmst	17_007	6. Meta
17_011	2. Imp Lmst	11_006	3. P Lmst	03_005	4. Non calc	26_003	6. Meta
18_001	2. Imp Lmst	11_010	3. P Lmst	04_001	4. Non calc	26_007	6. Meta
18_002	2. Imp Lmst	11_011	3. P Lmst	04_002	4. Non calc	27_001	6. Meta
18_008	2. Imp Lmst	12_002	3. P Lmst	04_005	4. Non calc	27_002	6. Meta
18_010	2. Imp Lmst	12_003	3. P Lmst	04_006	4. Non calc	27_007	6. Meta
19_004	2. Imp Lmst	13_004	3. P Lmst	04_008	4. Non calc	27_010	6. Meta
						27_011	6. Meta

S&G, sand and gravel; Imp Lmst, impure limestone; P Lmst, pure limestone; Non calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

were significant and, therefore, if the parameter should be reported nationally, or per lithological or other, group. The analysis was performed using Minitab 16.2.2 statistical software. Statistical significance was defined by a threshold of $p \leq 0.05$. Grouping

information for the ANOVA results was provided by Fisher's method, which uses individual confidence intervals. The results of the ANOVA tests and, therefore, the parameters that are considered to be affected by lithology are outlined in Chapter 3.

3 Results and Discussion

3.1 Summary of National Groundwater Chemistry

Natural groundwater chemistry varies as a function of a number of factors such as rainfall chemistry, aquifer lithology, geochemical environment, groundwater flow paths and residence time. As rainwater infiltrates through the soil, subsoils and bedrock, the chemistry evolves due to water–rock interactions. The degree to which groundwater becomes mineralised depends on a number of factors: the aquifer mineralogy, the permeability and nature of groundwater flow; the presence and nature of overlying deposits; the geochemical environment (especially the pH and redox conditions); groundwater flowpaths and the groundwater residence times (since most reactions are kinetically controlled).

The temperature of Irish groundwater does not vary considerably and groundwater is typically aerobic. Groundwater is typically near-neutral with a mean

pH of 7.0. A statistical summary of the major ion groundwater chemistry data for Ireland is shown in Figures 3.1 and 3.2. The plots show variation between lithological groups in alkalinity and calcium concentrations; with sands and gravels and the limestones groups having higher, well-defined concentrations. There is little variation within and between lithological groups for Cl, Na, Mg and K. The impure limestones show a high and variable SO_4 concentrations and low and variable NO_3 concentrations. This plot is constructed using data from all 217 monitoring points and therefore may reflect anthropogenic influences.

The Piper diagram (Figure 3.3) shows that, in general, the groundwater in Ireland is dominated by Ca-HCO_3 water type with a significant number of Ca-Mg-HCO_3 types. The groundwater derived from the pure limestones and sand and gravel of limestone gravel provenance have well-defined and similar groundwater chemistry and are dominated by Ca-HCO_3 water

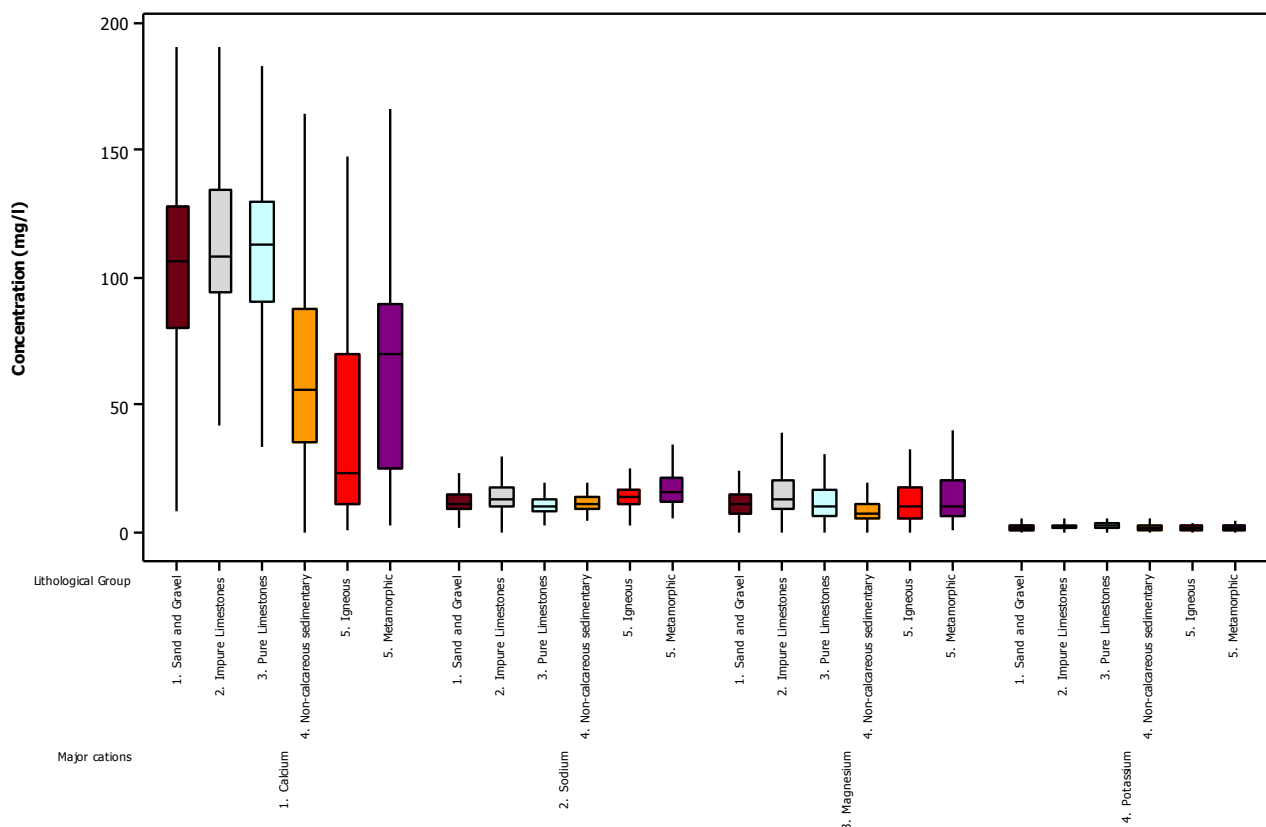


Figure 3.1. Box and whisker plot summarising the major ion groundwater chemistry.

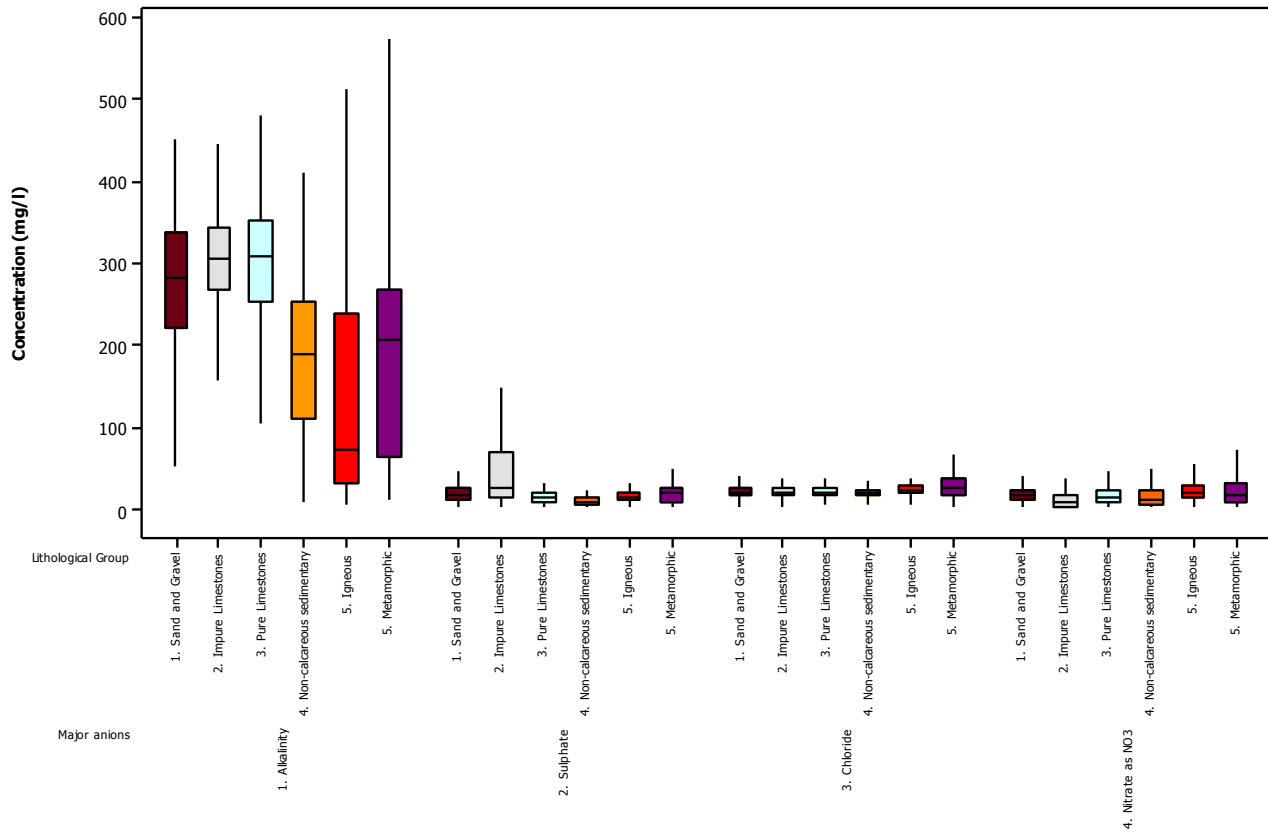


Figure 3.2. Box and whisker plot summarising the major anion groundwater chemistry.

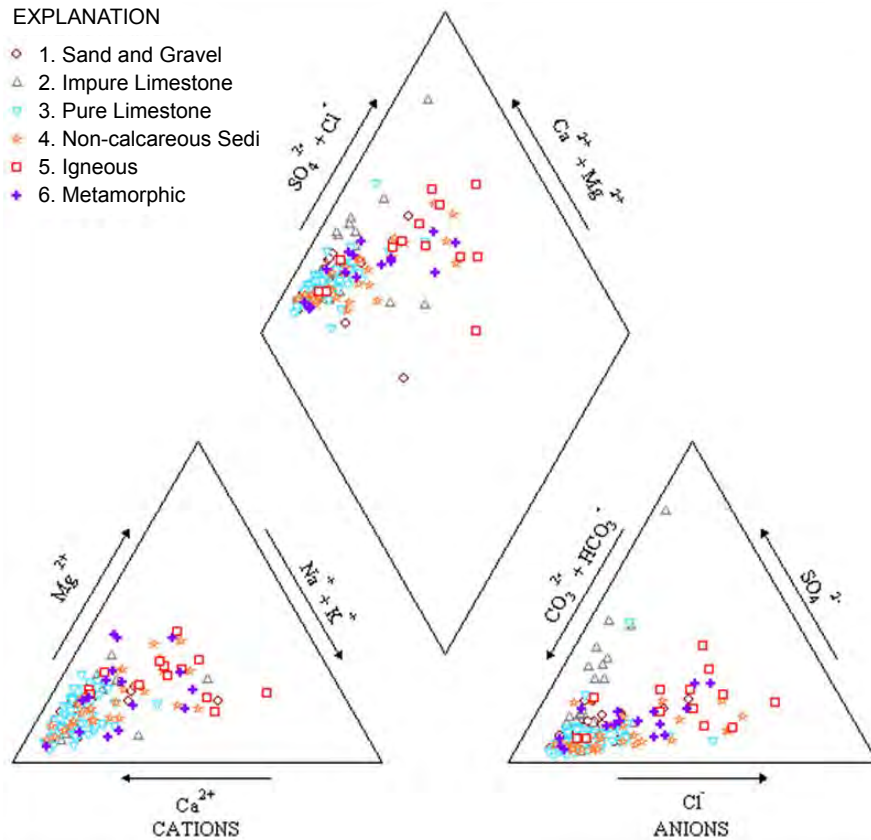


Figure 3.3. Piper plot summarising the major ion groundwater chemistry for each monitoring point grouped into lithological groups.

types. Sand and gravel aquifers with provenances other than limestone gravels have a more variable composition, varying from Ca-HCO_3 to Mg-Na/K-HCO_3 . The impure limestones have a similar chemistry to the pure limestones except that they show a slightly wider range with slightly higher SO_4 and Mg ranges. Groundwaters from the non-calcareous sedimentary, igneous and metamorphic aquifers tend to have a more variable composition than the limestones with groundwater types varying from Ca-HCO_3 to Mg-Na/K-HCO_3 .

3.2 Natural Background Level Results

The descriptions that follow are based on the pre-selected datasets as outlined in section 2.6. The descriptions make reference to Figures A1 to A120 (i.e. the maps, box and whisker plots and cumulative frequency plots) and Tables A1 to A40 in Appendix A. The individual box and whisker plots for the parameters that are not potentially impacted by anthropogenic activities are presented in Appendix B. It should be noted that, for the nutrients and for parameters that are potentially impacted by anthropogenic activities, the sand and gravel, igneous and metamorphic lithological groups are represented by only one or two monitoring points and therefore upper limits for the natural background levels are not set for these groups.

Table 3.1 presents summary statistics for each parameter for all lithologies. Table 3.2 presents summary statistics for each parameter for each lithological group. The upper limit of the natural background level is denoted as the 95th percentile; the lower limit (where applicable) of the natural background level is denoted as the 5th percentile. Table 4.1 in Chapter 4 details the upper (or lower where appropriate) limit of the natural background level established for each parameter.

3.3 Limits of Detection and Quantification

For a number of parameters, the limit of detection or quantification may affect the natural background level established. This is of particular relevance to trace elements where the concentrations measured are close to or below the limit of detection. An added

complication is the fact that there are often a number of different limits of detection or quantification for the same parameter depending on the date of sampling, analytical method and laboratory used. Table 3.3 outlines the different limits of detection or quantification used for each parameter and the percentage of samples which are below any limit of detection.

3.4 Physico-chemical Parameters

3.4.1 pH

pH represents the negative base-10 log of the hydrogen ion activity in moles per litre. The pH of pure water at 25°C is 7.00. The median pH of European reference aquifers varies from 6.5 to 7.5 in most aquifer types regardless of whether they are carbonate or siliclastic (Shand and Edmunds, 2008). This highlights the fact that only small amounts (approximately 2–3%) of carbonate minerals (calcite, dolomite) in an aquifer are sufficient to buffer the pH to nearly neutral values (Shand and Edmunds, 2008). Most groundwater in the USA has pH values ranging from about 6.0 to 8.5, but water with a lower pH is not uncommon in thermal springs (Hem, 1985).

Groundwater in the non-calcareous sedimentary and igneous lithological groups has the lowest pH values with medians of 6.03 and 6.07, respectively (see Table A1). Monitoring points 11_013 (Swan; confined Westphalian sandstones) and 03_005 (Whitegate; Devonian Old Red Sandstone) have high pH values relative to the other non-calcareous sedimentary monitoring points with medians of 7.3 and 6.7, respectively (see Figure A2). This is likely to be due to their calcareous nature as discussed further in section 3.5.6. Groundwater in the other lithological groups is nearly neutral, with medians between 7.1 and 7.3 (see Figure A2).

One-way ANOVA tests indicated that there were significant differences between the pH of the lithological groups. The lower and upper limits of the natural background levels, calculated from the unconfined monitoring points, for the pure limestone and non-calcareous sedimentary lithological groups are shown in Table 3.4.1. The 5th and 95th percentiles for the other lithological groups are included for information only. They have been calculated using data from two or fewer monitoring points and, therefore, are not defined as limits to natural background levels.

Table 3.1. Summary statistics calculated nationally for all parameters using unconfined monitoring points. The 95th percentile for confined monitoring points are also included. Relevant standards and values are included

Parameter	Unit	All lithologies							
		Unconfined							Confined
		Number of MPs	Number of data points	Minimum	5th percentile	Median	95th percentile	Maximum	95th percentile
Alkalinity	mg/l CaCO ₃	21	513	5.00	20.00	220	319	544	387.20
Aluminium	µg/l Al	217	4682	0.70	1.00	2.50	24.0	688	14.50
Ammonium	mg/l N	12	326	0.0015	0.0040	0.01	0.09	0.56	0.39
Antimony	µg/l Sb	217	4857	0.05	0.05	0.25	0.50	18.3	0.50
Arsenic	µg/l As	217	4853	0.05	0.10	0.25	2.00	92.1	0.50
Barium	µg/l Ba	217	4861	0.25	2.70	29.3	224	2099	78.60
Beryllium	µg/l Be	217	4862	0.05	0.25	0.50	0.50	1.20	0.50
Boron	µg/l B	21	416	1.50	1.50	10.0	15.0	66.0	572.50
Cadmium	µg/l Cd	21	416	0.03	0.05	0.05	0.20	1.10	0.20
Calcium	mg/l Ca	21	416	0.50	5.78	70.8	113	138	109.10
Chloride	mg/l Cl	21	520	1.30	8.00	14.3	21.0	33.9	15.40
Chromium	µg/l Cr	217	36	0.25	0.25	0.25	0.53	0.60	0.25
Cobalt	µg/l Co	217	4862	0.05	0.25	0.50	0.80	10.00	0.87
Conductivity	µS/cm	21	439	9.00	68.17	408	560	697	1074.00
Copper	µg/l Cu	21	416	0.25	0.25	1.50	16.00	231.00	8.70
Dissolved oxygen	mg/l O ₂	21	316	0.21	1.52	7.00	11.3	20.9	9.31
Fluoride	mg/l F	21	502	0.04	0.05	0.08	0.20	1.10	2.61
Iron	µg/l Fe	21	416	1.00	2.00	11.0	268	928	762.20
Lead	µg/l Pb	217	4861	0.10	0.15	0.25	2.81	84.10	2.56
Magnesium	mg/l Mg	21	416	0.15	1.43	5.40	16.5	28.3	42.46
Manganese	µg/l Mn	21	416	0.50	0.50	2.00	23.3	318	176.10
Mercury	µg/l Hg	217	4846	0.006	0.010	0.025	0.025	6.98	0.03
Molybdate reactive phosphorus	µg/l P	18	182	0.008	0.008	0.008	0.017	0.036	0.01
Molybdenum	µg/l Mo	21	416	0.25	0.25	0.50	0.63	4.90	1.02
Nickel	µg/l Ni	21	416	0.15	0.25	0.50	2.15	12.4	4.65
Nitrate	mg/l NO ₃	12	328	0.11	0.27	3.47	8.73	15.3	1.48
Nitrite	mg/l NO ₂	12	319	0.0005	0.0010	0.0025	0.03	0.15	0.03
pH	pH units	21	419	5.00	5.80	7.20	7.86	8.75	7.94
Potassium	mg/l K	21	416	0.10	0.23	1.12	2.10	4.39	5.86
Radon	Bq/l	214	579	0.25	1.31	17.95	122	355	10.075
Silica	mg/l SiO ₂	217	2970	0.02	3.20	6.91	14.0	42.6	18.60
Sodium	mg/l Na	21	416	0.25	5.60	9.00	13.1	21.4	105.44
Strontium	µg/l Sr	217	4856	0.25	44.5	187	763	25440	7026.20
Sulphate	mg/l SO ₄	21	513	0.50	0.50	5.80	13.16	216.00	223.00
Total hardness	mg/l CaCO ₃	21	510	1.50	27.98	219	310	391	434.07
Total organic carbon	mg/l C	21	446	0.06	0.44	1.80	26.3	588	69.55
Total phosphorus	µg/l P	18	176	0.0035	0.0035	0.0035	0.02	0.05	0.01
Turbidity	NTU	21	498	0.02	0.05	0.50	5.12	32.0	10.54
Uranium	µg/l U	217	4861	0.05	0.10	0.50	3.00	17.0	1.97
Zinc	µg/l Zn	21	192	0.25	1.60	6.90	40.0	98.6	53.86

Table 3.1. Continued

Parameter	Unit	Drinking water standards (Government of Ireland, 2004)	Overall threshold values (Government of Ireland, 2010)	Environmental quality standard (Government of Ireland, 2009)	Interim guideline values (EPA, 2003)	WHO guideline values (WHO, 2014)	Other
Alkalinity	mg/l CaCO ₃						
Aluminium	µg/l Al	200	150		200		
Ammonium	mg/l N	0.3	0.065–0.175	0.04–0.065	0.15		
Antimony	µg/l Sb	5				20	
Arsenic	µg/l As	10	7.5	25	10	10	
Barium	µg/l Ba					700	
Beryllium	µg/l Be						
Boron	µg/l B	1000	750		1000	2400	
Cadmium	µg/l Cd	5	3.75	0.08–0.25	5	3	
Calcium	mg/l Ca				200		
Chloride	mg/l Cl	250	24–187.5		30		
Chromium	µg/l Cr	50	37.5	3.4–4.7	30	50	
Cobalt	µg/l Co						
Conductivity	µS/cm	2500	800–1875				
Copper	µg/l Cu	2000	1500	5–30	30	2000	
Dissolved oxygen	mg/l O ₂						
Fluoride	mg/l F	0.8–1.5		0.5		1.5	
Iron	µg/l Fe	200			200		
Lead	µg/l Pb	10	18.75	7.2		10	
Magnesium	mg/l Mg				50		
Manganese	µg/l Mn	50			50		
Mercury	µg/l Hg	1	0.75	0.05	1	6	
Molybdate reactive phosphorus	µg/l P		35	25–35	30		30 ^a
Molybdenum	µg/l Mo						
Nickel	µg/l Ni	20	15	20	20	70	
Nitrate	mg/l NO ₃	50	37.5		50	50	11.5 ^b
Nitrite	mg/l NO ₂	0.5	0.375		0.2	3	
pH	pH units	6.5–9.5					
Potassium	mg/l K				5		
Radon	Bq/l						
Silica	mg/l SiO ₂						
Sodium	mg/l Na	200	150		150	50	
Strontium	µg/l Sr						
Sulphate	mg/l SO ₄	250	187.5		200		
Total hardness	mg/l CaCO ₃				200		
Total organic carbon	mg/l C						
Total phosphorus	µg/l P						20 ^c , 35 ^d
Turbidity	NTU						
Uranium	µg/l U					30	
Zinc	µg/l Zn			5–100	100		

^aMcGarrigle (1998).

^bChamp (1998).

^cOECD (1982).

^dEnvironmental quality standard for estuaries.

Table 3.2. Summary statistics for each parameter presented for each lithological group

Parameter	Unit	1. Sand and gravel					2. Impure limestones					3. Pure limestones				
		Number of MPs	Number of data points	5th percentile	Median	95th percentile	Number of MPs	Number of data points	5th percentile	Median	95th percentile	Number of MPs	Number of data points	5th percentile	Median	95th percentile
Alkalinity	mg/l CaCO ₃	1	25	227	266	350	2	65	144	246	290	10	278	95.7	216	322
Aluminium	µg/l Al	30	632	1.00	2.50	15.2	29	583	1.00	2.50	18.9	96	2145	1.00	2.50	26.0
Ammonium	mg/l N	0	0	–	–	–	2	66	0.004	0.01	0.05	4	163	0.004	0.02	0.09
Antimony	µg/l Sb	30	658	0.05	0.25	0.50	29	605	0.05	0.25	0.50	96	2227	0.05	0.25	0.50
Arsenic	µg/l As	30	659	0.10	0.25	1.00	29	605	0.10	0.30	3.00	96	2225	0.10	0.25	1.00
Barium	µg/l Ba	30	659	6.68	54.8	585.7	29	605	6.84	45.7	195	96	2230	3.00	21.2	179
Beryllium	µg/l Be	30	659	0.25	0.50	0.50	29	605	0.25	0.50	0.50	96	2230	0.25	0.50	0.50
Boron	µg/l B	1	25	1.50	10.0	11.8	2	44	1.50	5.00	10.9	10	216	1.50	10.0	16.0
Cadmium	µg/l Cd	1	25	0.05	0.05	0.20	2	44	0.05	0.05	0.20	10	216	0.05	0.05	0.20
Calcium	mg/l Ca	1	25	89.9	99.1	111	2	44	50.9	88.1	113	10	216	30.3	70.8	117
Chloride	mg/l Cl	1	25	13.0	15.0	17.0	2	66	10.3	14.7	19.0	10	283	8.42	14.0	22.4
Chromium	µg/l Cr	30	6	0.25	0.25	0.51	29	2	0.25	0.25	0.25	96	19	0.25	0.25	0.51
Cobalt	µg/l Co	30	659	0.25	0.50	0.50	29	605	0.25	0.50	1.24	96	2230	0.25	0.50	0.50
Conductivity	µS/cm	1	23	397	515	583	2	54	302	472	554	10	236	179	417	601
Copper	µg/l Cu	1	25	0.25	0.80	8.53	2	44	0.25	0.75	18.1	10	216	0.25	1.45	8.25
Dissolved oxygen	mg/l O ₂	1	19	3.82	6.00	7.19	2	33	5.40	7.63	11.3	10	166	1.07	6.22	10.5
Fluoride	mg/l F	1	25	0.05	0.08	0.20	2	65	0.05	0.08	0.20	10	275	0.05	0.08	0.20
Iron	µg/l Fe	1	25	1.20	5.00	37.6	2	44	1.23	9.50	62.7	10	216	2.50	28.0	347
Lead	µg/l Pb	30	659	0.15	0.25	2.41	29	605	0.15	0.25	2.08	96	2230	0.15	0.25	2.92
Magnesium	mg/l Mg	1	25	6.49	7.00	7.83	2	44	3.86	5.17	11.3	10	216	1.76	4.89	17.6
Manganese	µg/l Mn	1	25	0.50	1.30	4.60	2	44	0.50	0.50	12.9	10	216	0.50	2.00	33.1
Mercury	µg/l Hg	30	656	0.01	0.03	0.03	29	603	0.01	0.03	0.03	96	2227	0.01	0.03	0.03
Molybdate reactive phosphorus	µg/l P	4	43	7.50	7.50	7.50	3	31	7.50	7.50	7.50	8	86	7.50	7.50	20.0
Molybdenum	µg/l Mo	1	25	0.25	0.50	0.50	2	44	0.25	0.38	0.50	10	216	0.25	0.50	1.08
Nickel	µg/l Ni	1	25	0.25	0.25	2.00	2	44	0.25	0.38	2.00	10	216	0.25	0.60	2.53
Nitrate	mg/l NO ₃	0	0	–	–	–	2	66	1.58	5.10	7.78	4	165	0.26	3.50	10.2
Nitrite	mg/l NO ₂	0	0	–	–	–	2	63	0.001	0.003	0.03	4	159	0.001	0.003	0.03
pH	pH units	1	22	6.84	7.18	7.48	2	50	6.79	7.30	8.25	10	223	6.71	7.30	7.90
Potassium	mg/l K	1	25	0.75	0.89	1.10	2	44	0.41	0.95	1.80	10	216	0.30	1.28	2.22
Radon	Bq/l	31	87	0.80	10.8	33.5	25	69	1.32	11.5	28.2	94	253	0.90	15.4	35.1

Table 3.2. Continued

Parameter	Unit	1. Sand and gravel				2. Impure limestones				3. Pure limestones			
		Number of MPs	Number of data points	5th percentile	Median	95th percentile	Number of MPs	Number of data points	5th percentile	Median	95th percentile	Number of MPs	Number of data points
Silica	mg/l SiO ₂	30	399	4.70	7.23	12.9	29	372	4.10	8.42	17.2	96	1367
Sodium	mg/l Na	1	25	8.36	9.00	10.2	2	44	6.82	8.50	10.6	10	216
Strontium	µg/l Sr	30	659	83.9	203	651	29	605	84.5	487	2900	96	2227
Sulphate	mg/l SO ₄	1	25	4.44	8.20	11.4	2	65	1.36	7.40	10.8	10	280
Total hardness	mg/l CaCO ₃	1	25	175.40	283	310	2	65	144	250	29	10	279
Total organic carbon	mg/l C	1	25	0.74	1.00	3.40	2	46	0.75	2.05	46.1	10	234
Total phosphorus	µg/l P	4	42	3.50	3.50	12.0	3	31	3.50	3.50	13.0	8	82
Turbidity	NTU	1	24	0.05	0.25	1.72	2	62	0.06	0.50	3.09	10	267
Uranium	µg/l U	30	659	0.20	0.50	5.00	29	604	0.30	0.50	3.10	96	2230
Zinc	µg/l Zn	1	11	1.30	7.00	16.1	2	22	1.64	6.70	30.0	10	99
Parameter	Unit	4. Non-calcareous sedimentary				5. Igneous				6. Metamorphic			
		Number of MPs	Number of data points	5th percentile	Median	95th percentile	Number of MPs	Number of data points	5th percentile	Median	95th percentile	Number of MPs	Number of data points
Alkalinity	mg/l CaCO ₃	3	73	16.8	60.00	216	1	24	6.00	14.5	43.4	2	48
Aluminium	µg/l Al	31	688	1.00	2.50	16.0	13	288	1.00	2.50	131	16	346
Ammonium	mg/l N	3	73	0.002	0.01	0.05	1	24	0.004	0.01	0.10	0	0
Antimony	µg/l Sb	31	711	0.05	0.25	0.50	13	296	0.05	0.25	0.50	16	360
Arsenic	µg/l As	31	707	0.10	0.30	2.00	13	297	0.10	0.50	52.1	16	360
Barium	µg/l Ba	31	711	4.80	45.2	427	13	297	0.86	7.00	179	16	359
Beryllium	µg/l Be	31	711	0.25	0.50	0.50	13	297	0.25	0.50	0.50	16	360
Boron	µg/l B	3	59	4.65	8.50	11.0	1	24	1.50	5.00	21.9	2	48
Cadmium	µg/l Cd	3	59	0.05	0.05	0.50	1	24	0.05	0.05	0.20	2	48
Calcium	mg/l Ca	3	59	6.17	15.6	63.6	1	24	1.71	3.33	8.17	2	48
Chloride	mg/l Cl	3	74	12.7	17.0	20.1	1	24	1.30	8.00	10.9	2	48
Chromium	µg/l Cr	31	3	0.25	0.25	0.25	13	3	0.25	0.25	0.25	16	3
Cobalt	µg/l Co	31	711	0.25	0.50	0.60	13	297	0.25	0.50	0.50	16	360
Conductivity	µS/cm	3	59	98.8	184	392	1	22	19.7	49.5	60.5	2	45
Copper	µg/l Cu	3	59	0.25	2.00	44.2	1	24	0.25	0.90	2.93	2	48
Dissolved oxygen	mg/l O ₂	3	44	1.04	5.52	9.40	1	17	8.68	10.7	13.2	2	37
Fluoride	mg/l F	3	66	0.05	0.05	0.08	1	23	0.05	0.05	0.08	2	48
Iron	µg/l Fe	3	59	2.50	5.00	16.1	1	24	1.23	24.4	71.2	2	48

Table 3.2. Continued

Parameter	Unit	4. Non-calcareous sedimentary					5. Igneous					6. Metamorphic				
		Number of MPs	Number of data points	5th percentile	Median	95th percentile	Number of MPs	Number of data points	5th percentile	Median	95th percentile	Number of MPs	Number of data points	5th percentile	Median	95th percentile
Lead	µg/l Pb	31	710	0.15	0.25	3.00	13	297	0.15	0.40	3.00	16	360	0.15	0.25	2.20
Magnesium	mg/l Mg	3	59	1.90	6.14	11.3	1	24	0.28	0.89	1.68	2	48	2.65	5.70	13.7
Manganese	µg/l Mn	3	59	0.50	3.00	13.5	1	24	3.00	5.00	9.90	2	48	0.50	0.50	8.76
Mercury	µg/l Hg	31	712	0.01	0.03	0.03	13	297	0.01	0.03	0.03	16	351	0.01	0.03	0.03
Molybdate reactive phosphorus	µg/l P	1	11	7.50	7.50	7.50	0	0	–	–	–	1	11	7.50	7.50	7.50
Molybdenum	µg/l Mo	3	59	0.25	0.50	0.50	1	24	0.25	0.50	0.50	2	48	0.25	0.50	0.50
Nickel	µg/l Ni	3	59	0.25	0.70	2.31	1	24	0.25	0.25	0.67	2	48	0.25	0.38	2.08
Nitrate	mg/l NO ₃	3	73	1.33	3.39	8.00	1	24	0.18	0.62	1.23	0	0	–	–	–
Nitrite	mg/l NO ₂	3	73	0.001	0.001	0.03	1	24	0.001	0.02	0.03	0	0	–	–	–
pH	pH units	3	57	5.35	6.03	7.13	1	23	5.35	6.07	7.53	2	44	6.68	7.10	7.73
Potassium	mg/l K	3	59	0.48	1.09	2.12	1	24	0.10	0.20	0.45	2	48	1.03	1.50	1.80
Radon	Bq/l	38	95	3.65	45.0	141	12	36	21.4	85.9	268	14	39	8.13	43.4	164
Silica	mg/l SiO ₂	31	442	4.60	7.91	13.7	13	179	3.87	9.40	19.3	16	211	3.81	9.29	16.0
Sodium	mg/l Na	3	59	8.25	10.0	12.5	1	24	2.79	5.60	6.95	2	48	7.61	9.60	12.2
Strontium	µg/l Sr	31	708	29.1	101	320	13	297	8.95	56.0	498	16	360	50.2	164	772
Sulphate	mg/l SO ₄	3	71	0.50	4.40	5.90	1	24	0.50	3.00	4.17	2	48	0.72	5.15	7.38
Total hardness	mg/l CaCO ₃	3	70	25.1	70.5	212	1	24	5.84	13.8	42.1	2	47	222	250	303
Total organic carbon	mg/l C	3	69	0.13	0.75	3.60	1	24	0.79	1.78	9.97	2	48	0.71	1.00	16.0
Total phosphorus	µg/l P	0	11	5.75	10.0	16.0	0	0	–	–	–	1	10	3.50	3.50	25.2
Turbidity	NTU	3	74	0.05	0.25	1.73	1	24	0.05	0.25	1.88	2	47	0.05	0.25	4.75
Uranium	µg/l U	31	711	0.05	0.50	3.75	13	297	0.05	0.50	1.00	16	360	0.05	0.50	2.60
Zinc	µg/l Zn	3	28	2.71	11.4	66.9	1	11	2.00	5.40	16.8	2	21	1.90	5.00	37.2

Table 3.3. Limits of detection for each parameter and the percentage of samples that are recorded as less than the limits of detection

Parameter	Unit	Limits of detection	Percentage below limit of detection
Alkalinity	mg/l CaCO ₃	12, 25	1.3
Aluminium	µg/l Al	11, 2, 5	80.2
Ammonium	mg/l N	0.003, 0.007, 0.008, 0.009, 0.01, 0.026, 0.03, 0.1, 0.2	40.5
Antimony	µg/l Sb	0.1, 0.12, 0.2, 0.5, 1	79.0
Arsenic	µg/l As	0.1, 0.2, 0.37, 0.5, 1, 5	66.8
Barium	µg/l Ba	0.5, 1, 4	1.6
Beryllium	µg/l Be	0.1, 0.12, 0.5, 1	99.6
Boron	µg/l B	10, 17, 20, 3	66.5
Cadmium	µg/l Cd	0.06, 0.1, 0.4, 1	95.7
Calcium	mg/l Ca	1	0.3
Chloride	mg/l Cl	2.6	0.6
Chromium	µg/l Cr	0.1, 0.5, 0.7, 1	69.7
Cobalt	µg/l Co	0.1, 0.5, 0.8, 1	93.6
Conductivity	µS/cm	–	–
Copper	µg/l Cu	0.5, 1, 10, 2.7, 3	49.3
Dissolved oxygen	mg/l O ₂	10	1.4
Fluoride	mg/l F	0.1, 0.15, 0.3	63.7
Iron	µg/l Fe	10, 2, 5, 7	39.1
Lead	µg/l Pb	0.2, 0.3, 0.5, 1, 1.5	72.9
Magnesium	mg/l Mg	0.3	0.2
Manganese	µg/l Mn	1, 1.5	34.0
Mercury	µg/l Hg	0.012, 0.02, 0.05	94.5
Molybdate reactive phosphorus	µg/l P	3, 5, 6, 8, 9, 10, 15, 20, 40	57.5
Molybdenum	µg/l Mo	0.5, 1	93.9
Nickel	µg/l Ni	0.3, 0.5, 0.9, 1	49.7
Nitrate	mg/l NO ₃	0.04, 0.1, 0.21, 0.22, 0.27, 0.3, 0.36, 0.44, 0.443, 0.53	21.7
Nitrite	mg/l NO ₂	0.001, 0.002, 0.003, 0.004, 0.005, 0.03, 0.043, 0.05	79.8
pH	pH units	–	–
Potassium	mg/l K	0.2, 0.25	2.9
Radon	Bq/l	0.5, 0.6	2.9
Silica	mg/l SiO ₂	0.04, 1	0.2
Sodium	mg/l Na	0.5	0.2
Strontium	µg/l Sr	0.5, 1	0.1
Sulphate	mg/l SO ₄	1, 10, 3	7.3
Total hardness	mg/l CaCO ₃	3	0.2
Total organic carbon	mg/l C	0.12, 0.25, 0.5, 1.5, 2, 2.5	26.4
Total phosphorus	µg/l P	7, 10	55.8
Turbidity	NTU	0.01, 0.1, 0.11, 0.2, 0.4, 0.5, 1	30.8
Uranium	µg/l U	0.1, 1, 2	41.2
Zinc	µg/l Zn	0.5, 1	14.3

NTU, Nephelometric Turbidity Unit.

Table 3.4.1. The upper and lower limits of the natural background level for pH for pure limestone and non-calcareous sedimentary lithological groups. The 5th and 95th percentiles for other lithological groups are included for information

pH (pH units)	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non-calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	1	2	10	3	1	2
Number of data points	22	50	223	57	23	44
5th percentile	6.8	6.8	6.7	5.4	5.4	6.7
95th percentile	7.5	8.3	7.9	7.1	7.5	7.7

3.4.2 Electrical conductivity

Electrical conductivity is the ability of an aqueous solution to conduct an electrical current. The presence of charged ionic species in a solution makes the solution conductive and as such electrical conductivity is a proxy measure of the total dissolved ions (Hem, 1985).

The confined groundwater at Tydavnet (18_010; Dinantian mixed sandstones, shales and limestones) has the highest electrical conductivity of all samples examined, with a median of 914 $\mu\text{S}/\text{cm}$; this is likely to reflect the longer residence time, as indicated by the apparent softening as a result of ion exchange along the groundwater flow path (Misstear *et al.*, 2008). Groundwater in the pure limestone aquifers has a relatively low electrical conductivity with a median of 417 $\mu\text{S}/\text{cm}$ for this lithological group. This may reflect the short residence time of groundwater passing through the karstified aquifers. Groundwater in the igneous and non-calcareous sedimentary lithological groups (with the exception of monitoring

points 11_013 Swan and 03_005 Whitegate) has the lowest electrical conductivity; with medians between 50 and 184 $\mu\text{S}/\text{cm}$ (see Figure A5). Monitoring points 11_013 (Swan; confined Westphalian sandstones) and 03_005 (Whitegate; Devonian Old Red Sandstone) have higher electrical conductivities than the other non-calcareous sedimentary monitoring points with medians of 509 and 378 $\mu\text{S}/\text{cm}$, respectively (Figure A5). This is likely to be due to their calcareous nature as discussed further in section 3.5.6. The metamorphic lithological group has a relatively high electrical conductivity with a median of 479 $\mu\text{S}/\text{cm}$. Again, this is likely to reflect their calcareous nature (section 3.5.6).

One-way ANOVA tests indicated that there were significant differences between the electrical conductivity of the lithological groups. The upper limits of the natural background levels, calculated from the unconfined monitoring points, for the pure limestone and non-calcareous sedimentary lithological groups are shown in Table 3.4.2. The 95th percentiles for the other lithological groups are included for information only. They have been calculated using data from

Table 3.4.2. The upper limits of the natural background level for electrical conductivity for pure limestone and non-calcareous sedimentary lithological groups

Electrical conductivity ($\mu\text{S}/\text{cm}$)	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non-calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	1	2	10	3	1	2
Number of data points	23	54	236	59	22	45
95th percentile	<i>583</i>	<i>554</i>	601	392	60	<i>546</i>

The 95th percentiles for the other lithological groups are included for information only. They have been calculated using data from two or fewer monitoring points and are therefore not defined as limits to natural background levels (shown in blue italics).

two or fewer monitoring points and are therefore not defined as limits to natural background levels.

3.4.3 Turbidity

Turbidity is an expression of the optical property that causes light to be scattered and absorbed by particles and molecules rather than transmitted in straight lines through a water sample. It is caused by suspended matter or impurities that interfere with the clarity of the water (US EPA, 1999). These impurities may include clay, silt, finely divided inorganic and organic matter, soluble coloured organic compounds, and plankton and other microscopic organisms (Wilde and Radtke, 2005).

In general, turbidity values are low. Overall, 42% of turbidity samples show levels below the limit of detection. The most frequent limit of detection is 0.5 NTU (Nephelometric Turbidity Unit) (Table 3.3). Median values for the sand and gravel, non-calcareous sedimentary, igneous and metamorphic lithological groups are all 0.25 (i.e. <0.5 NTU). The pure and impure limestones groups both have median values of 0.9 NTU. The impure limestones have a larger range in turbidity than the other groups, driven in part by the high values and large range at Tydavnet (18_010), which has a median value of 3.75 NTU (see Figure A8).

One-way ANOVA tests indicated that turbidity levels in the pure and impure limestone lithological groups were significantly different from the levels in other lithological groups. The upper limit of the natural background levels for pure limestones and non-calcareous sedimentary lithological groups were 5.8 and 1.7 NTU, respectively (Table 3.4.3). The 95th percentiles for the

other lithological groups are included for information only. They have been calculated using data from two or fewer monitoring points and, therefore, are not defined as limits to natural background levels.

3.4.4 Dissolved oxygen

The concentration of dissolved oxygen in water is affected by many factors, including ambient temperature, atmospheric pressure and the ion activity of the water body (Wilde and Radtke, 2005). The atmosphere has a PO_2 of 0.21 atm (atmospheric pressure), and, therefore, a dissolved oxygen concentration of 8.6 mg/l at 25°C, increasing to 13 mg/l at 5°C (Appelo and Postma, 2005). Oxygen is supplied to groundwater through recharge and by movement of air through unsaturated material above the water table. This oxygen reacts with oxidisable material encountered along the flow path of the water. Water containing measurable amounts of dissolved oxygen may penetrate long distances into the system if little reactive material is available. The principal reacting species are organic materials and reduced inorganic minerals such as pyrite and siderite. As time passes, the oxidisable material in the aquifer will be removed or altered for long distances from the point of recharge (Hem, 1985). Higher forms of aquatic life require oxygen for survival, and dissolved oxygen is used widely in evaluations of the biochemistry of streams and lakes (Hem, 1985). For example, high dissolved oxygen concentrations are essential for freshwater pearl mussels (*Margaritifera margaritifera*). The contribution of groundwater, which typically has low dissolved oxygen concentration relative to surface water, to the surface water column and hyporheic zone can affect the survival of adult and juvenile mussels

Table 3.4.3. The upper limits of the natural background level for turbidity for pure limestone and non-calcareous sedimentary lithological groups

Turbidity (NTU)						
	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non-calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	1	2	10	3	1	2
Number of data points	24	62	267	74	24	47
95th percentile	<i>1.7</i>	<i>3.1</i>	5.8	1.7	<i>1.9</i>	<i>4.7</i>

The 95th percentiles for the other lithological groups are included for information only. They have been calculated using data from two or fewer monitoring points and therefore are not defined as limits to natural background levels (shown in blue italics).

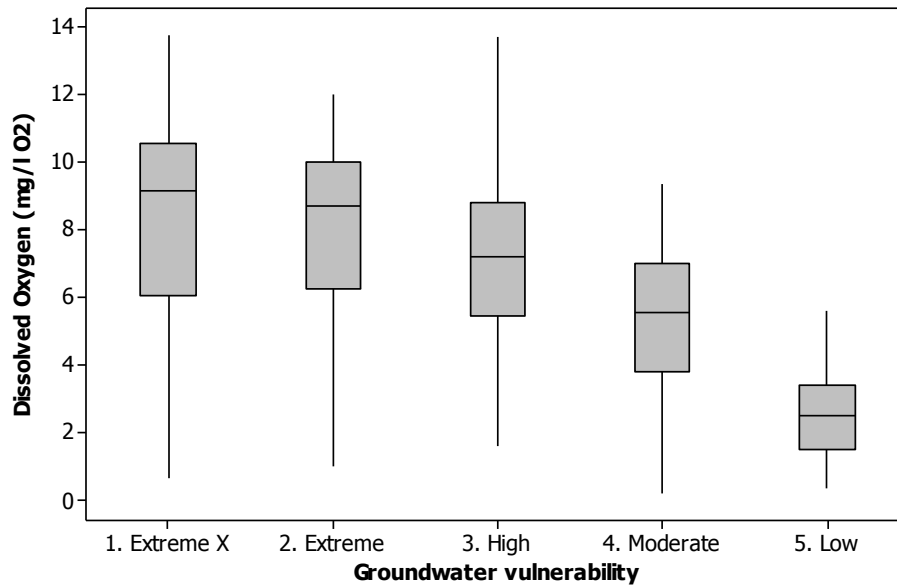


Figure 3.4. The relationship between dissolved oxygen concentration in groundwater and groundwater vulnerability.

(Skinner *et al.*, 2003; Soulsby *et al.*, 2009; Degerman *et al.*, 2013).

Figure 3.4 shows that dissolved oxygen content of groundwater in the monitoring points studied seems to be controlled, to some extent, by the groundwater vulnerability. Monitoring points defined as having “extreme X” [bedrock is at or near the surface, within 30 m of a location of point recharge (DELG, EPA and GSI, 1999)], “extreme” [subsoil is less than 3 m thick (DELG, EPA and GSI, 1999)] or “high” groundwater vulnerability have the highest dissolved oxygen concentrations with median concentrations of 9.1, 8.7 and 7.2 mg/l O₂, respectively. Exceptions include monitoring point 11_013 (Swan; Westphalian sandstones) which is confined by overlying shales in the Coolbaun Formation (Wright, 2000a). Monitoring points with moderate groundwater vulnerability have

moderate dissolved oxygen concentrations with a median concentration of 5.5 mg/l O₂. Monitoring points with low groundwater vulnerability have the lowest dissolved oxygen concentrations with a median of 2.5 mg/l O₂.

One-way ANOVA tests indicated that there were significant differences between the dissolved oxygen concentrations of monitoring points with (1) extreme and high, (2) moderate and (3) low groundwater vulnerabilities. The upper and lower limits of the natural background levels for the different groundwater vulnerability groups are shown in Table 3.4.4. The 5th and 95th percentiles for the low groundwater vulnerability category are included for information only. They have been calculated using data from two monitoring points and therefore do not define the limits to natural background levels.

Table 3.4.4. The lower and upper limits of natural background levels for dissolved oxygen for each groundwater vulnerability category

Dissolved oxygen (mg/l O ₂)					
Groundwater vulnerability	Extreme X	Extreme	High	Moderate	Low
Number of MPs	4	4	5	6	2
Number of data points	62	54	89	110	34
5th percentile	4.4	0.8	3.9	0.7	<i>0.5</i>
95th percentile	12.0	11.3	12.3	8.1	<i>5.9</i>

The 5th and 95th percentiles for the low groundwater vulnerability category are included for information only. The 95th percentiles shown in blue italics have been calculated using data from two or fewer monitoring points and are therefore not defined as limits to natural background levels.

3.5 Major Ions

3.5.1 Calcium

Calcium is an abundant element in the Earth's crust and a major component of many rock-forming minerals. In limestones it occurs most commonly in the minerals calcite and dolomite; in non-calcareous sedimentary rocks it occurs in plagioclase feldspars; and in evaporites it occurs in gypsum and anhydrite (Deer *et al.*, 1996). It also occurs in igneous and metamorphic rocks chiefly in the silicate minerals of plagioclase feldspars, amphiboles, pyroxenes and garnets (Deer *et al.*, 1996). Ca^{2+} is an abundant dissolved ion in sea water but levels in rainfall inputs are typically negligible for most groundwater. For example, the national rainfall-weighted mean annual concentration of calcium in bulk precipitation samples collected in Irish monitoring stations between 1992 and 1994 is 1.0 mg/l (Jordan, 1995).

The upper limiting factor in most freshwater systems is saturation with respect to calcite (Hem, 1985), which will limit the maximum concentration; the flattening off in many of the distributions at around 70–120 mg/l is due to this (Shand and Edmunds, 2008). Aquifer freshening (ion-exchange mainly with sodium) decreases calcium in solution and mixing with saline water may lead to an increase in concentrations (Shand and Edmunds, 2008).

Calcium concentrations vary across the lithologies by up to two orders of magnitude. The cumulative probability diagram shows that the upper limit is likely to be controlled by mineral solubility (Figure A15). In contrast, European aquifers show a range in calcium concentrations over four orders of magnitude (Shand and Edmunds, 2008). Groundwater from the pure

and impure limestone aquifers show similar calcium concentrations with interquartile ranges from 40 to 90 mg/l and 70 to 100 g/l, respectively. Groundwater from the non-calcareous sedimentary aquifers shows lower calcium concentrations than the limestones, with an interquartile range from 15 to 50 mg/l. The spatial distribution of calcium reflects the lithological differences.

One-way ANOVA tests indicated that calcium concentrations in the non-calcareous sedimentary, pure limestone and impure limestone aquifers were significantly different from each other. The upper limit of the natural background levels for the pure limestone and non-calcareous sedimentary lithological groups was 117 and 64 mg/l Ca, respectively (Table 3.5.1). The 95th percentiles for the other lithological groups are included for information only. They have been calculated using data from two or fewer monitoring points and therefore are not defined as limits to natural background levels.

3.5.2 Magnesium

Magnesium is the eighth most abundant element in the Earth's crust. In sedimentary rocks it is present in the mineral dolomite and forms a solid solution with other carbonate minerals such as calcite. In igneous and metamorphic rocks it is present in silicate minerals such as olivine, pyroxene, amphiboles and micas (Deer *et al.*, 1996; Shand *et al.*, 2007). It is an abundant cation in seawater (median of 1350 mg/l (Hem, 1985), but rainfall inputs are usually negligible (0.9 mg/l Jordan, 1995).

Magnesium concentrations are highest in the confined monitoring points of Tydavnet and Swan,

Table 3.5.1. The upper limits of the natural background level for calcium for pure limestone and non-calcareous sedimentary lithological groups

Calcium (mg/l Ca)						
	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non-calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	1	2	10	3	1	2
Number of data points	25	44	216	59	24	48
95th percentile	<i>111</i>	<i>113</i>	117	64	<i>8</i>	<i>114</i>

The 95th percentiles for the other lithological groups are included for information only. They have been calculated using data from two or fewer monitoring points and are therefore not defined as limits to natural background levels (shown in blue italics).

with interquartile ranges of 32.5–39.5 mg/l Mg and 23.2–25.5 mg/l Mg, respectively. The high magnesium concentrations at Tydavnet are due to ion exchange along the groundwater flow path (Kelly, 2001). The magnesium ions are probably sourced from dolomites in the Meenymore Formations (Misstear *et al.*, 2008). Magnesium concentrations across the other monitoring points show a relatively narrow range, with medians ranging from 0.9 to 17.2 mg/l. The pure limestone, impure limestone, non-calcareous sedimentary and the metamorphic lithological groups show bimodal distributions (Figure A18).

The upper limit of the natural background levels for magnesium, which is defined nationally for the unconfined monitoring points and calculated using data collected since 2007, is 17 mg/l Mg (Table 3.5.2). It should be noted that the magnesium concentrations from confined aquifers may be higher. For example, the 95th percentile for the confined aquifers (two monitoring points) is 42 mg/l Mg. This has been calculated using data from two monitoring points and, therefore, is not defined as a limit to natural background levels.

3.5.3 Total hardness

Total hardness is the concentration of dissolved calcium and magnesium. It is expressed as an equivalent concentration of calcium carbonate. Carbonate hardness includes that part of the total hardness equivalent to the bicarbonate and carbonate (or alkalinity). If the total hardness exceeds the alkalinity (in mg/l CaCO₃ or other equivalent units), the excess is termed “non-carbonate hardness” and may be suggestive of ion exchange.

The distribution of total hardness across the lithological groups is similar to the distribution of calcium concentration (see Figures A14, A15, A20 and A21), indicating that calcium is the dominant component of the total hardness. The influence of the high magnesium concentrations observed in, for example, the confined monitoring points where ion exchange is likely to be occurring, may also be observed.

One-way ANOVA tests indicated that there were significant differences between the total hardness of the lithological groups. The upper limit of the natural background levels for the pure limestone and

Table 3.5.2. The upper limit of natural background levels for magnesium for unconfined conditions

	Magnesium (mg/l Mg)	
	Unconfined	Confined
Number of MPs	19	2
Number of data points	416	48
95th percentile	17	<i>42</i>

The 95th percentile for confined conditions is included for information only. The 95th percentile shown in blue italics has been calculated using data from two or fewer monitoring points and is therefore not defined as limit to natural background levels.

Table 3.5.3. The upper limits of the natural background level for total hardness for pure limestone and non-calcareous sedimentary lithological groups

	Total hardness (mg/l CaCO ₃)					
	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non-calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	1	2	10	3	1	2
Number of data points	25	65	279	70	24	47
95th percentile	<i>310</i>	<i>294</i>	328	212	<i>42</i>	<i>303</i>

The 95th percentiles for the other lithological groups are included for information only. They have been calculated using data from two or fewer monitoring points and are therefore not defined as limits to natural background levels (shown in blue italics).

non-calcareous sedimentary lithological groups are 328 and 212 mg/l CaCO₃, respectively (Table 3.5.3). The 95th percentiles for the other lithological groups are included for information only. They have been calculated using data from two or fewer monitoring points and, therefore, are not defined as limits to natural background levels.

3.5.4 Sodium

Sodium is the most abundant cation in seawater [median of 10500 mg/l (Hem, 1985)]; the dominant control on sodium in most groundwater is mixing with more saline water. Ion exchange reactions are important controls on sodium, especially during aquifer freshening and seawater intrusion (Shand *et al.*, 2007). The dominant sodium containing mineral phases are clay minerals, alkali and plagioclase feldspars and halite. Rainfall inputs of sodium vary with distance from the coast. For example, the national rainfall-weighted mean annual concentration of sodium in bulk precipitation samples collected in Irish coastal monitoring stations between 1992 and 1994 is 16 mg/l compared to 4 mg/l for inland monitoring stations (Jordan, 1995).

Groundwater from the confined monitoring points of Tydavnet and Swan show the highest sodium concentrations with interquartile ranges of 75–100 mg/l and 22–25 mg/l, respectively (see Figures A23 and A24). The high sodium concentrations at Tydavnet are due to ion exchange along the groundwater flow path (Kelly, 2001). The sodium ions are probably sourced from clay minerals in the Meenymore and Benbulbin Formations (Misstear *et al.*, 2008). Sodium concentrations across the other monitoring points show a relatively narrow range, with medians ranging from 5 to 12 mg/l. There is little variation between lithological groups. While there is little correlation

between sodium concentration and distance from the coast, as might be expected from the variation in rainfall chemistry, there is a similarity between the sodium and chloride concentrations for the unconfined monitoring points (Figure 3.5), perhaps indicating a shared sodium chloride (NaCl) control on the hydrochemistry. In contrast, European aquifers show a range in sodium concentrations over four orders of magnitude (Shand and Edmunds, 2008). A positive skew indicating saline mixing (or pollution) is not observed for any of the lithological groups.

The upper limit of the natural background levels for sodium, which is defined nationally for the unconfined monitoring points and calculated using data collected since 2007, is 13 mg/l Na (Table 3.5.4). It should be noted that the sodium concentrations from confined aquifers may be higher. For example, the 95th percentile for the confined aquifers (2 monitoring points) is 105 mg/l Na. This has been calculated using data from two monitoring points and, therefore, is not defined as a limit to natural background levels.

3.5.5 Potassium

Potassium occurs in silicate minerals such as clays, alkali feldspars and micas; it is also contained in the evaporite sylvite (KCl) (Deer *et al.*, 1996). It is therefore present in minerals that are relatively stable in the weathering environment and concentrations are usually low in groundwater. As well as uptake by vegetation, potassium's mobility is limited by incorporation into clay minerals (Shand and Edmunds, 2008).

Again, the groundwater from the confined monitoring points of Tydavnet and Swan show the highest potassium concentrations with interquartile ranges of 3.8–5.5 mg/l and 3.7–4.0 mg/l, respectively (Figure A26). The high potassium concentrations at Tydavnet

Table 3.5.4. The upper limit of natural background levels for sodium for unconfined conditions

	Sodium (mg/l Na)	
	Unconfined	Confined
Number of MPs	19	2
Number of data points	416	48
95th percentile	13	<i>105</i>

The 95th percentile for confined conditions is included for information only. The 95th percentile shown in blue italics has been calculated using data from two or fewer monitoring points and is therefore not defined as limits to natural background levels.

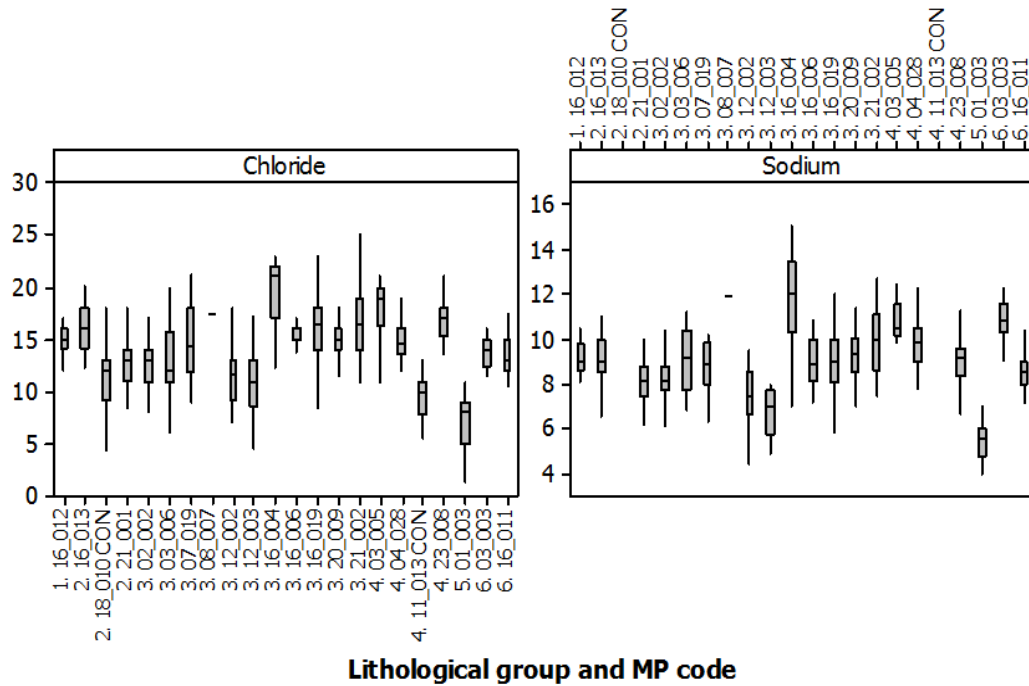


Figure 3.5. Similarity between the distribution of sodium (in mg/l Na) and chloride (in mg/l Cl). MPs 18_010 and 11_013 are confined (CON).

Table 3.5.5. The upper limit of natural background levels for potassium for unconfined conditions

	Potassium (mg/l K)	
	Unconfined	Confined
Number of MPs	19	2
Number of data points	416	48
95th percentile	2.1	5.9

The 95th percentile for confined conditions is included for information only. The 95th percentile shown in blue italics has been calculated using data from two or fewer monitoring points and is therefore not defined as limits to natural background levels.

are due to ion exchange along the groundwater flow path (Kelly, 2001). The potassium ions are probably sourced from clay minerals in the Meenymore and Benbulbin Formations (Misstear *et al.*, 2008). Potassium concentrations across the other monitoring points show a relatively narrow range, with medians ranging from 0.2 to 1.8 mg/l.

The upper limit of the natural background levels for potassium, which is defined nationally for unconfined monitoring points and calculated using data collected since 2007, is 2.1 mg/l K. It should be noted that the potassium concentrations from confined aquifers may be higher. For example the 95th percentile for the confined aquifers (2 monitoring points) is 5.9 mg/l K. This has been calculated using data from two

monitoring points and, therefore, is not defined as a limit to natural background levels.

3.5.6 Bicarbonate (alkalinity)

Alkalinity is defined as the acid neutralising capacity of water. It is determined by titrating with acid to a pH of 4.5 and is equivalent to the concentration of HCO_3^- and CO_3^{2-} ions in most samples (Appelo and Postma, 2005).

The distribution of alkalinity varies across lithological groups (Figure A30). The pure and impure limestones groups have the highest alkalinity values as expected, but show a relatively large range of alkalinities with medians from 125 to 330 mg/l as CaCO_3 . The igneous

Table 3.5.6. The upper limits of the natural background level for bicarbonate (alkalinity) for pure limestone and non-calcareous sedimentary lithological groups

Bicarbonate (alkalinity) (mg/l CaCO ₃)						
	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non-calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	1	2	10	3	1	2
Number of data points	25	65	278	73	24	48
95th percentile	<i>350</i>	<i>290</i>	322	216	<i>43</i>	<i>310</i>

The 95th percentiles for the other lithological groups are included for information only. They have been calculated using data from two or fewer monitoring points and are therefore not defined as limits to natural background levels (shown in blue italics).

lithological group has the lowest alkalinity value at a median of 15 mg/l as CaCO₃. The sand and gravel lithological group has a median of 266 mg/l as CaCO₃, which is likely to reflect the provenance of the gravels. The metamorphic lithological group has a relatively high alkalinity with a median of 250 mg/l as CaCO₃ (Figure A29). This is likely to be due to the influence of carbonates contained in the subsoils overlying the Silurian metasediments and volcanics in County Clare (MP 03_003; Scarriff) and the possible presence of thin marble bands in the Precambrian quartzites, gneisses and schist metamorphic units in County Mayo (MP 16_011; Killasser) (Working Group on Groundwater, 2004b). The non-calcareous sedimentary lithological group has a bimodal distribution. Monitoring points 03_005 (Whitegate; Devonian Old Red Sandstone; Co. Clare) and 11_013 (Swan; confined Westphalian shales; Co. Laois) have high alkalinities with medians of 175 and 230 mg/l CaCO₃, respectively. These high alkalinities are likely to be due to (1) carbonates contained in the subsoils overlying the Devonian Old Red Sandstone aquifer and (2) carbonate cement in otherwise siliceous Westphalian shales coupled with long residence times (Working Group on Groundwater, 2004b). Carbon isotope dating of water from Swan determined a corrected age of 1440 (± 170) years (Wright, 2000).

One-way ANOVA tests indicated that concentrations in the non-calcareous sedimentary aquifers were significantly different from concentrations in the pure and impure limestone aquifers. The upper limit of the natural background levels for pure limestones and non-calcareous sedimentary lithological groups are 322 and 216 mg/l CaCO₃, respectively (Table 3.5.6).

The 95th percentiles for the other lithological groups are included for information only. They have been calculated using data from two or fewer monitoring points and, therefore, are not defined as limits to natural background levels.

3.5.7 Chloride

Chloride occurs in evaporite minerals such as halite and sylvite (Deer *et al.*, 1996). It is the most abundant ion in seawater (median of 19000 mg/l; Hem, 1985). Chloride is considered to behave conservatively in most aquifers because of its unreactive nature and high solubility. The source of natural chloride in groundwater is generally from rainfall or due to mixing with formation waters, although concentrations may be high where evaporite minerals are present and in geothermal areas (Shand *et al.*, 2007). Rainfall inputs of chloride vary with distance from the coast. For example, the national rainfall-weighted mean annual concentration of chloride in bulk precipitation samples collected in Irish monitoring stations between 1992 and 1994 vary from 3.8 to 44.5 mg/l Cl (Jordan, 1995).

Chloride concentrations across the monitoring points show a relatively narrow range, with medians ranging from 5.1 to 17.0 mg/l Cl (Figure A32). There is little variation between the lithological groups. While there is little correlation between chloride concentration and distance from the coast, as might be expected from the variation in rainfall chemistry, there is a similarity between the sodium and chloride concentrations for the unconfined monitoring points (Figure 3.5), perhaps indicating a shared sodium chloride (NaCl) control on the hydrochemistry. The upper limit of the

natural background levels for chloride, which is defined nationally for data from all pre-selected monitoring points, is 21 mg/l Cl.

Table 3.5.7. The upper limits of natural background levels for chloride calculated from all pre-selected data

	Chloride (mg/l Cl)
Number of MPs	21
Number of data points	613
95th percentile	21

3.5.8 Sulphate

Sulphate may be released by the weathering of evaporite minerals such as gypsum and anhydrite or by the oxidation of sulphide minerals such as pyrite (FeS_2), sphalerite (ZnS) or galena (PbS) (Dickinson and Patrick, 1986; Deer *et al.*, 1996). It is an abundant dissolved ion in sea water [median of 2700 mg/l (Hem, 1985)] but rainfall inputs are usually negligible [median of 0.9 mg/l (Jordan, 1995)]. It is the only major ion that is affected by redox reactions and, as such, its behaviour is complex (Shand *et al.*, 2007).

Groundwater from the confined monitoring points of Tydavnet and Swan show the highest sulphate concentrations with medians of 118 mg/l and 29 mg/l SO_4 , respectively (Figure A35). The high values may represent local geology [e.g. evaporite sources in the case of Tydavnet (Misstear *et al.*, 2008)] or the longer residence times in confined sources. Sulphate concentrations across the other monitoring points show a relatively narrow range, with medians ranging from 3 to 12 mg/l SO_4 .

The upper limit of the natural background levels for sulphate, which is defined nationally and calculated

for the unconfined monitoring points, is 13 mg/l SO_4 . It should be noted that the sulphate concentrations from the two confined aquifer monitoring points are higher: the 95th percentile for the confined aquifers (2 monitoring points) is 223 mg/l SO_4 . This has been calculated using data from two monitoring points and, therefore, is not defined as a limit to natural background levels.

The 95th percentile for the confined aquifers is greater than both the EPA's 2003 interim guideline value of 200 mg/l SO_4 and the 2010 Groundwater Regulations overall threshold value of 187.5 mg/l SO_4 (Table 3.1).

3.6 Minor Ions

3.6.1 Barium

Barium is an alkaline earth metal. The most common barium minerals are baryte (barium sulphate, BaSO_4) and witherite (barium carbonate, BaCO_3), which occur in hydrothermal veins in limestones, sandstones, shales and clays (Deer *et al.*, 1996). Barium's solubility is largely controlled by saturation with respect to baryte: where SO_4 concentrations are high, barium concentrations are low (Hem, 1985).

Barium shows a wide range of concentrations over four orders of magnitude (see Figure A39). The observed variation appears to be controlled by both lithology and location (Figure A37). Figure A37 shows that high concentrations tend to be associated with the Devonian Old Red Sandstone, Dinantian Kiltorcan-type Sandstone or gravels derived from those parent materials, which are located in the anticline that forms the Slieve Bloom and Silvermines mountains. This area is proximal to the Rathdowney trend, an approximately 80 km north-east to south-west trending belt in the south-central Irish midlands noted for its abundance of mineral occurrences (Sevastopulo

Table 3.5.8. The upper limit of natural background levels for sulphate for unconfined conditions

	Sulphate (mg/l SO_4)	
	Unconfined MPs	Confined MPs
Number of MPs	19	2
Number of data points	513	91
95th percentile	13	223

The 95th percentile for confined conditions is included for information only. The 95th percentile shown in blue italics has been calculated using data from two or fewer monitoring points and is therefore not defined as limits to natural background levels.

Table 3.6.1. The upper limits of natural background levels for barium for each lithological group

Barium ($\mu\text{g/l Ba}$)						
	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non-calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	30	29	96	31	13	16
Number of data points	659	605	2230	711	297	359
95th percentile	586	195	179	427	179	114

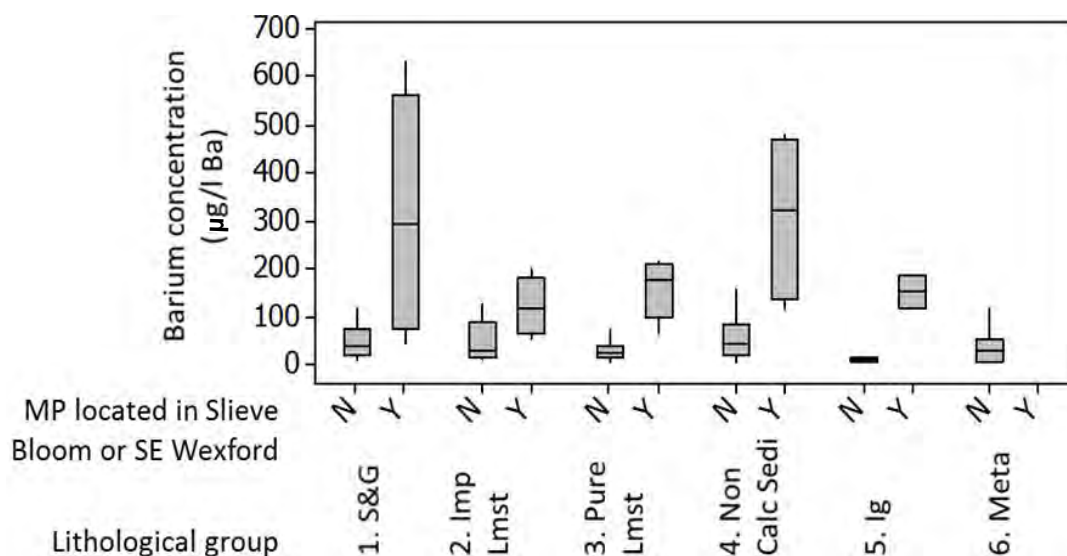


Figure 3.6. Elevated groundwater barium concentration observed in monitoring points located in the Slieve Bloom and Silvermines mountains and south-east Wexford compared to monitoring points in other areas. MP, monitoring point; S&G, sand and gravel; Imp Lmst, impure limestone; Pure Lmst, pure limestone; Non Calc Sedi, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

and Redmond, 1999; Bonson *et al.*, 2005) including many baryte (BaSO_4) deposits (Archer *et al.*, 1996). High concentrations are also observed in south-east Wexford (Figure 3.6) where vein type barytes are hosted in the Carboniferous dolomitic limestones (Tietzsch-Tyler *et al.*, 1994). Monitoring point 26_009 [S. Wexford RWS (Ballykelly)] has a median concentration of $653 \mu\text{g/l Ba}$ and a number of individual samples have exceeded the WHO's guideline value of $700 \mu\text{g/l Ba}$ (WHO, 2011). Monitoring points located in these rock units away from these areas show lower barium concentrations. For example, sand and gravel and non-calcareous sedimentary monitoring points in the Slieve Bloom and Silvermines area have medians of 292 and $321 \mu\text{g/l}$, respectively, compared to 35 and $78 \mu\text{g/l}$ for the rest of the country. Other lithological groups show a similar pattern, with monitoring points in the Slieve Bloom and Silvermines area showing

higher concentrations than for the rest of the country (Figure 3.6). The bimodal distributions for the different lithological groups seen in the frequency plot (see Figure A39) are a reflection of this.

One-way ANOVA tests indicated that there were significant differences between the lithological groups. The upper limits of the natural background levels, calculated including data from monitoring points in Slieve Bloom and Silvermines area and south-east Wexford, for the different lithological groups are shown in Table 3.6.1.

3.6.2 Fluoride

The principle mineral source of fluoride is the fluorite (CaF_2) and fluoroapatite [$\text{Ca}_5(\text{PO}_4)_3\text{F}$], which are common accessory minerals, particularly in granites

(Deer *et al.*, 1996). Fluoride is also released from weathering of primary silicates such as biotite and hornblende, where it replaces OH in the mineral lattices (Shand and Edmunds, 2008). Igneous and volcanic rocks have a fluoride concentration from 100 ppm (ultramafic) up to >1000 ppm (alkalic). Sedimentary rocks have a fluoride concentration from 200 ppm (limestone) up to 1000 ppm (shales). Metamorphic rocks have a fluoride concentration from 100 ppm (regional metamorphism) up to >5000 ppm (contact metamorphism) (Frencken, 1992). Its occurrence in groundwater is almost entirely due to water–rock interactions (Shand and Edmunds, 2008) and, therefore, largely depends on reaction times with aquifer minerals (Frencken, 1992). Concentrations in most groundwater are limited by saturation with respect to fluorite, which is relatively insoluble. High-fluoride groundwaters are mainly associated with a sodium-bicarbonate water type and relatively low calcium and magnesium concentrations. Fluoride is an essential element for humans at low concentrations but can be harmful, causing mottling of teeth and skeletal fluorosis, at higher concentrations. The Irish drinking water standard is 1.5 mg/l F for supplies with naturally occurring fluoride and 0.8 mg/l F for fluorinated supplies (Government of Ireland, 2014).

Groundwater from the confined monitoring point of Tydavnet has a median F concentration of 2.0 mg/l F. This is an order of magnitude higher than the other monitoring points (Figure A41) and would require blending to meet the Irish drinking water standard. The origin of the fluoride is not clear. Misstear *et al.* (2008) reported that the high fluoride concentrations correlated with high alkalinity and low calcium concentrations and that slightly elevated phosphorus concentrations (up to 31 mg/l) may indicate the presence of fluorapatite, as both a source of

phosphorus and fluoride, but that this has not been confirmed. High groundwater fluoride concentrations have also been reported in County Fermanagh, across the border, where a well with fluoride concentrations of 10 mg/l F was affecting school children's teeth in the 1970s (McKay, 1974). Groundwater from the other confined monitoring point at Swan has a median of 0.075 mg/l F, which is equivalent to the 0.15 mg/l F limit of detection. Fluoride concentrations across the other monitoring points show a relatively narrow range, with medians ranging from 0.1 to 0.3 mg/l. 58% of samples have concentrations below the limit of detection.

The upper limit of the natural background levels for fluoride, which is defined nationally and calculated for the unconfined monitoring points, is 0.20 mg/l F. It should be noted that the fluoride concentrations from the Tydavnet monitoring point are higher than this limit and are believed to be of natural origin. The 95th percentile for this monitoring point is 2.6 mg/l F. This has been calculated using data from one monitoring point and, therefore, is not defined as a limit to natural background levels.

3.6.3 Iron

Iron is the second most abundant metallic element in the Earth's crust. Igneous rock minerals with high iron content include the pyroxenes, amphiboles, biotite, magnetite and olivine. Secondary iron oxides and oxyhydroxides are ubiquitous in most rock types in oxidising environments. The chemical behaviour of iron and its solubility depend strongly on the oxidation and pH conditions of the system in which it occurs (Hem, 1985; Shand *et al.*, 2007).

Five of the monitoring points (23%) have medians concentrations of iron greater than 100 µg/l, including

Table 3.6.2. The upper limits of natural background levels for fluoride for unconfined monitoring conditions

	Fluoride (mg/l F)	
	Unconfined	Tydavnet MP (18_010)
Number of MPs	19	1
Number of data points	502	44
95th percentile	0.2	2.6

The 95th percentile of data from the Tydavnet monitoring point is included for information only. The 95th percentile shown in blue italics has been calculated using data from two or fewer monitoring points and is therefore not defined as limits to natural background levels.

Table 3.6.3. The upper limits of natural background levels for iron for unconfined conditions

	Iron (µg/l Fe)	
	Unconfined	Confined
Number of MPs	19	2
Number of data points	416	48
95th percentile	268	<i>762</i>

The 95th percentile for confined conditions is included for information only. The 95th percentile shown in blue italics has been calculated using data from two or fewer monitoring points and is therefore not defined as limits to natural background levels.

the confined monitoring points of Tydavnet and Swan, which have medians of 183 and 160 µg/l Fe, respectively (Figure A44). Individual samples from these monitoring points would require blending to meet the Irish drinking water standard of 200 µg/l Fe (Government of Ireland, 2014). Monitoring point 03_006 (Killeany, Co Clare) has a median concentration of 132 µg/l Fe. For this monitoring point it is likely that the high iron concentration originates from the streams that run off the Namurian shales uphill of the spring and sink at the limestone boundary (Cronin and Deakin, 2000). Further details are not available for the other two monitoring points with high iron. Groundwater concentrations in the other monitoring points are much lower. 59% of samples have concentrations below the limit of detection. 10 µg/l is the most frequent limits of detection used since 2007 (Table 3.3).

The upper limit of the natural background levels for iron, which is defined nationally and calculated using data collected since 2007 from unconfined monitoring points, is 268 µg/l Fe. The natural background level established exceeds the Irish drinking water standard of 200 µg/l (Government of Ireland, 2014; Table 3.1).

It should be noted that the iron concentrations from confined aquifers may be higher. For example, the 95th percentile for the confined aquifers (two

monitoring points) is 762 µg/l Fe. This has been calculated using data from two monitoring points and, therefore, is not defined as a limit to natural background levels.

3.6.4 Manganese

Manganese is an essential element in plants and animals. It is less abundant than iron, but shows similar geochemical behaviour as both are redox sensitive and largely controlled by pH and redox conditions. Manganese substitutes for iron, magnesium and calcium in silicate minerals (Shand *et al.*, 2007).

Groundwater from the confined monitoring points of Swan and Tydavnet show the highest manganese concentrations with medians of 150 µg/l and 65 µg/l Mn, respectively (Figure A47). These medians are both higher than the Irish drinking water standard of 50 µg/l Mn (Government of Ireland, 2014). This is likely to reflect the reducing conditions in these confined aquifers. Manganese concentrations across the other monitoring points show a relatively narrow range, with medians ranging from 0.5 to 7.0 µg/l Mn.

The upper limit of the natural background levels for manganese for unconfined monitoring points, which is defined nationally and calculated using data collected

Table 3.6.4. The upper limits of natural background levels for manganese for unconfined conditions

	Manganese (µg/l Mn)	
	Unconfined	Confined
Number of MPs	19	2
Number of data points	416	47
95th percentile	23	<i>176</i>

The 95th percentile for confined conditions is included for information only. The 95th percentile shown in blue italics has been calculated using data from two or fewer monitoring points and is therefore not defined as limits to natural background levels.

since 2007, is 23 µg/l Mn. It should be noted that the manganese concentrations from confined aquifers may be higher. For example, the 95th percentile for the confined aquifers (two monitoring points) is 176 µg/l Mn. This has been calculated using data from two monitoring points and, therefore, is not defined as a limit to natural background levels.

3.6.5 Silica

Silicon is the second most abundant element in the Earth's crust (after oxygen). Silica is silicon oxide (SiO_2). The chemical bond between silicon and oxygen is very strong and the SiO_4^{4-} tetrahedron is the fundamental building block of most of the minerals making up igneous and metamorphic rocks and is present in some form in most other rock types, soils and in natural water (Hem, 1985). The solubility of silica is generally low, except in geothermal waters. The presence of silica, up to a few mg/l, in nearly all natural waters testifies to its natural abundance, so an under-saturation with respect to calcite minerals denotes either an absence of silica minerals (a rare occurrence) or very short residence times (Davis, 1964).

Groundwater from the pure limestones shows the lowest silica concentrations with a median of 5.9 mg/l SiO_2 for the lithological group (Figure A51). The pure limestones also show the lowest variation in concentration with medians for individual monitoring points ranging from 1.4 to 11.8 mg/l SiO_2 . The igneous and metamorphic lithological groups show the highest silica concentrations (medians for the groups of 9.4 and 9.3 mg/l SiO_2) and the largest variations. The impure limestones and the non-calcareous sedimentary groups have median silica concentrations of 8.5 and 8.1 mg/l SiO_2 (Figure A50).

One-way ANOVA tests indicated that there were significant differences between the lithological groups.

The upper limits of the natural background levels for the different lithological group are shown in Table 3.6.5.

3.6.6 Strontium

Strontium is an alkaline earth metal, which displays similar geochemical behaviour to calcium because of their similar ionic radii. Strontium is mainly derived from calcium-rich minerals such as calcite, calcium-rich feldspars, and especially aragonite (which may hold 8000 ppm strontium) (Deer *et al.*, 1996) and gypsum/anhydrite (Shand and Edmunds, 2008). The principle mineral source of strontium is Celestine (SrSO_4), which occurs in dolomites and evaporite deposits (Deer *et al.*, 1996). In fresh groundwater, there are generally no solubility controls on strontium and it typically increases with residence time (Shand *et al.*, 2007). As strontium is typically derived from water-rock interactions, it is a good indicator of processes taking part in the aquifer (Shand and Edmunds, 2008). There is no established drinking water guideline value for strontium (WHO, 2012; EU, 2011).

Strontium groundwater concentrations in most lithological groups vary over approximately two orders of magnitude up to a maximum of approximately 1000 µg/l Sr. Concentrations are relatively high in the impure limestone lithological group which vary over three orders of magnitude up to a maximum of approximately 10,000 µg/l Sr. Concentrations are relatively low in the carbonate poor igneous and non-calcareous sedimentary groups (see Figure A53).

Strontium concentrations in monitoring points 02_004 (Milltown Well in the Dinantian Lower Impure Limestone) are an order of magnitude above the other impure limestone monitoring points with an interquartile range between 6500 and 18,650 µg/l Sr and a median of 7470 µg/l Sr. It is possible that the high strontium levels are from interactions with the

Table 3.6.5. The upper limits of natural background levels for silica for each lithological group

Silica (mg/l SiO_2)	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non-calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	30	29	96	31	13	16
Number of data points	399	372	1367	442	179	211
95th percentile	13	17	10	14	19	16

Table 3.6.6. The upper limits of natural background levels for strontium for each lithological group

Strontium ($\mu\text{g/l Sr}$)	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non-calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	30	29	96	31	13	16
Number of data points	659	605	2227	708	297	360
95th percentile	651	2900	575	320	498	772

evaporitic sediments deposited in Counties Leitrim, Cavan and Fermanagh, perhaps with the nearby Meenymore Formation [part of the Dinantian mixed sandstones, shales and limestones (Geraghty, 1997)], which contains gypsum and celestine (West *et al.*, 1968). Monitoring point 18_010 (Tydavnet in the confined Dinantian mixed sandstones, shales and limestones) also has a high strontium concentration relative to the other impure limestone monitoring points with an interquartile range between 4810 and 6266 $\mu\text{g/l Sr}$ and a median of 5210 $\mu\text{g/l Sr}$. This may be due to exposure to the evaporitic beds within the Meenymore Formation, which is exposed in the Tydavnet area (Misstear *et al.*, 2008) or due to the longer residence time in the confined aquifer. Confined monitoring points in other lithological groups also show higher strontium concentrations. For example, the median strontium concentrations for confined and unconfined sand and gravel monitoring points are 494 $\mu\text{g/l}$ and 121 $\mu\text{g/l Sr}$, respectively.

Generally, pure limestone in the north-west of the country, i.e. in Counties Mayo, Roscommon, Sligo and particularly Galway, has both higher strontium concentrations and larger concentration ranges compared to pure limestones elsewhere in the country (see Figure A52).

Figure A54 shows that the igneous and metamorphic lithological groups have a bimodal distribution. For the igneous group this is due to higher concentrations in the basalt and other volcanic rocks in County Limerick and County Laois (possibly due to the prevalence of calcium-rich feldspars) relative to the concentrations in the granites and Ordovician volcanics in the south-east of the country (see Figure A52). For the metamorphic group, this is due to higher concentrations in the Precambrian marble and Precambrian quartzites, gneisses and schists in County Donegal and County Mayo relative to the concentrations in the Ordovician

and Silurian metasediments in the north-east and south-east of the country (see Figure A52).

One-way ANOVA tests indicated that concentrations in the impure limestone lithological group were significantly different to concentrations in the other lithological groups. The upper limit of the natural background levels for the impure limestone lithological group, calculated for data collected since 2007, is 2900 $\mu\text{g/l Sr}$; the upper limit for the other lithological groups range between 320 and 772 $\mu\text{g/l Sr}$ (Table 3.6.6).

3.7 Nutrient Species

3.7.1 Nitrogen species

Nitrogen may be present in water as a number of dissolved species: nitrate (NO_3), ammonium (NH_4), nitrite (NO_2), which is metastable, nitrogen gas (N_2) and organic nitrogen. The occurrence and mobility of the inorganic nitrogen species is largely dependent on the redox conditions of the water, with NO_3 being stable under oxidising conditions and NH_4 under reducing conditions.

Nitrogen is essential for life and often is a limiting factor for plant growth. To increase crop yields, the application of nitrogen-based fertilisers is common in agricultural practice. However, use of nitrogen also increases the pressure on soil and water quality. High nitrate concentrations in soils result in soil acidification, changes in soil quality and loss of soil biodiversity. When applied in excess, the nitrogen not used by plants may leach through the root zone and contaminate groundwater resources, usually in the form of nitrate (NO_3). High nitrate concentrations in groundwater have public health and environmental implications and have become a common problem in many parts of the world.

Table 3.7.1. The upper limits of natural background levels established for nitrate for unconfined conditions.

	Nitrate (mg/l NO ₃)	
	Unconfined	Confined
Number of MPs	10	2
Number of data points	328	93
95th percentile	8.7	<i>1.5</i>

The 95th percentile for confined conditions is included for information only. The 95th percentile shown in blue italics has been calculated using data from two or fewer monitoring points and therefore is not defined as limits to natural background levels.

As discussed in the introduction (Chapter 1), the determination of natural background levels for nitrogen is difficult because of the widespread and variable use of organic and inorganic fertilisers, the significant increase in atmospheric nitrogen inputs due to the burning of fossil fuels, as well as the impact of denitrification. The annual mean nitrate concentration in Irish rain water has increased from 0.21 mg/l N (10.9 mg/l as NO₃) in 1986–1988 to 0.25 mg/l N (1.1 mg/l as NO₃) in 1992–1994 (Jordan 1995).

As outlined in section 2.6, when establishing natural background levels for the nitrogen species parameters, monitoring points were pre-selected to reflect low agricultural pressure and low nitrate susceptibility. In the case of the nitrogen species parameters, 6% of monitoring points (12) were pre-selected for the assessment based on the screening criteria. This is a small number of monitoring points available to perform this type of analysis; also, statistical confidence in the natural background levels established for the nitrogen species parameters is low. However, the methodology follows best practice and has made best use of the available data.

Nitrate

Nitrate concentrations in the pre-selected monitoring points range from 0.02 mg/l NO₃ to 15 mg/l NO₃. Monitoring points 16_013 (Kilkelly), 07_002 (Ballygar) and 08_021 (Portmagee) show the highest nitrate concentrations (with median concentrations of 5.8, 5.8 and 5.9 mg/l NO₃, respectively) and the largest range in nitrate concentration (Figure A56). The upper limit of natural background levels for nitrate, which is defined nationally for unconfined groundwater, is 8.7 mg/l NO₃.

Within the selected monitoring points, the influence of confined conditions may be seen as groundwater

in confined aquifers; 11_013 (Swan), and 18_010 (Tydavnet) have the low nitrate concentrations with medians of 0.18, and 0.40 mg/l NO₃, respectively (Figure A56). A median concentration of 0.18 mg/l indicates that most samples are below the 0.36 mg/l NO₃ limit of detection. Given the hydrogeological settings at these monitoring points and the groundwater concentrations, it is likely that denitrification is occurring in the confined aquifers sampled by these monitoring points. It should be noted that nitrate concentrations from confined aquifers is lower than the natural background level established for the unconfined monitoring points. For example, the 95th percentile for the confined aquifers (two monitoring points) is 1.5 mg/l NO₃. This has been calculated using data from two monitoring points and, therefore, is not defined as a limit to natural background levels.

There is a wide range in the natural background levels (or equivalents) for nitrate from international literature. For example, those summarised in Table 1.1 range from 0.1 to 18.5 mg/l NO₃. Published estimates of background or threshold values for nitrate in groundwater compiled by Panno *et al.* (2006) (Table 3.7.2) range from 0.008 mg/l to 19.9 mg/l NO₃. In addition, Pauwels *et al.* (2006) note that natural pre-industrial concentrations in aerobic water would be unlikely to have exceeded 2 mg/l N (8.8 mg/l NO₃). Shand *et al.* (2007) indicate that the baseline range of nitrate is likely to vary from < 1 mg/l N (4.4 mg/l NO₃) to possibly around 3 to 4 mg/l N (13.2 to 17.7 mg/l NO₃). Gemitzi (2001) established a nitrate natural background level of 7.7 mg/l NO₃ using data from a pristine mountainous area in Greece. The natural background level of 8.7 mg/l NO₃ established for Irish groundwater falls within the range of equivalent values from international literature.

Table 3.7.2. Published estimates of background and threshold concentrations for NO₃ (mg/l). Some of the publications also determined concentrations indicating anthropogenic contamination. After Panno *et al.*, 2006

Reference	Background/threshold (mg/l)		Anthropogenic events (mg/l)		Sources and locations (number of samples or sample dates)
	N	NO ₃	N	NO ₃	
Large data sets					
George and Hastings (1951)	1–2	4.4–8.9	4.5	20	Wells, Texas (>20,000)
Madison and Brunett (1985)	0.2	0.9	3	13	Wells, United States (>87,000)
Parlman (1988)	1	4.4	2	8.9	Wells, Idaho (1678)
Baker <i>et al.</i> (1989)	<0.3	<1.3			Wells, Ohio (>14,000)
Nolan (2001)			4	18	Wells, United States (1230)
Levine <i>et al.</i> (2002)	0.08	0.35			Wells, Ohio (466)
Nolan and Hitt (2005)	1.1	4.9			Wells in undeveloped areas, United States (>12,000)
Historical data sets					
Hallberg and Keeney (1993)	<1	<4.4			Wells and springs, Iowa (1930s)
Katz <i>et al.</i> (2002)	0.1	0.44			Springs, northern Florida (1950s)
Limbrick (2003)	1	4.4			Springs, UK (1880–1940s)
Jones and Smart (2005)	<2.1	<9.3			Karst springs, UK (1930s)
Pristine areas					
McKenna <i>et al.</i> (1988)	<1.3	<5.8			Wells in natural areas, Illinois
Postma <i>et al.</i> (1991)	<0.1	<0.44			Pristine wells, Denmark
Mueller and Helsel (1996)	<2	<8.9			Wells, United states
Panno <i>et al.</i> (1996)	1.4	6.2			Springs and wells, Illinois
Leenhouts <i>et al.</i> (1998)	4.5	19.9			Background wells, Arizona
Cho <i>et al.</i> (2000)	<1.0	<4.4			Upgradient well, South Korea
Brye <i>et al.</i> (2001)	<0.3	<1.3			Prairie soil water, Wisconsin
Perakis and Hedin (2002)	0.0019	0.0084			Pristine streams, South America

Nitrite

91% of samples have nitrite concentrations below the limit of detection (see Figure A59). A level of 0.002 mg/l NO₂ is the most frequent limit of detection, but it should be noted that many data have a higher limit of detection (Table 3.3).

The upper limit of the natural background levels for nitrite for unconfined monitoring points, which is defined nationally, is <0.05 mg/l NO₂. The 95th percentile for the confined aquifers (two monitoring points) is also <0.05 mg/l NO₂. This has been calculated using data from two monitoring points and, therefore, is not defined as a limit to natural background levels.

Ammonium

Ammonium is stable under reducing conditions and, as such, is observed in relatively high concentrations in the two confined monitoring points of 18_010 (Tydavnet) and 11_013 (Swan), which have median concentration of 0.17 and 0.12 mg/l N, respectively (Figure A62). In all of the other (unconfined) monitoring points, the median concentration is 0.013 mg/l (Figure A62). A median concentration of 0.013 mg/l indicates that most samples are below the 0.026 mg/l N limit of detection (Table 3.3).

The upper limit of the natural background levels for ammonium, which is defined nationally for unconfined groundwater, is 0.09 mg/l N. The natural background

Table 3.7.3. The upper limits of natural background levels established for nitrite for unconfined conditions

	Nitrite (mg/l NO ₂)	
	Unconfined	Confined
Number of MPs	10	2
Number of data points	319	87
95th percentile	<0.05	<i><0.05</i>

The 95th percentile for confined conditions is included for information only. The 95th percentile shown in blue italics has been calculated using data from two or fewer monitoring points and therefore is not defined as limits to natural background levels.

Table 3.7.4. The upper limits of natural background levels established for ammonium for unconfined conditions

	Ammonium (mg/l N)	
	Unconfined	Confined
Number of MPs	10	2
Number of data points	326	92
95th percentile	0.09	<i>0.4</i>

The 95th percentile for confined conditions is included for information only. The 95th percentile shown in blue italics has been calculated using data from two or fewer monitoring points and therefore is not defined as limits to natural background levels.

level established exceeds the environmental quality standard for total ammonia of 0.065 mg/l (Government of Ireland, 2009) (Table 3.1). The ammonium concentrations from the confined aquifers are higher than both these levels: the 95th percentile for the confined aquifers (two monitoring points) is 0.4 mg/l N. This has been calculated using data from two monitoring points and, therefore, is not defined as a limit to natural background levels.

3.7.2 Phosphorus species

Phosphorus is an essential element for life and major nutrient for plants. The dominant natural source of phosphorus in groundwater is apatite, which is a common accessory mineral in many rock types, especially igneous rocks (Deer *et al.*, 1996), and exchangeable phosphorus on iron oxides. It occurs in concentrations of several hundred mg/kg in all common rock types but its concentration in natural waters is usually low due to the low solubility of most of its inorganic compounds (Hem, 1985). Under alkaline conditions phosphorus is easily sorbed to carbonates and iron oxide minerals; as a result, its mobility is likely to be low (Shand and Edmunds, 2008). However, in some situations, phosphorus

can transfer into groundwater (Holman *et al.*, 2008). In some cases seawater can provide a source of phosphorus (median concentration of 0.09 mg/l) (Hem, 1985).

In some instances in Ireland, groundwater can provide a pathway of phosphorus transfer to ecologically sensitive surface waters. This is particularly likely to occur in vulnerable karst situations due to leaching of phosphorus through the thin, organic soils or point recharge bypassing the protective soil cover altogether and rapid transfer via conduits (Coxon, 2011).

Total phosphorus samples comprise a number of different fractions of phosphorus, including orthophosphate, condensed phosphates, organic phosphates, colloidal phosphates and biotic and abiotic particulate phosphorus (Jones and Mulholland, 2000). The orthophosphate fraction is the simplest form of phosphate and biologically readily available phosphorus (Nollet and De Gelder, 2000). This is often equated to molybdate reactive phosphorus.

As outlined in section 2.6, when establishing natural background levels for the phosphorus species parameters, monitoring points were pre-selected to reflect low agricultural pressure and low phosphorus

susceptibility. In the case of the phosphorus species parameters, 8% of monitoring points (18) were pre-selected for the assessment based on the screening criteria. This is a small number of monitoring points to perform this type of analysis; statistical confidence in the natural background levels established for the phosphorus species parameters is low. However the methodology follows best practice and has made best use of the available data.

Total phosphorus

Total phosphorus is typically higher in groundwater from karstified flow. The median total phosphorus concentration from monitoring points within karstified regimes is 13 µg/l P; compared to a median of 3.5 µg/l for the other flow regime types regimes (see Figures 3.7 and A65). A median concentration of 3.5 µg/l indicates that most samples are below the 7 µg/l P

limit of detection. This may reflect the high degree of variation in the conduit systems of karstified flow regime. Alternatively, the ZOCs of the karstified systems may contain unknown point sources which were not filtered out during the pre-selection process.

The upper limit of the natural background levels for total phosphorus for karstic regime groundwater, which is calculated for data collected since 2010, is 26 µg/l P. The upper limit of the natural background levels for total phosphorus, for intergranular and poorly productive groundwater flow regimes, is 13 and 16 µg/l P, respectively (Table 3.7.5). It should be noted that no monitoring points with the productive fissured flow regime category were pre-selected; therefore, this flow regime category does not feature in Figure 3.7 or Table 3.7.5. The natural background level in this category is most likely to be similar to the poorly productive fractured aquifers, given the absence of karst conduit flow.

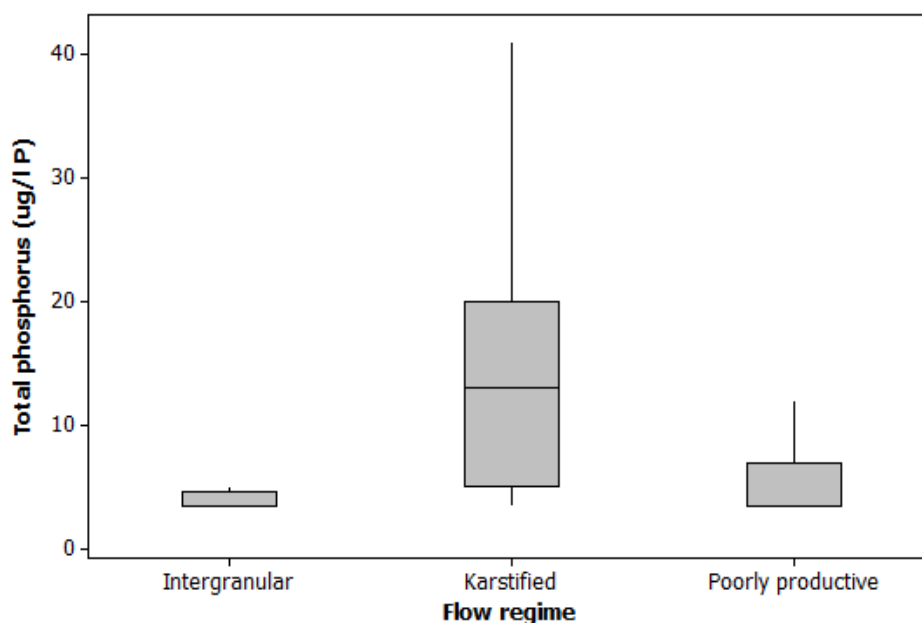


Figure 3.7. The concentration of total phosphorus in groundwater from karstified flow regimes in comparison with groundwater from other flow regimes.

Table 3.7.5. The upper limits of natural background levels established for total phosphorus for the intergranular, karstified and poorly productive flow regime categories. The productive fissured flow regime was not represented in the pre-selected dataset

Total phosphorus (µg/l P)			
Flow regime	Intergranular	Karstified	Poorly productive
Number of MPs	5	6	7
Number of data points	52	61	72
95th percentile	13	26	16

Molybdate reactive phosphorus

71% of samples have molybdate reactive phosphorus concentrations below the limit of detection of 15 µg/l P. All samples from 16 of the 18 pre-selected monitoring points have phosphorus concentrations that are below the limit of detection (Figure A68). Molybdate reactive phosphorus has been detected in two of the pre-selected monitoring points since 2010, namely 02_002 (Bawnboy) and 07_010 (Kilbannon), which have median molybdate reactive phosphorus concentrations of 20 and 7.5 µg/l P, respectively. A median concentration of 7.5 µg/l indicates that most samples are below the 15 µg/l P limit of detection. These monitoring points are located in karstic flow regimes in the Dinantian pure bedded limestone.

Table 3.7.6. The upper limits of natural background levels established for molybdate reactive phosphorus calculated from all pre-selected data

Molybdate reactive phosphorus (µg/l P)	
Number of MPs	18
Number of data points	193
95th percentile	17

The upper limit of the natural background levels for molybdate reactive phosphorus, which is defined nationally and calculated using data collected since 2010, is 17 µg/l P. The upper limit of the natural background levels was defined nationally rather than for different flow regime categories (as was the case for total phosphorus) as 71% of samples have molybdate reactive phosphorus concentrations below the limit of detection.

There are not many estimates of natural background level for molybdate reactive phosphorus in international literature, possibly because of limitations of the knowledge of phosphorus behaviour and the multiple natural and pollutant sources (Shand *et al.*, 2007). Edmunds *et al.* (2003) established an upper limit to the baseline orthophosphorus concentration range of 6.5 and 12.7 µg/l P for the unconfined and confined Berkshire Chalk aquifer respectively (Table 1.1). Wendland *et al.* (2008) derived a natural background level of 170 µg/l PO₄ (55 µg/l P) for groundwater bodies in the Upper Rhine Valley (France,

Switzerland and Germany). SNIFFER (2008) suggests an upper background limit for orthophosphate of 40 µg/l P for the Tamar groundwater body in south-west England. The natural background level of 17 µg/l P established for Irish groundwater falls within the range of equivalent values from international literature.

3.7.3 Total organic carbon

Organic carbon is present in all natural waters and plays an important role in many geochemical processes such as redox reactions, weathering, diagenesis and the transport of trace metals (Gooddy and Hinsby, 2008). Natural organic carbon in shallow groundwater is derived mostly from the overlying soils and consists of a mixture of macromolecules of humic and fulvic substances; deeper and older groundwater may contain organic material that has been mobilised from the matrix (Gooddy and Hinsby, 2008). Total organic carbon (TOC) measurements include all organic compounds in the analysed water sample including, for example, suspended particles and bacteria.

Groundwater from the pure limestone lithological group has the highest TOC concentrations with a median of 5.0 mg/l C (see Figure A71 and A72). These high TOC values may be a result of a combination of peat subsoils and active forestry within the zones of contribution of most of these monitoring points [D. Drew, Trinity College Dublin (retired), March 2015, personal communication]. Impure limestones and igneous lithological groups have median TOC concentrations of 1.9 and 1.8 mg/l C, respectively. The other lithological groups have median TOC concentrations of 1 mg/l C or less. For comparison, European groundwater samples were found to have a median TOC of 2.69 mg/l C and a range from 0.12 to 59.4 mg/l C (Gooddy and Hinsby, 2008).

Summary statistics (Table A24) have been calculated for TOC using the pre-selection criteria for parameters which are potentially impacted by anthropogenic activities (see section 2.6.3). The criteria considers nitrate concentration and pressure within the zones of contribution. It does not consider factors such as active forestry within the zones of contribution and as such is an inappropriate pre-selection for TOC. Therefore, an upper limit of the natural background levels was not defined for TOC.

Table 3.8.1. The upper limits of natural background levels established for aluminium for each lithological group

Aluminium (µg/l Al)	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non-calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	30	29	96	31	13	16
Number of data points	632	583	2145	688	288	346
95th percentile	15	19	26	16	131	19

3.8 Trace Elements

3.8.1 Aluminium

Aluminium is the third most abundant element in the Earth's crust (Hem, 1985). It is present in most of the silicate minerals: pyroxenes, amphiboles, micas, clays and plagioclase feldspars; as well as in gibbsite $[\text{Al}(\text{OH})_3]$ (Deer *et al.*, 1996). Despite its geochemical abundance, aluminium occurs at low concentrations, typically in the µg/l range, because of the low solubility of aluminium bearing minerals at the near-neutral pH values of most groundwater. Aluminium is most soluble under acidic conditions but is, to a lesser extent, also soluble under alkaline conditions (Shand and Edmunds, 2008).

Monitoring points in the igneous lithological group, particularly in the “granites and other igneous intrusive rocks” rock unit, have the highest aluminium concentrations (Figures A74 and A75) and some of the lowest pH values. For example, Glynn/St. Mullins and Graiguenamanagh have median aluminium concentrations of 88.5 and 82.0 µg/l Al, respectively, and median pH values of 6.1 and 6.4, respectively. Aluminium concentrations across the other lithological groups are low, with median concentrations for the other lithological groups being 2.5 µg/l. This reflects the fact that 80% of samples are below the limit of detection. The most frequent limit of detection since 2007 is 5 µg/l (see Table 3.3).

One-way ANOVA tests indicated that concentrations in the igneous lithological group were significantly different from concentrations in the other lithological groups. The upper limit of the natural background levels for the igneous lithological group, which is calculated using data collected since 2007, is 131 µg/l Al. The upper limits for the other lithological groups are between 15 and 26 µg/l Al (Table 3.8.1).

3.8.2 Antimony

Antimony is a trace metal with geochemical behaviour similar to arsenic (Luoma and Rainbow, 2008). It is commonly associated with ferric hydroxides, sulphides (Shand *et al.*, 2007) or lead minerals (Blum, 2006).

The concentration of antimony in the majority of the monitoring points is low with 80% of samples being below the limit of detection. 0.5 µg/l is the most frequent limit of detection since 2007 (see Table 3.3). The median antimony concentration in 12 monitoring points exceeds the limits of detection. Of those, Pettigo MP (05_004) has the highest median concentration (4.0 µg/l) and individual samples have exceeded the Irish drinking water standard of 5 µg/l for antimony (Government of Ireland, 2014) on a number of occasions.

The upper limit of the natural background levels for antimony, which is defined nationally and calculated using data collected since 2007, is 0.5 µg/l Sb.

Table 3.8.2. The upper limits of natural background levels established for antimony for all pre-selected data

Antimony (µg/l Sb)	
Number of MPs	217
Number of data points	4905
95th percentile	0.5

3.8.3 Arsenic

Arsenic is a trace metal known for its toxicity. Sulphide minerals (such as pyrite) and iron oxides are the most common sources and sinks of arsenic in groundwater. Arsenic is redox sensitive: it is released from sulphide minerals via oxidation reactions and released from iron

oxides via reductive dissolution or desorption reactions (Shand and Edmunds, 2008).

The concentration of arsenic in the majority of the monitoring points is low with 67% of samples being below the limit of detection. 0.5 µg/l is the most frequent limit of detection in data collected since 2007 (see Table 3.3). The median arsenic concentration in 20 monitoring points exceeds 1 µg/l As. Of those, Ballyogarty WS MP (24_004; in the Campile Formation of the Ordovician volcanics) has the highest median concentration (54.0 µg/l) and individual samples routinely exceed the groundwater threshold value of 7.5 µg/l As (Government of Ireland, 2010) and the Irish drinking water standard of 10 µg/l As (Government of Ireland, 2014) (Figure A81). The elevated levels of arsenic at this monitoring point are considered to be of natural origin (Conroy, 2010). Shale units in the Campile Formation have been identified as being rich in pyrite (GSI, 2012) and are a possible source.

The upper limit of the natural background levels for arsenic, which is defined nationally and calculated using data collected since 2007, including data from Ballyogarty WS MP, is 2 µg/l As.

A review of EPA, county council and HSE (Health and Safety Executive) data (Liam Morrison, National University of Ireland, Galway, March 2015, personal communication) found incidences of high arsenic concentrations in groundwater (> 50 µg/l) in Counties Louth, Meath, Wicklow, Waterford, Cork, Limerick, Kerry, Mayo and Sligo. The source of the arsenic is believed to be natural in the majority of cases and may be associated with arsenopyrite in quartz veins or with metasediments.

Table 3.8.3. The upper limits of natural background levels established for arsenic for all pre-selected data

	Arsenic (µg/l As)
Number of MPs	217
Number of data points	4901
95th percentile	2

3.8.4 Beryllium

Beryllium is an alkaline earth metal; it may occur in silicates or hydroxy-silicates, the most important of

which is beryl, which occurs in granite pegmatites (Deer *et al.*, 1996). Beryllium concentrations in groundwater are typically low as a result of the insolubility of beryllium oxides and hydroxides in the normal pH range (Hem, 1985).

99.6% of samples have concentrations below the limit of detection. 1.0 µg/l Be is the most frequent limit of detection since 2007 (see Table 3.3). Only one monitoring point has a median concentration above the limit of detection (Pilltown WS MP; 20_015) which has a median of 1 µg/l Be (Figure A84).

The upper limit of the natural background levels for Be, which is defined nationally and calculated using data collected since 2007, is < 1.0 µg/l Be.

Table 3.8.4. The upper limits of natural background levels established for beryllium for all pre-selected data

	Beryllium (µg/l Be)
Number of MPs	217
Number of data points	4910
95th percentile	< 1

3.8.5 Boron

Boron is important at low concentrations for plant growth. The most widely distributed mineral in which boron is an essential constituent is tourmaline, which is present in granite pegmatites and granites. Boron may also be present as an accessory constituent of biotite and the amphiboles (Hem, 1985; Deer *et al.*, 1996). It is a relatively abundant dissolved ion in sea water (median of 4.5 mg/l; Hem, 1985).

Groundwater from the confined monitoring points of Tydavnet and Swan show the highest boron concentrations, with medians of 495 and 28 µg/l B, respectively (Figures A86 and A87). Natural enrichment of boron in water supplies can result from hydrothermal influence on infiltrating waters, dissolution of evaporites, the presence of residual seawater and mineral weathering (Ravenscroft and McArthur, 2004). Boron concentrations across the other monitoring points show a relatively narrow range, with medians ranging from 6.8 to 13 µg/l (Figures A86 and A87). These concentrations are relatively low when compared to aquifers in the UK (Shand *et al.*,

Table 3.8.5. The upper limits of natural background levels established for boron for unconfined conditions

	Boron ($\mu\text{g/l B}$)	
	Unconfined	Confined
Number of MPs	19	2
Number of data points	416	48
95th percentile	15	<i>573</i>

The 95th percentile for confined conditions is included for information only. The 95th percentile shown in blue italics has been calculated using data from two or fewer monitoring points and therefore is not defined as limit to natural background levels.

2007) and may reflect the relatively short residence times of Irish aquifers.

The upper limit of the natural background levels for boron, which is defined nationally for unconfined groundwater and calculated using data collected since 2007, is $15 \mu\text{g/l B}$. It should be noted that the boron concentrations from confined aquifers might be higher. For example, the 95th percentile for the confined aquifers (two monitoring points) is $573 \mu\text{g/l B}$. This has been calculated using data from two monitoring points and, therefore, is not defined as a limit to natural background levels.

3.8.6 Cadmium

Cadmium is a transition metal with chemical similarities to zinc. It is present in zinc and copper ore minerals, such as sphalerite (Hem, 1985). It is considered to be harmful and has an Irish drinking water standard of $5 \mu\text{g/l}$ and a WHO threshold value of $3 \mu\text{g/l}$.

96% of samples have concentrations below the limit of detection (Figures A89 and A90). $0.4 \mu\text{g/l Cd}$ is the most frequent limit of detection (Table 3.3).

The upper limit of the natural background levels for cadmium, which is defined nationally and calculated using data collected since 2007, is $<0.4 \mu\text{g/l Cd}$.

Table 3.8.6. The upper limits of natural background levels established for cadmium for all pre-selected data

	Cadmium ($\mu\text{g/l Cd}$)
Number of MPs	21
Number of data points	464
95th percentile	<0.4

3.8.7 Chromium

Chromium is an essential nutrient for animal and plant metabolism but is also toxic at high concentrations. High chromium concentrations are found in ferromagnesian minerals such as olivine, pyroxene and amphibole. Chromium is also present at higher than average concentrations in shales and other argillaceous rocks. Chromium can exist in a number of oxidation states (0 to 6+), but only the trivalent and hexavalent states are important in the range of Eh-pH values found in natural waters (Richard and Bourg, 1991). Like other metal cations, Cr^{3+} is easily adsorbed onto clay and Fe and Mn hydroxide surfaces, and adsorption increases with pH. It is generally more mobile under acidic oxidising conditions and can also form a number of inorganic and organic complexes. Under highly oxidising conditions, chromate (CrO_4^{2-}), a toxic form of chromium, is stable (Shand and Edmunds, 2008).

69% of samples have concentrations below the limit of detection (Figure A93). $0.25 \mu\text{g/l Cr}$ and $0.5 \mu\text{g/l Cr}$ are the most frequent limits of detection (see Table 3.3).

One-way ANOVA tests indicate that there were significant differences between the chromium concentrations of the lithological groups. The upper limits for each lithological group are shown in Table 3.8.7.

3.8.8 Cobalt

Cobalt is a transition metal. Cobalt ions can substitute for iron in ferromagnesian rock minerals. Cobalt precipitation or adsorption of cobalt by oxides of manganese and iron appear to be an important factor in controlling the amounts that can occur in solution in natural waters (Hem, 1985).

Table 3.8.7. The upper limits of natural background levels established for chromium for each lithological group

Chromium ($\mu\text{g/l Cr}$)	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non-calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	30	29	95	31	13	16
Number of data points	659	605	2230	711	297	360
95th percentile	11	11	11	9	4	8

94% of samples have concentrations below the limit of detection (Figure A96). $1.0 \mu\text{g/l Co}$ is the most frequent limit of detection since 2007 (see Table 3.3). Five of the monitoring points (2%) have median concentrations of greater than $1 \mu\text{g/l}$. Monitoring point 27_007 (Kerry Foods, Shillelagh in the Ordovician metasediments) has the highest cobalt concentrations with a median of $3.1 \mu\text{g/l Co}$.

One-way ANOVA tests indicated that concentrations in the metamorphic lithological group were significantly different from concentrations in the other lithological groups (Figure A96). However, because 94% of the samples are less than the limit of the detection the natural background level has been defined nationally. The upper limit of the natural background levels, which have been calculated using data collected since 2007, is $< 1 \mu\text{g/l Co}$.

Table 3.8.8. The upper limits of natural background levels established for cobalt for all pre-selected data

Cobalt ($\mu\text{g/l Co}$)	
Number of MPs	217
Number of data points	4910
95th percentile	< 1

3.8.9 Copper

Copper is an essential element in plant and animal metabolism. In nature it occurs as native copper and in sulphide minerals of ore deposits. It forms a range of inorganic and especially organic complexes in water. Copper is usually immobile in organic soils due to strong adsorption onto organic matter. Under oxidising conditions, it is soluble under acidic conditions, but solubility is limited at high pH by relatively insoluble

carbonate or hydroxide phases (Hem, 1985; Shand *et al.*, 2007).

Copper groundwater concentrations vary over 3 orders of magnitude up to approximately $100 \mu\text{g/l}$. Concentrations are highest in the non-calcareous sedimentary group (see Figures A98 and A99) with median concentrations varying between 1.2 and $10 \mu\text{g/l Cu}$. Copper concentrations for the other groups are lower; median concentrations are less than $3 \mu\text{g/l}$ and often represent a limit of detection (see Figure A98). 41% of samples have concentrations below the limit of detection. $3.0 \mu\text{g/l Cu}$ is the most frequent limit of detection since 2007 (see Table 3.3).

Table 3.8.9. The upper limits of natural background levels established for copper for all pre-selected data

Copper ($\mu\text{g/l Cu}$)	
Number of MPs	21
Number of data points	464
95th percentile	16

The upper limit of the natural background levels for copper, which is defined nationally and calculated using data collected since 2007, is $16 \mu\text{g/l Cu}$.

3.8.10 Lead

Lead is toxic and may affect aquatic organisms at relatively low concentrations. It forms a major component of ore minerals such as galena (PbS) and secondary sulphate, carbonate and chloride minerals. It is also a trace constituent of potassium feldspars and micas (Deer *et al.*, 1996; Shand *et al.*, 2007). Its natural mobility is low owing to the low solubility of lead hydroxy carbonates and phosphates. The adsorption

of lead on sediment surfaces also tends to maintain low concentrations in groundwater (Hem, 1985).

Concentrations of lead vary over 3 orders of magnitude up to a maximum of approximately 100 µg/l Pb. There is very little variation between the lithological groups (Figure A102). 73% of sample concentrations are below the limit of detection. 0.5 µg/l Pb is the most frequent limit of detection since 2007 (see Table 3.3). Monitoring points with a median greater than 0.5 µg/l are all located south of a line between Dublin Bay and Galway Bay (see Figure A100). Occasionally, individual samples exceed the Irish drinking water standard of 10 µg/l (Government of Ireland, 2014).

High groundwater lead concentrations have been reported in County Clare with lead values in the Mountshannon Spring frequently exceeding the Irish drinking water standard of 10 µg/l (Jones, 1998; Cronin and Deakin, 1999). A high lead anomaly in the subsoils was found over much of the area by an exploration company and is considered to be largely associated with the east-west fault and also disseminated in the sandstone (Cronin and Deakin, 1999).

The upper limit of the natural background levels for lead, which is defined nationally and calculated using data collected since 2007, is 2.9 µg/l Pb.

Table 3.8.10. The upper limits of natural background levels established for lead for all pre-selected data

	Lead (µg/l Pb)
Number of MPs	217
Number of data points	4909
95th percentile	2.9

3.8.11 Mercury

In most natural water systems, the stable form mercury is the free metal, $Hg_{(aq)}$. Mercury may form chloride or hydroxide complexes depending on pH and total chloride concentrations. It is an environmental pollutant and is concentrated in successive biological species along aquatic food chains (Hem, 1985).

94% of samples have concentrations below the limit of detection (Figures A104 and A105). 0.05 µg/l Hg is the

most frequent limit of detection since 2007 (see Table 3.3). Monitoring point 13_010 (Fedamore, located in the Dinantian pure unbedded limestones) has the highest median concentration at 0.15 µg/l Hg. The other monitoring points all have a median of 0.025 µg/l or less.

The upper limit of the natural background levels for Hg, which is defined nationally and calculated using data collected since 2007, is <0.05 µg/l Hg.

Table 3.8.11. The upper limits of natural background levels established for mercury for all pre-selected data

	Mercury (µg/l Hg)
Number of MPs	217
Number of data points	4894
95th percentile	<0.05

3.8.12 Molybdenum

Molybdenum is a rare element [1.2 ppm in igneous rocks (Hem, 1985)] that can occur in a number of oxidation states. It occurs as a sulphide mineral in some ore deposits. The dominant species is pH dependent. It is an essential trace element in animal and plant nutrition (Shand *et al.*, 2007).

90% of samples have concentrations below the limit of detection. 1.0 µg/l Mo is the most frequent limit of detection since 2007 (Table 3.3 and Figure A108). All monitoring points have a median of 0.5 µg/l or less (Figure A107).

The upper limit of the natural background levels for molybdenum, which is defined nationally and calculated using data collected since 2007, is <1.0 µg/l Mo.

Table 3.8.12. The upper limits of natural background levels established for molybdenum for all pre-selected data

	Molybdenum (µg/l Mo)
Number of MPs	19
Number of data points	416
95th percentile	<1

3.8.13 Nickel

Nickel has similar geochemical properties to cobalt in that they both may substitute for iron in ferromagnesian igneous rock minerals and tend to be co-precipitated with iron and manganese oxides. Sulphide minerals are among the most important mineral sources of nickel, particularly pyrite.

Groundwater from the monitoring points 18_010 (Tydavnet) and 23_008 (Kilcoran) show the highest nickel concentrations with medians of 1.9 and 1.8 µg/l, respectively (Figure A110). Nickel concentrations across the other monitoring points show a relatively narrow range, with medians ranging from 0.15 to 1.0 µg/l Ni, with little variation between lithological units (Figure A111).

The upper limit of the natural background levels for nickel, which is defined nationally for unconfined groundwater and calculated using data collected since 2007, is 2.1 µg/l Ni. The 95th percentile for the confined aquifers (2 monitoring points) is 4.7 µg/l Ni. This has been calculated using data from two monitoring points and, therefore, is not defined as a limit to natural background levels.

3.8.14 Radon

Radon is a naturally occurring radioactive gas. It is produced by the radioactive decay of uranium. Its most stable isotope, ²²²Rn, has a half-life of 3.8 days. Long-term exposure to high levels of radon gas increases the risk of developing lung cancer. Ingestion of dissolved radon will result in a radiation dose to the lining of the stomach.

Data for establishing the natural background level of radon came from the Radiological Protection Institute of Ireland (which has since become the Office of Radiological Protection of the Environmental Protection Agency) survey of the natural radioactivity of groundwater sources in Ireland. The survey was carried out between 2007 and 2011 and analysed samples from over 200 groundwater sources. The reader is referred to Radiological Protection Institute of Ireland (2013) for further information.

Radon concentration in the groundwater monitoring points surveyed varied between <0.5 Bq/l and 355 Bq/l. None of the samples exceeded the Office of Radiological Protection's recommended guideline of 500 Bq/l for drinking water supplies. Groundwater

Table 3.8.13. The upper limits of natural background levels established for nickel for unconfined conditions.

	Nickel (µg/l Ni)	
	Unconfined	Confined
Number of MPs	19	2
Number of data points	416	48
95th percentile	2.1	<i>4.7</i>

The 95th percentile for confined conditions is included for information only. The 95th percentile shown in blue italics has been calculated using data from two or fewer monitoring points and therefore is not defined as limits to natural background levels.

Table 3.8.14. The upper limits of natural background levels established for radon for each lithological group

	Radon (Bq/l)					
	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non-calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	31	25	94	38	12	14
Number of data points	87	69	253	95	36	39
95th percentile	33	28	35	141	268	164

from the igneous, non-calcareous sedimentary and metamorphic lithological groups tend to have higher radon concentrations (medians of 80, 44 and 43 Bq/l, respectively) than groundwater from the pure and impure limestone and sand and gravel lithological groups (medians of 15, 11 and 11 Bq/l respectively) (Figure A113 and A114).

One-way ANOVA tests indicated that concentrations in the igneous, non-calcareous sedimentary and metamorphic lithological groups were significantly different from concentrations in the other lithological groups. The upper limits of the natural background levels for the different lithological groups are outlined in Table 3.8.14.

3.8.15 Uranium

Natural uranium is composed of several isotopes, of which uranium-238 is predominant. This nuclide is the starting point in the radioactive decay series which ends with the stable lead isotope lead-206 (Hem, 1985). Uranium is present in ores, such as uraninite, which are relatively rare. Uranium (VI) partitions strongly with phosphate minerals, including hydroxyapatite. High concentrations are also found in zircons, sphenes and monazites. These minerals occur in granitic rocks but, as they are poorly soluble, they are unlikely to be a significant influence on uranium concentration in water. The strong affinity of iron oxides for uranium is also well established (Shand *et al.*, 2007) and this may mean that uranium is more mobile from sedimentary rocks (Adams and Weaver, 1958). Uranium is redox sensitive. Reduced species are only slightly soluble whereas more highly oxidised forms are more soluble (Hem, 1985).

The average crustal concentration of uranium is approximately 2–3 ppm. In Ireland, the highest rock concentrations have been measured in the County

Clare shales (greater than 100 ppm). Relatively high rock concentrations (greater than 10 ppm) have been measured in granites in the Mourne Mountains, the Carnsore granites and parts of the County Galway and County Donegal granites (Wilmot Noller *et al.*, 2015).

Groundwater uranium concentrations show a variation across three orders of magnitude within each lithological group (Figure A117). The results for each lithological group show a bimodal distribution (see Figure A117) with 41% of samples having concentrations below the limit of detection. It should be noted that a number of limits of detection have been used since 2007 (0.1, 1.0 and 2.0 µg/l U), but 1.0 µg/l U is the most frequent limit of detection (Table 3.3 and Figure A117). Each lithological group, except for the igneous and metamorphic groups, have at least one monitoring point with a median greater than 3 µg/l U. In contrast, monitoring points in the igneous lithological group all have medians of less than 0.9 µg/l U (Figure A116 and Appendix B). This may be due to the stability of uranium in igneous rocks, relative to sedimentary rocks, despite the higher rock concentrations. It may also be due to bias in the sampling network. The majority of the EPA's monitoring points are public water supplies and, as such, the network represents high yielding sources of potable water. In 2008, the EPA introduced monitoring of a set of "poorly productive" aquifers into its long-term monitoring programme (CDM and OCM, 2009). These monitoring points have not been routinely analysed for this report; however, an inspection of their uranium values shows that the Newvillage monitoring points, situated in the Oughterard Granite, Co. Mayo, have very high uranium values with an interquartile range between 11 and 132 µg/l U. The report by EPA "Water Quality in Ireland 2001–2003" (EPA, 2005) noted relatively high levels of uranium in County Wicklow (132 µg/l), County Carlow (53 µg/l) and County Kildare (60 µg/l).

Table 3.8.15. The upper limits of natural background levels established for uranium for each lithological group

Uranium (µg/l U)						
	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non-calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	30	29	96	31	13	16
Number of data points	659	604	2230	711	297	360
95th percentile	5.0	3.1	2.8	3.8	1.0	2.6

These values are in excess of the WHO's provisional guideline value for uranium which is 30 µg/l (WHO, 2012) and the report states that alternative supplies have been sourced. It should be noted there is no national drinking water standard for uranium (Government of Ireland, 2014).

One-way ANOVA tests indicated that there are significant differences between the uranium concentrations in groundwater from the different lithological groups, using the EPA national monitoring network (excluding the EPA's poorly productive aquifer monitoring points). The upper limit of the natural background levels for each lithological group are shown in Table 3.8.15. It should be noted that the literature and data from the EPA's poorly productive aquifer monitoring points suggest that the uranium concentration in groundwater from igneous rocks may be higher. For example, the Newvillage monitoring point has an interquartile range between 11 and 132 µg/l U.

3.8.19 Zinc

Zinc is essential in plant and animal metabolism (Hem, 1985). It is a primary constituent of the zinc sulphide and a range of zinc carbonates and oxides. It also occurs as a trace constituent in a number of common minerals including clays, shales and calcite. It only has one oxidation state (Zn²⁺) and, therefore, is not affected by redox conditions.

Groundwater from the non-calcareous sedimentary lithological group tends to have higher zinc concentrations than groundwater from other lithological groups (Figure A119 and A120). Monitoring points 03_005 and 11_013 have median zinc concentrations

of 44 and 18 µg/l Zn, respectively. Median concentrations in the majority of the other monitoring points are less than 10 µg/l Zn.

One-way ANOVA tests indicated that concentrations in the non-calcareous sedimentary lithological group were significantly different from concentrations in the other lithological groups. The upper limit of the natural background levels for the non-calcareous sedimentary and pure limestone sedimentary groups are shown in Table 3.8.10. The 95th percentile for the other lithological groups are included for information only. They have been calculated using data from two or fewer monitoring points and are therefore not defined as limits to natural background levels.

3.9 Summary of Natural Background Level Results

Natural background levels have been established for 39 parameters comprising field parameters, major ions, minor ions, nutrients and trace elements. The upper limits (and lower limits where appropriate) are presented in Table 3.9. The natural background levels are grouped based on how the natural background level was established: (a) by lithological group; (b) by groundwater vulnerability categories; (c) by flow regime categories; (d) nationally for unconfined conditions; and (e) nationally for all pre-selected data. These groups reflect the potential influence of hydrogeological and hydrogeochemical settings on the concentration of each parameter.

The natural background levels established are typically comparable to natural background levels established for other countries or regions (Table 1.1). The Irish natural background levels of some major ions (such

Table 3.8.16. The upper limits of natural background levels established for zinc for pure limestone and non-calcareous sedimentary lithological groups

Zinc (µg/l Zn)						
	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non-calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	1	2	10	3	1	2
Number of data points	11	22	99	28	11	21
95th percentile	<i>16</i>	<i>30</i>	31	67	<i>17</i>	<i>37</i>

The 95th percentiles for the other lithological groups are included for information only. They have been calculated using data from two or fewer monitoring points and are therefore not defined as limits to natural background levels (shown in blue italics).

Table 3.9. Natural background levels established for parameters defined (a) by lithological group; (b) by groundwater vulnerability categories; (c) by flow regime categories; (d) nationally for unconfined conditions; and (e) nationally for all pre-selected data. The groups are outlined in Chapter 4

(a) Lithological groups							
Parameter	Unit	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non-calcareous sedimentary	5. Igneous	6. Metamorphic
pH	pH units	7.5	8.3	7.9	7.1	7.5	7.7
Electrical conductivity	µS/cm	583	554	601	392	60	546
Turbidity	NTU	1.7	3.1	5.8	1.7	1.9	4.7
Calcium	mg/l Ca	111	113	117	64	8.2	114
Alkalinity	m/l CaCO ₃	350	290	322	216	43	310
Silica	mg/l SiO ₂	13	17	10	14	19	16
Aluminium	µg/l Al	15	19	26	16	131	19
Barium	µg/l Ba	586	195	179	427	179	114
Chromium	µg/l Cr	11	11	11	9.0	4.3	8.0
Radon	Bq/l	33	28	35	141	268	164
Strontium	µg/l Sr	651	2900	575	320	498	772
Total hardness	mg/l CaCO ₃	310	294	328	212	42	303
Uranium	µg/l U	5.0	3.1	2.8	3.8	1.0	2.6
Zinc	µg/l Zn	16	30	31	67	17	37
(b) Groundwater vulnerability							
Parameter	Unit	Extreme X	Extreme	High	Moderate	Low	
Dissolved oxygen (mg/l O ₂)	mg/l O ₂	Lower limit	4.4	0.8	3.9	0.7	0.5
		Upper limit	12	11	12	8.1	5.9
(c) Flow regime							
Unit	Parameter	Inter-granular	Karstified	Poorly productive	Productive fissured		
µg/l P	Total phosphorus (µg/l P)	Upper limit	13	26	16	-	

Values which are shown in blue italics are included for information only. They have been calculated using data from two or fewer monitoring points and are therefore not defined as natural background levels.

Table 3.9. Continued

(d) Influence of unconfined and confined aquifers			
Parameter	Unit	Unconfined	Confined
Sodium	mg/l Na	13	105
Magnesium	mg/l Mg	17	42
Potassium	mg/l K	2.1	5.9
Sulphate	mg/l SO ₄	13	223
Fluoride	mg/l F	0.2	2.6
Nitrate	mg/l NO ₃	8.7	1.5
Ammonium	mg/l N	0.1	0.4
Boron	µg/l B	15	573
Iron	µg/l Fe	268	762
Manganese	µg/l Mn	23	176
Nickel	µg/l Ni	2.1	4.7
(e) National parameters			
Parameter	Unit	All pre-selected data	
Chloride	mg/l Cl	21	
Molybdate reactive phosphorus	µg/l P	17	
Antimony	µg/l Sb	0.5	
Arsenic	µg/l As	2.0	
Copper	µg/l Cu	16	
Lead	µg/l Pb	2.9	
Nitrite	mg/l NO ₂	<0.05	
Beryllium	µg/l Be	<1	
Cadmium	µg/l Cd	<0.4	
Cobalt	µg/l Co	<1	
Mercury	µg/l Hg	<0.05	
Molybdenum	µg/l Mo	<1	

Values which are shown in blue italics are included for information only. They have been calculated using data from two or fewer monitoring points and are therefore not defined as natural background levels.

as electrical conductivity, calcium, potassium, chloride and sulphate) and trace elements (such as copper,

molybdenum and nickel) are relatively low with respect to the values established for other countries or regions.

4 Conclusions and Recommendations

The ranges in natural background levels for 39 parameters in Irish groundwater are presented. These natural background levels may be used as a basis for updating threshold values for groundwater pollutants as well as a standard against which future pollution events may be assessed. The upper (and lower where appropriate) limits of natural background levels are presented in Table 3.9.

The parameters may be grouped based on how the natural background levels have been established:

1. Lithologically controlled: the concentrations of the majority of the field parameters (pH, electrical conductivity, turbidity), some major ions (calcium, total hardness and alkalinity), minor ions (barium, silica, strontium) and some trace elements (aluminium, chromium, radon, uranium and zinc) appear to be controlled by lithology and the natural background is defined for each lithological group.
2. National parameters:
 - (a) there is little spatial variation in the concentration of chloride, copper, molybdate reactive phosphorus, antimony, arsenic and lead. The natural background levels for these parameters are defined nationally;
 - (b) below the limit of detection: more than 90% of samples for nitrite, beryllium, cobalt, mercury, molybdenum and cadmium have concentrations below the limit of detection. The natural background levels for these parameters are defined nationally and defined as below the limit of detection.
3. Variation noted between confined and unconfined groundwater: natural background levels are defined nationally with a note regarding the likely impact of confined aquifers:
 - (a) the concentration of nitrate, ammonium, iron, manganese and nickel (by proxy) may be influenced by redox conditions and the difference in concentrations between confined and unconfined groundwater has been noted;
 - (b) the concentration of sodium, magnesium, potassium (and boron) may be affected by ion exchange and the difference in concentrations between confined and unconfined groundwater has been noted; and
 - (c) the concentration of sulphate may be affected by residence times and the difference in concentrations between confined and unconfined groundwater has been noted.
4. Other controls: the concentration of some parameters appear to be controlled by something other than lithology and the natural background levels for the following parameters have been defined accordingly:
 - (a) natural background levels for dissolved oxygen are defined using groundwater vulnerability;
 - (b) natural background levels for total phosphorus are defined using flow regime;

Most parameters show a large variation in natural groundwater chemistry with concentrations varying over a number of orders of magnitude. This variation reflects the complex interactions between rainfall input, soils, subsoils and aquifers. Because of this large natural variation, caution should be exercised when applying the results of this report. Where anomalous, naturally high concentrations were identifiable from the data (e.g. barium) or from literature (e.g. arsenic, fluoride, lead and uranium) details have been included. However, the list of anomalies included is not exhaustive.

The results were produced using subsets of the EPA's national groundwater monitoring network. The natural background levels for parameters which are not potentially influenced by anthropogenic activities (Al, Sb, As, Ba, Be, Cr, Co, Pb, Hg, Si, Sr and U) were established using the largest dataset and, therefore, confidence in those parameters is highest. Even so, caution should be exercised when applying the results for these parameters particularly to different, typically smaller scale studies. The results presented here are established at a national or regional scale and, as

such, average out the spatial variability of parameters, which include topography, vegetation, recharge rates, aquifer type, well depths and proximity to natural sources of the parameter of interest (Kelly and Panno, 2008). Therefore, when interpreting the results, emphasis should be placed on understanding the local geochemical setting and its relevance nationally.

Natural background levels for nutrients (NO_3 , NO_2 , NH_4 , molybdate reactive phosphorus and total phosphorus) and parameters that are potentially influenced by anthropogenic activities (alkalinity, B, Cd, Ca, Cl, electrical conductivity, Cu, dissolved oxygen, F, Fe, Mg, Mn, Mo, Ni, pH, K, Na, SO_4 , total hardness, turbidity and Zn) were established using less than 10% of the monitoring network. This reflects the extensive nature of anthropogenic activities in Ireland and hence the potential alteration of groundwater chemistry. This is a small number of monitoring points to perform this type of analysis and statistical confidence in the natural background levels established for these parameters is low. However, the methodology follows best practice and has made best use of the available data, and results are comparable to natural background levels established in other countries or regions. The nutrients (nitrate and phosphorus) are

of particular interest from a WFD perspective. In the 2008 WFD cycle, 16% of groundwater bodies, mostly in the south-east, were designated at risk of poor status due to the potential deterioration of estuarine surface water quality by nitrate from groundwater. 13% of groundwater bodies, mostly in the west, were designated poor status due to the potential deterioration of surface water quality by phosphorus from groundwater.

To improve the confidence in the results for the nutrients and the parameters that are potentially influenced by anthropogenic activities it would be useful to:

- analyse data from appropriate monitoring points from other data sources such as the EPA's poorly productive monitoring network (EPA and CDM, 2010), public or group water supplies and the Tellus first order stream data; while there will be difficulties compiling the different sampling and analytical techniques used in different networks, confidence will be improved by a larger dataset; and
- analyse historical data where available for individual parameters.

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Abbreviations

ANOVA	Analysis of variance
BRIDGE	Background cRiteria for the Identification of Groundwater thrEsholds
BaSeLiNe	Natural Baseline Quality in European Aquifers
CFC	Chlorofluorocarbon
CSO	Central Statistics Office
EPA	Environmental Protection Agency
GSI	Geological Survey of Ireland
GWDD	Groundwater Daughter Directive
GWWG	Groundwater Working Group
LAWA	Working Group of the Federal States of Germany on Water Problems
LPIS	Land Parcel Identification System
MP	Monitoring point
NaCl	Sodium chloride
NTU	Nephelometric Turbidity Units
OCM	O'Callaghan Moran & Associates
OSI	Ordnance Survey Ireland
TOC	Total organic carbon
WFD	Water Framework Directive
ZOC	Zone of contribution

List of Appendices

Appendix A

- Bubble plots for each parameter showing the spatial variation in concentration across the country.
- Descriptive statistics for each dataset and for each lithological group.
- Box and whisker plots for each monitoring point or lithological group.
- Cumulative frequency plots for each lithological group.

Appendix A is included as part of the main report and starts on page 75.

Appendix B

Box and whisker plots for each monitoring point for parameters whose concentrations are unlikely to be influenced by anthropogenic activities.

Appendix B is available from <http://erc.epa.ie/safer/iso19115/displayISO19115.jsp?isoID=3091> (Excel format).

Appendix C

Groundwater monitoring data used to establish natural background levels.

Appendix C is available from <http://erc.epa.ie/safer/iso19115/displayISO19115.jsp?isoID=3091> (Access format).

Other Outputs Arising from Research Fellowship

Evaluation and Interpretation of Groundwater Monitoring Data and the Implications for Groundwater in Ireland (2007-FS-WQ-16-S4)

The research fellowship evaluated the EPA's groundwater quality and level monitoring data. In addition to "Assessing and Developing Natural Background Levels for Chemical Parameters in Irish Groundwater", presented in this report, other outputs from the fellowship include:

Water Framework Directive Groundwater Tests

Assistance was provided to the EPA Groundwater and Hydrometric Unit with the design and implementation of groundwater tests, which defined the 2008 groundwater body status. This information fed into the first cycle of the River Basin Management Plans required by the Water Framework Directive. Information on the results is available from www.epa.ie/water/watmg/wfd/rbmp/ and www.wfdireland.ie/documents.html.

Groundwater Level Investigations

Groundwater level data available to the EPA was reviewed, investigated and published. The results were published in the following outputs:

Tedd, K., Misstear, B., Coxon, C., Daly, D., Hunter Williams, N.H., Craig, M. and Mannix, A., 2011. *Review of Groundwater Level Data in the South Eastern River Basin District*. EPA STRIVE Programme 2007–2013. Environmental Protection Agency, Johnstown Castle, Ireland. Available online: www.epa.ie

Tedd, K., Misstear, B., Coxon, C., Daly, D. and Hunter Williams, N., 2012. Hydrogeological insights from groundwater level hydrographs in southeast Ireland. *Quarterly Journal of Engineering Geology and Hydrogeology* 45: 19–30. DOI: <http://doi.org/10.1144/1470-9236/10-026>

Groundwater Phosphorus Investigations

A review of EPA groundwater phosphorus monitoring data was undertaken in consultation with EPA groundwater and hydrometric staff. The results of the review were presented in an internal EPA report circulated in May 2010. The report aimed to raise awareness and promote discussion of the issues associated with phosphorus sampling and analysis, and to provide recommendations on phosphorus sampling and analysis based on international best practice. As a result of this review the remaining planned phosphorus investigations were not carried out.

Groundwater Nitrate Investigations

An investigation of EPA groundwater nitrate monitoring data in the South Eastern River Basin District was carried out and presented in the journal *Science for the Total Environment*.

Tedd, K., Coxon, C.E., Misstear, B.D.R., Daly, D., Craig, M., Mannix, A. and Hunter Williams, N., 2014. An integrated pressure and pathway approach to the spatial analysis of groundwater nitrate: a case study from the southeast of Ireland. *Science of The Total Environment* 476–477: 460–476. DOI: <http://dx.doi.org/10.1016/j.scitotenv.2013.12.085>

Investigation of Field Parameters at Selected Springs

Groundwater flow and quality relationships were investigated at four EPA spring monitoring sites. The sites comprised Shanballymore, Cork; Paulstown, Kilkenny; Rockingham, Roscommon; and Killeglan, Roscommon and were selected because of their contrasting settings. The research involved the installation and regular maintenance of OTT Hydrolab MiniSonde 5 multi-parameter probes. Temperature, conductivity, pH, dissolved oxygen and turbidity were collected over a 4-year period. However the data was not sufficiently reliable to carry out the proposed

analysis. The methodology, data and challenges were presented in an International Association of Hydrogeologists (Irish Group) Technical Discussion

Meeting in December 2013. This presentation is available at <http://erc.epa.ie/safer/iso19115/displayISO19115.jsp?isoID=3092#files>

Appendix A

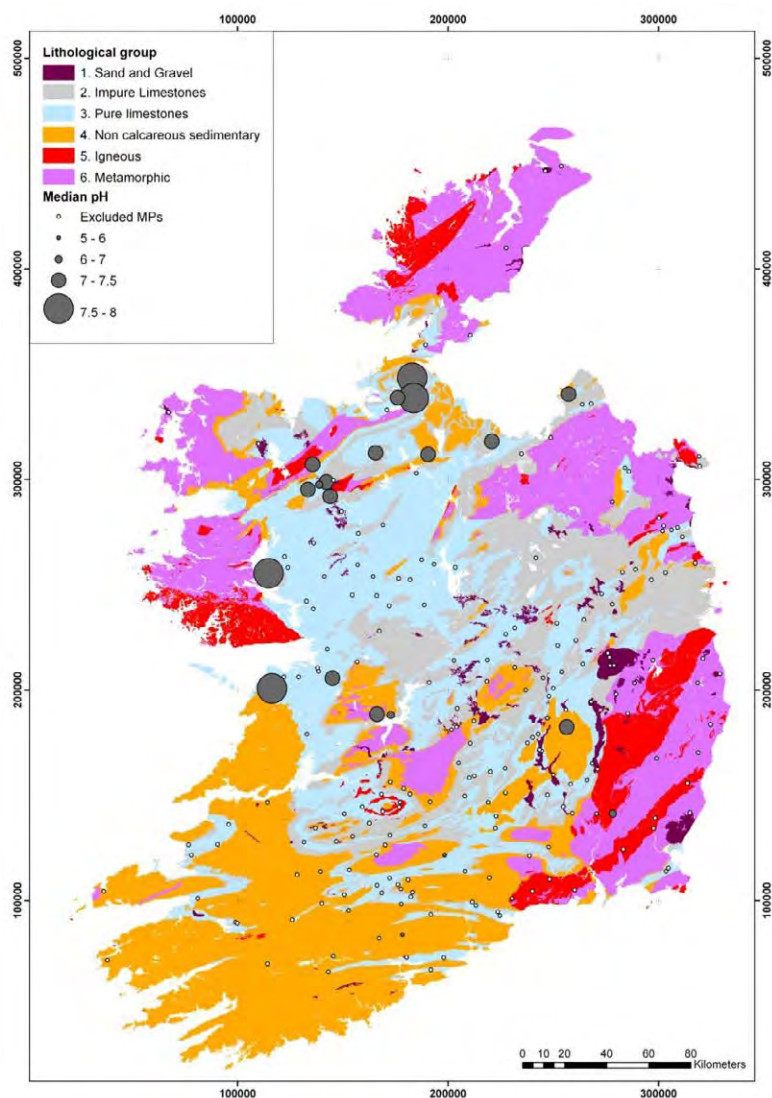


Figure A1. Location and median pH values of the monitoring points used to establish natural background levels for pH in Irish groundwater.

Table A1. Descriptive statistics of pH for monitoring points used to establish natural background levels for pH in Irish groundwater presented for all unconfined monitoring points and by lithological group

pH (pH units)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	419	61	22	50	223	57	23	44
5th percentile	5.80	6.90	6.84	6.79	6.71	5.35	5.35	6.68
Median	7.20	7.30	7.18	7.30	7.30	6.03	6.07	7.10
95th percentile	7.86	7.94	7.48	8.25	7.90	7.13	7.53	7.73

MP, monitoring point.

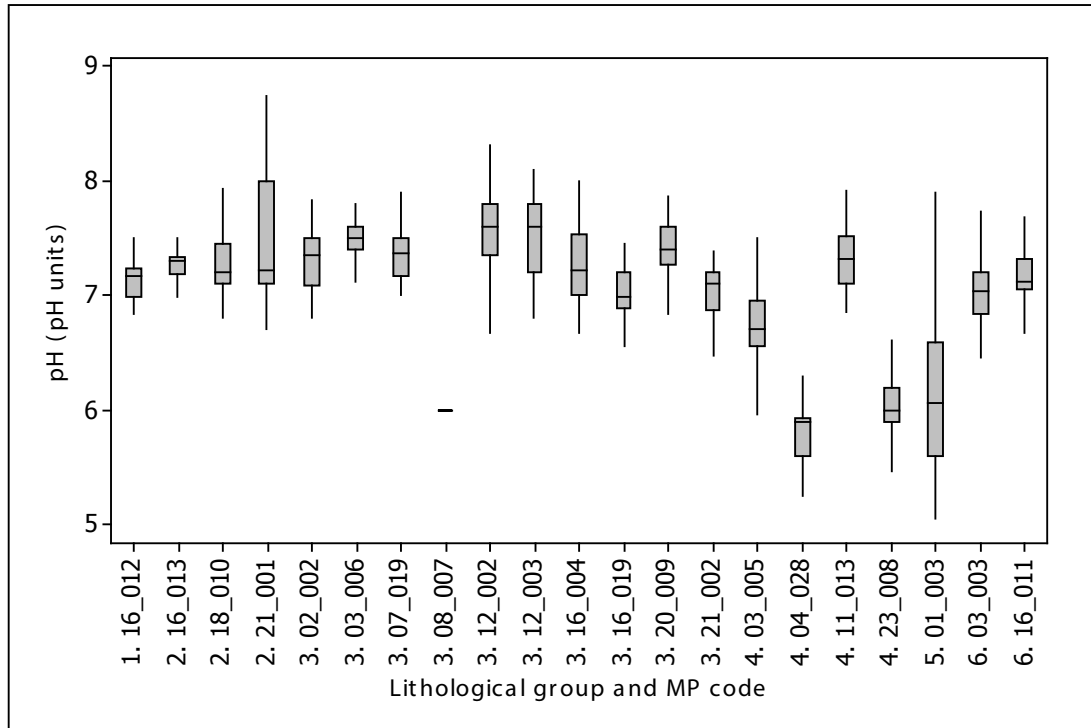


Figure A2. Box and whisker plot summarising pH data from each monitoring point used to establish natural background levels for pH in Irish groundwater. Lithological groups: 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

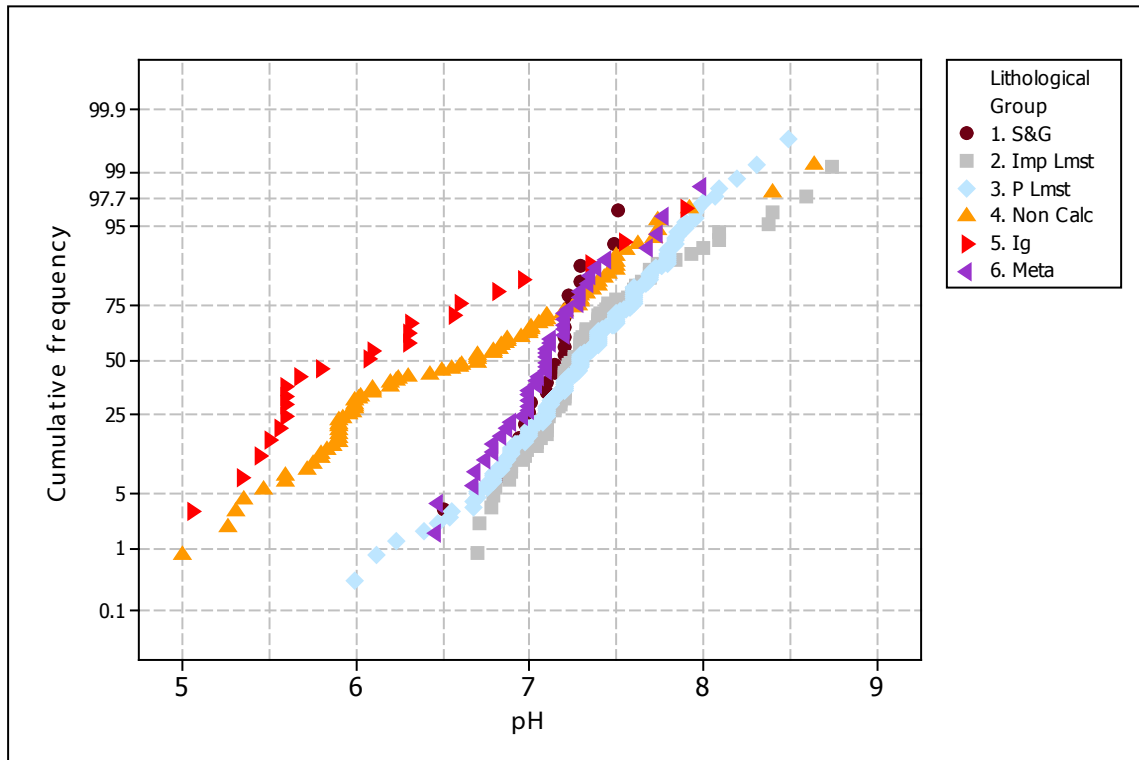


Figure A3. Cumulative frequency diagram showing the distribution of pH data used to establish natural background levels for pH in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Electrical Conductivity

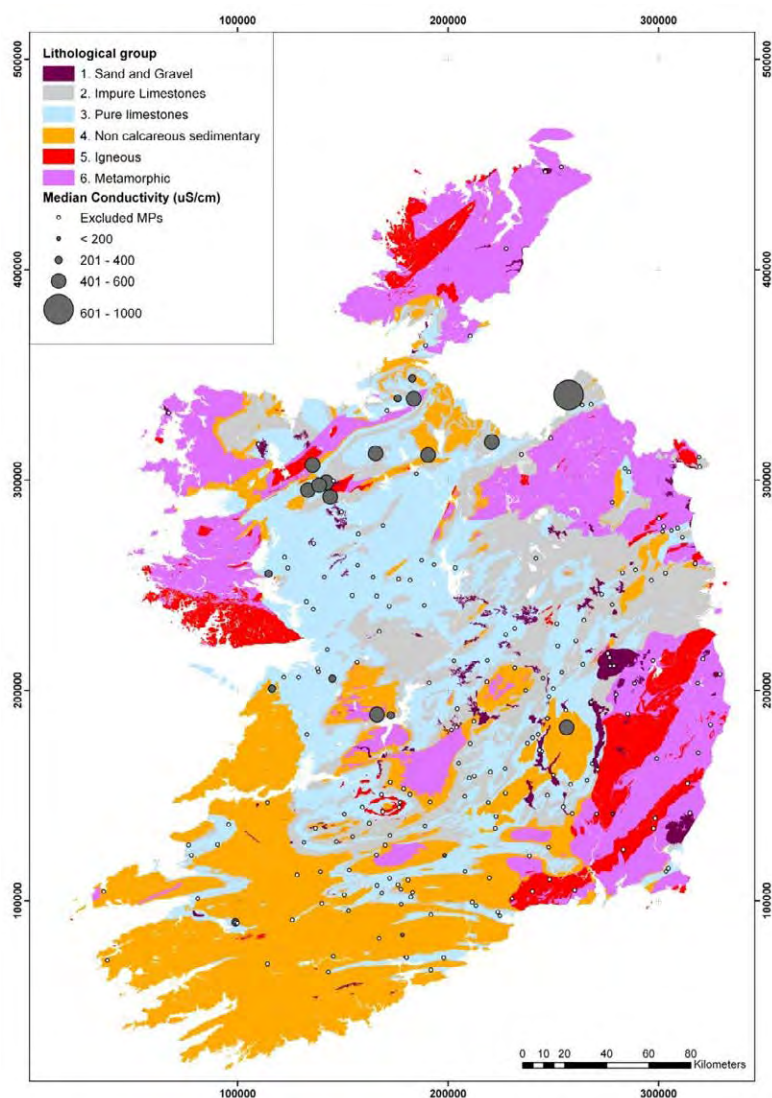


Figure A4. Location and median electrical conductivity values of the monitoring points used to establish natural background levels for electrical conductivity in Irish groundwater.

Table A2. Descriptive statistics of electrical conductivity for monitoring points used to establish natural background levels for electrical conductivity in Irish groundwater presented for all unconfined monitoring points and by lithological group

Electrical conductivity ($\mu\text{S}/\text{cm}$)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	439	61	23	54	236	59	22	45
5th percentile	68.17	457.00	396.80	301.60	179.43	98.80	19.70	327.80
Median	408.00	651.00	515.00	472.00	417.00	184.00	49.50	479.00
95th percentile	560.00	1074.00	583.10	554.35	600.75	391.56	60.47	546.00

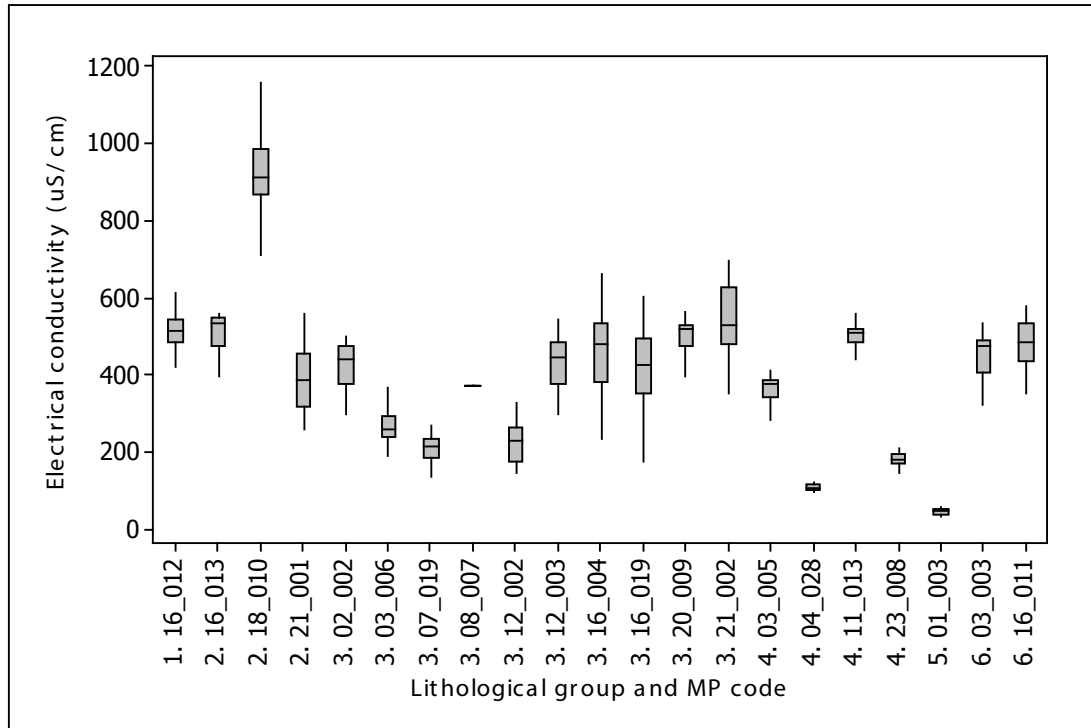


Figure A5. Box and whisker plot summarising electrical conductivity data from each monitoring point used to establish natural background levels for electrical conductivity in Irish groundwater. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

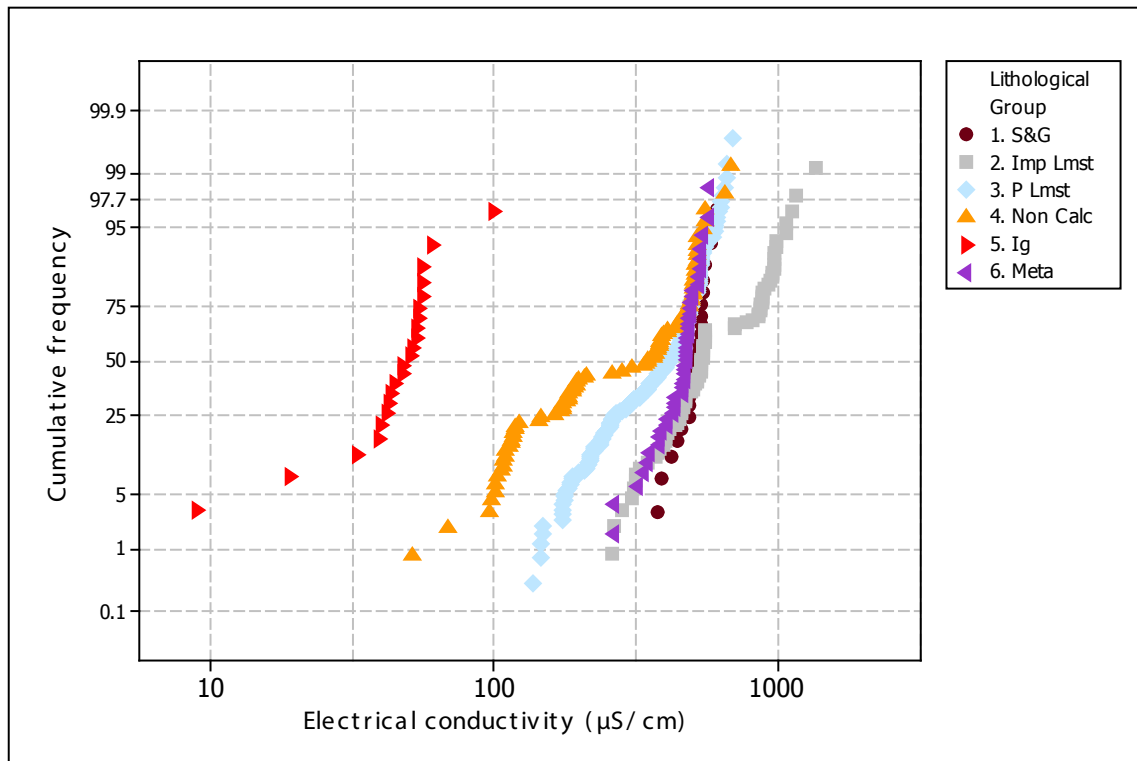


Figure A6. Cumulative frequency diagram showing the distribution of electrical conductivity data used to establish natural background levels for electrical conductivity in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Turbidity

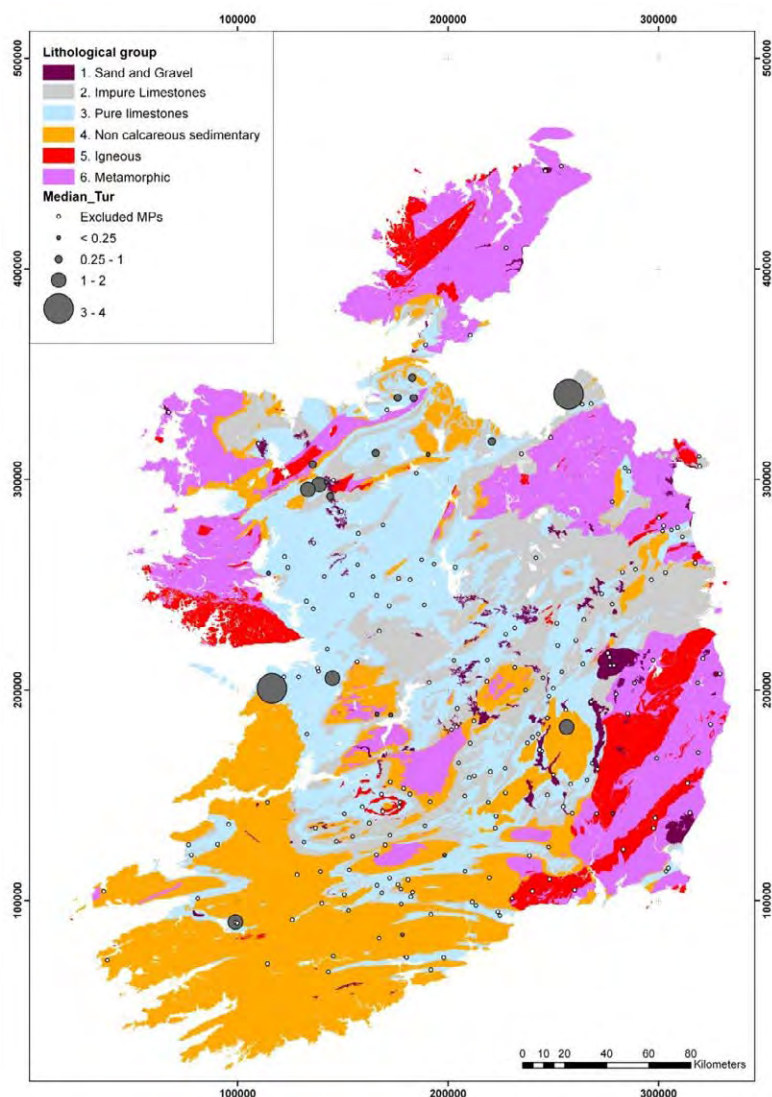


Figure A7. Location and median turbidity values of the monitoring points used to establish natural background levels for turbidity in Irish groundwater.

Table A3. Descriptive statistics of turbidity for monitoring points used to establish natural background levels for turbidity in Irish groundwater presented for all unconfined monitoring points and by lithological group

Turbidity (NTU)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	498	74	24	62	267	74	24	47
5th percentile	0.05	0.15	0.05	0.06	0.06	0.05	0.05	0.05
Median	0.50	2.00	0.25	0.50	0.90	0.25	0.25	0.25
95th percentile	5.12	10.54	1.72	3.09	5.80	1.73	1.88	4.75

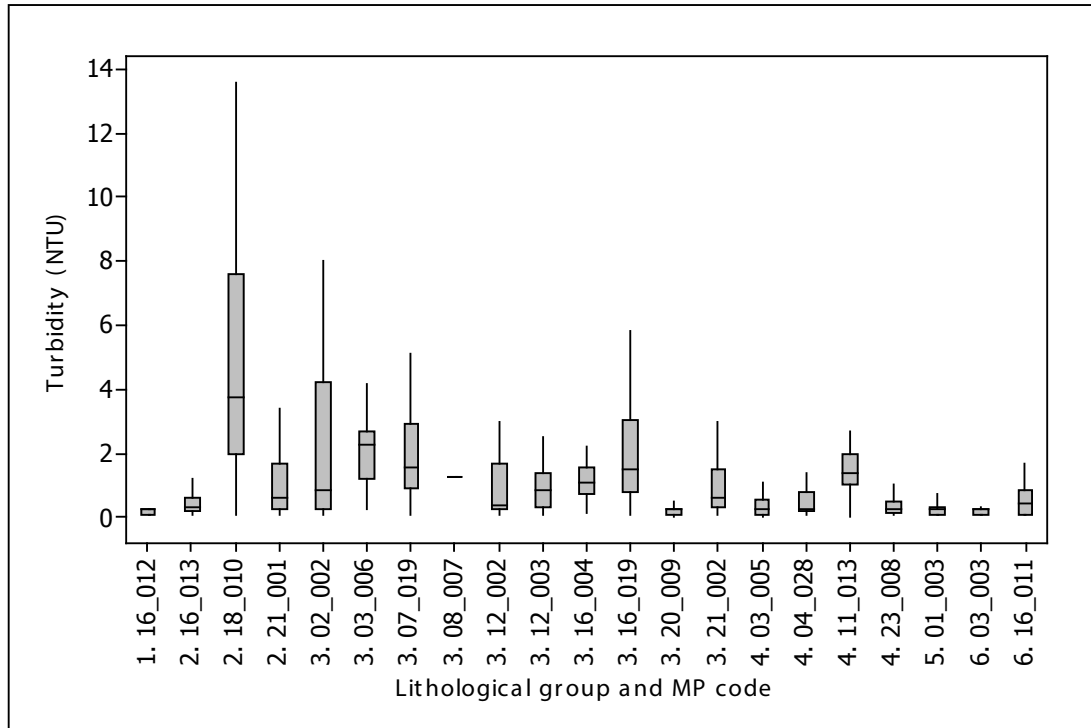


Figure A8. Box and whisker plot summarising turbidity data from each monitoring point used to establish natural background levels for turbidity in Irish groundwater. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

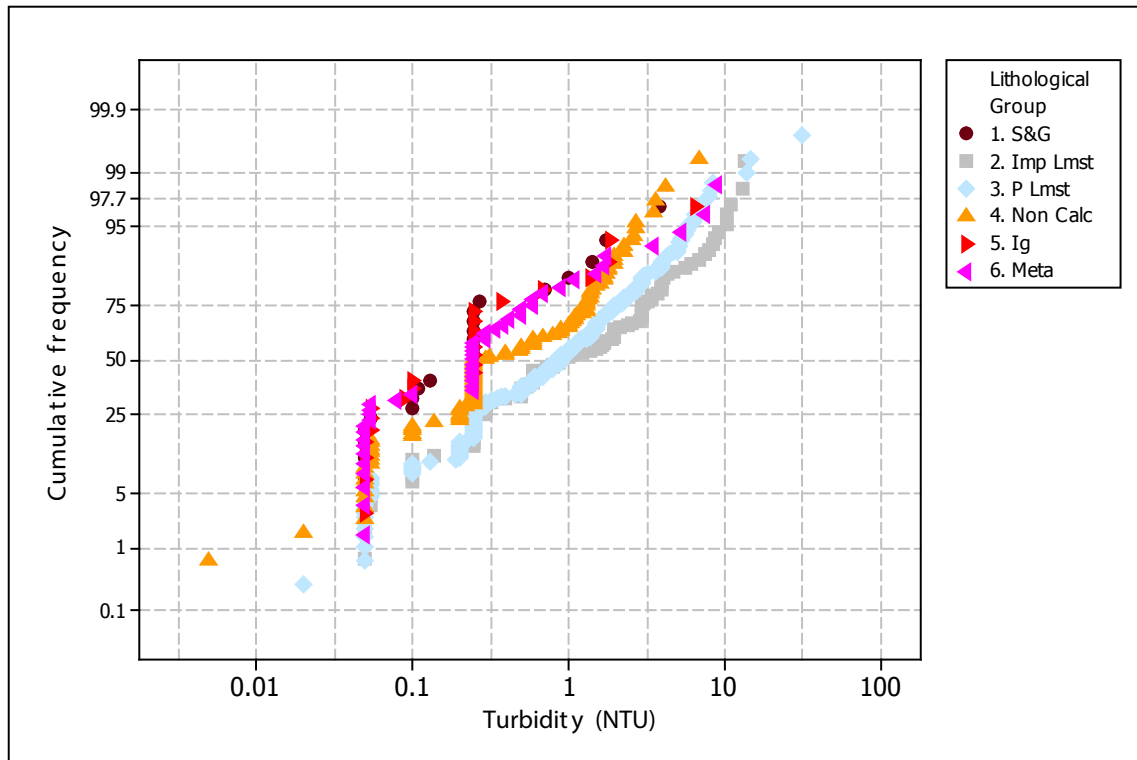


Figure A9. Cumulative frequency diagram showing the distribution of turbidity data used to establish natural background levels for turbidity in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Dissolved Oxygen

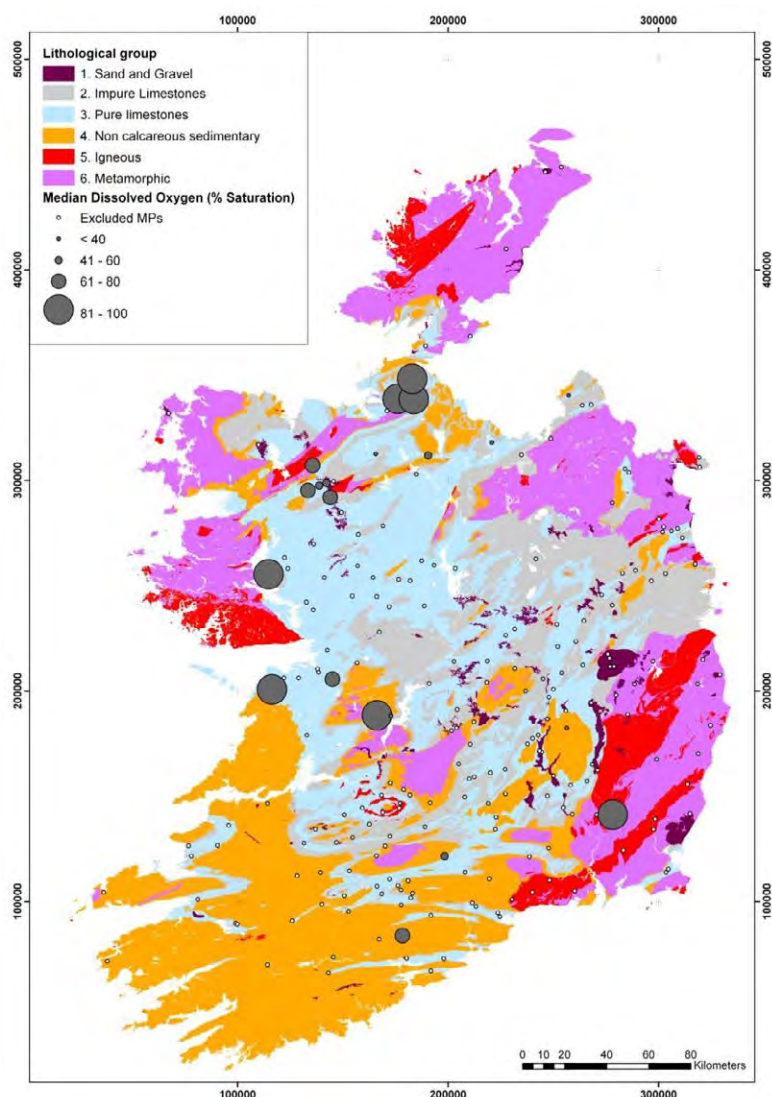


Figure A10. Location and median dissolved oxygen values of the monitoring points used to establish natural background levels for dissolved oxygen in Irish groundwater.

Table A4. Descriptive statistics of dissolved oxygen for monitoring points used to establish natural background levels for dissolved oxygen in Irish groundwater presented for all monitoring points and by lithological group

Dissolved oxygen (mg/l O ₂)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	316	33	19	33	166	44	17	37
5th percentile	1.52	0.46	3.82	5.40	1.07	1.04	8.68	3.87
Median	7.00	3.95	6.00	7.63	6.22	5.52	10.70	8.10
95th percentile	11.33	9.31	7.19	11.32	10.51	9.40	13.15	13.14

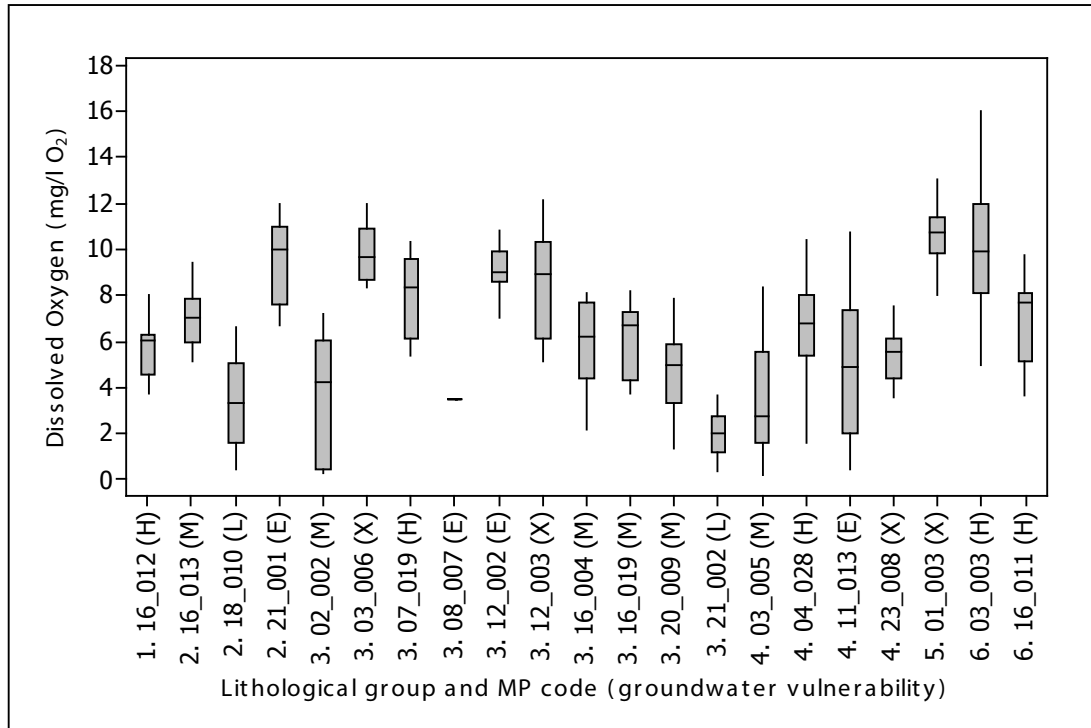


Figure A11. Box and whisker plot summarising dissolved oxygen data from each monitoring point used to establish natural background levels for dissolved oxygen in Irish groundwater. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

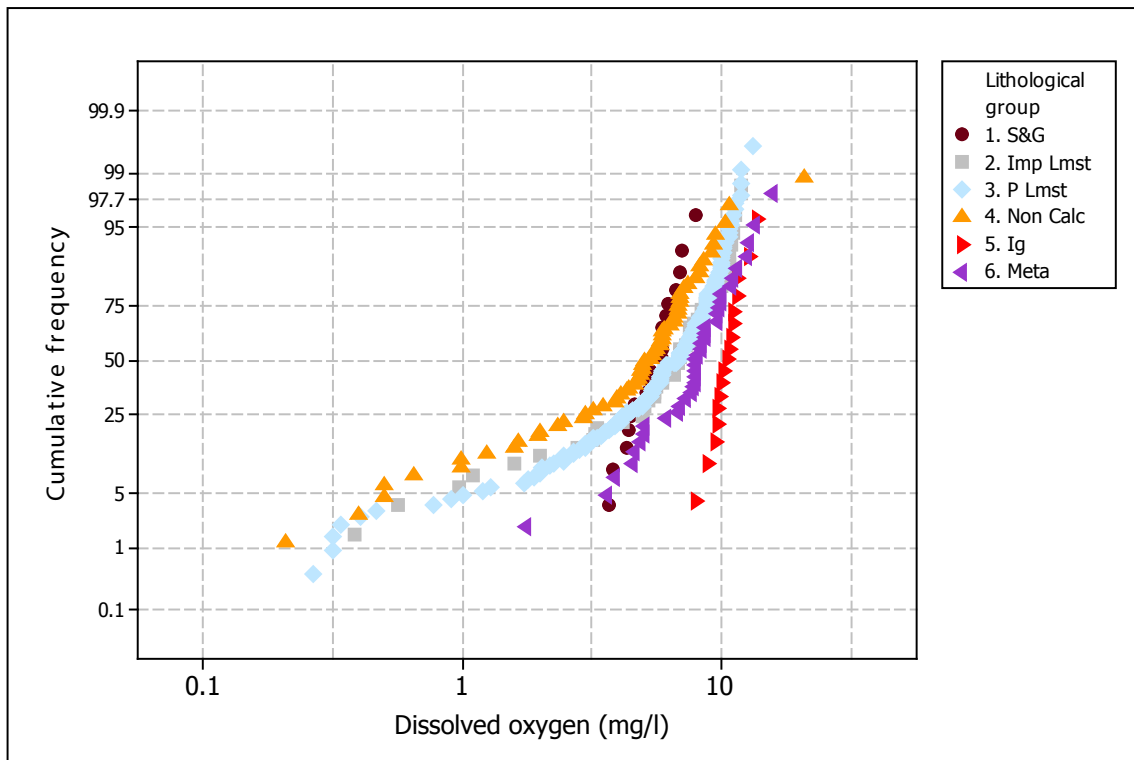


Figure A12. Cumulative frequency diagram showing the distribution of dissolved oxygen data used to establish natural background levels for dissolved oxygen in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Calcium

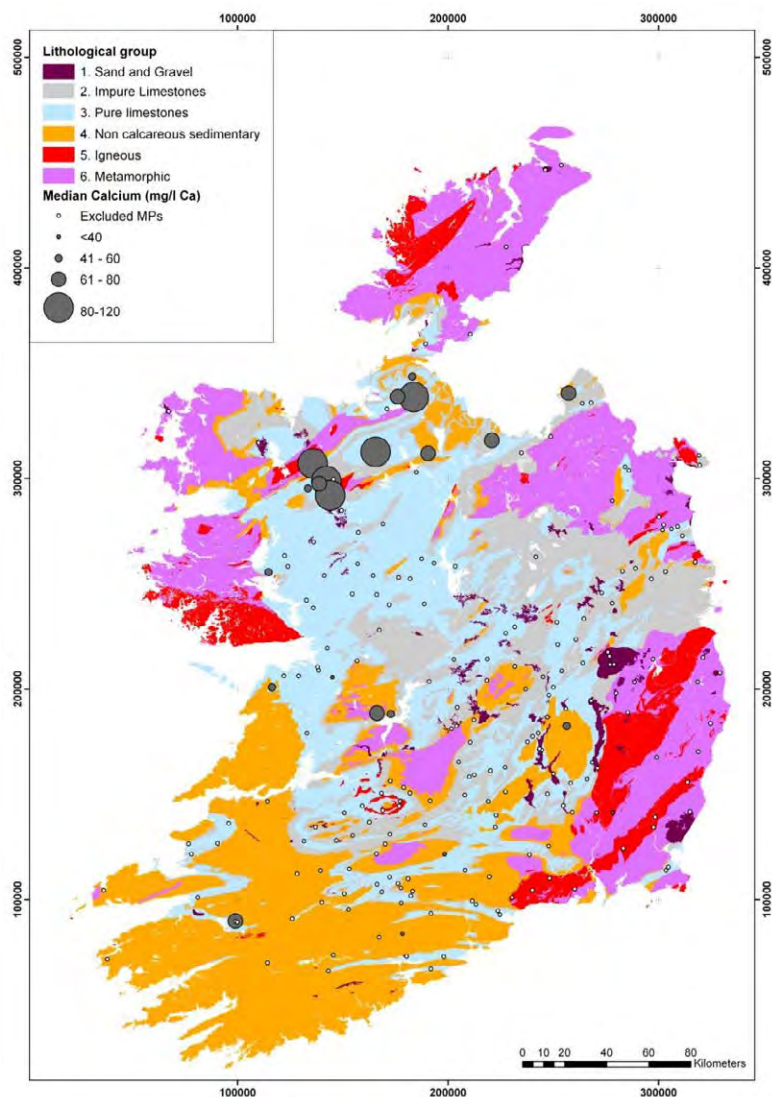


Figure A13. Location and median calcium values of the monitoring points used to establish natural background levels for calcium in Irish groundwater.

Table A5. Descriptive statistics of calcium for monitoring points used to establish natural background levels for calcium in Irish groundwater presented for all unconfined monitoring points and by lithological group

Calcium (mg/l Ca)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	416	48	25	44	216	59	24	48
5th percentile	5.78	43.98	89.90	50.91	30.28	6.17	1.71	68.20
Median	70.81	56.41	99.10	88.10	70.81	15.60	3.33	83.95
95th percentile	112.93	109.10	111.24	112.85	117.30	63.63	8.17	114.16

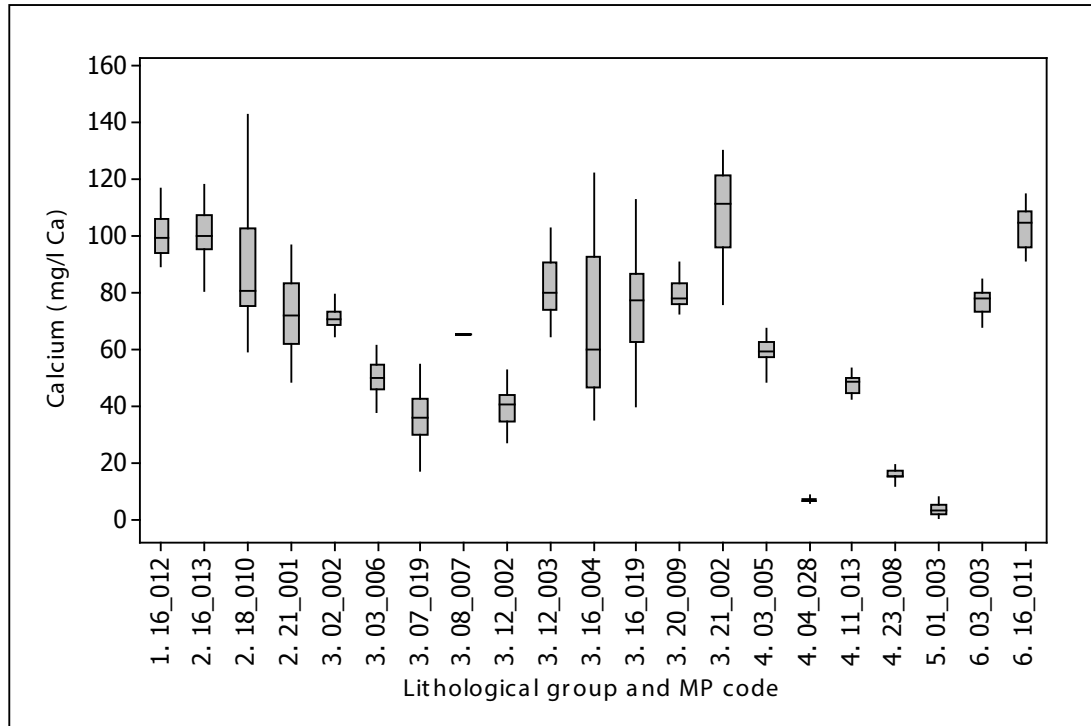


Figure A14. Box and whisker plot summarising calcium data from each monitoring point used to establish natural background levels for calcium in Irish groundwater. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

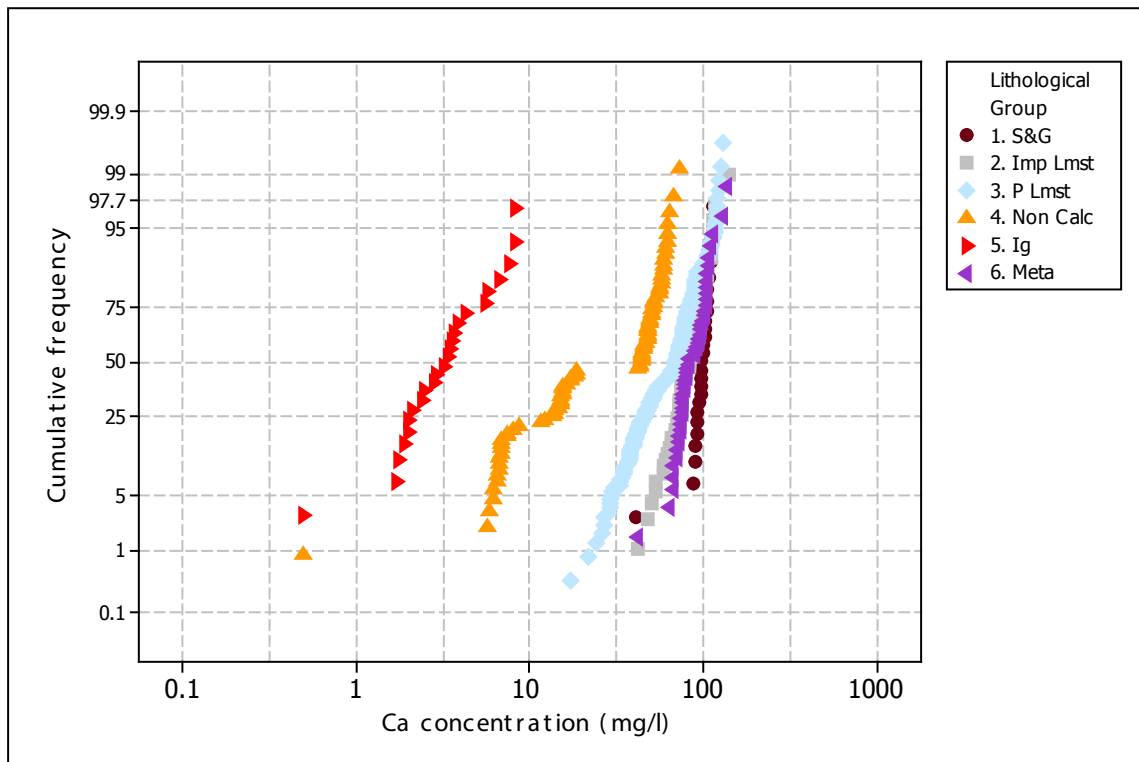


Figure A15. Cumulative frequency diagram showing the distribution of calcium data used to establish natural background levels for calcium in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Magnesium

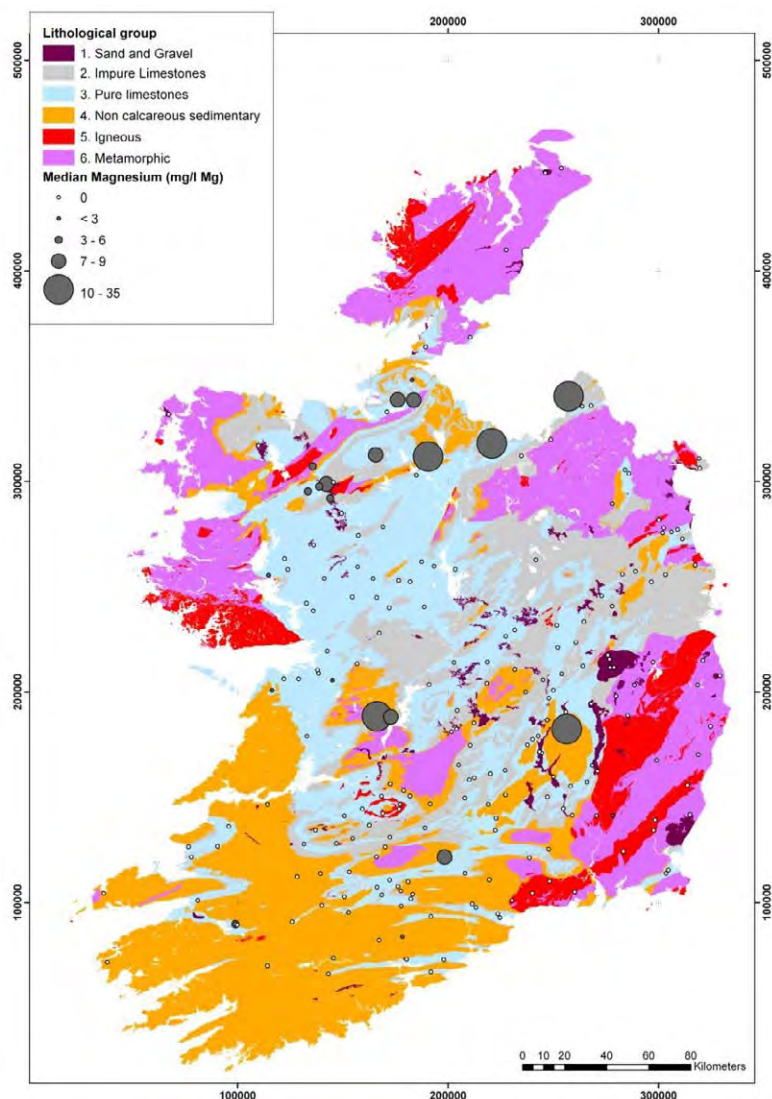


Figure A16. Location and median magnesium values of the monitoring points used to establish natural background levels for magnesium in Irish groundwater.

Table A6. Descriptive statistics of magnesium for monitoring points used to establish natural background levels for magnesium in Irish groundwater presented for all monitoring points and by lithological group

Magnesium (mg/l Mg)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	416	48	25	44	216	59	24	48
5th percentile	1.43	21.82	6.49	3.86	1.76	1.90	0.28	2.65
Median	5.40	28.65	7.00	5.17	4.89	6.14	0.89	5.70
95th percentile	16.53	42.46	7.83	11.32	17.55	11.32	1.68	13.67

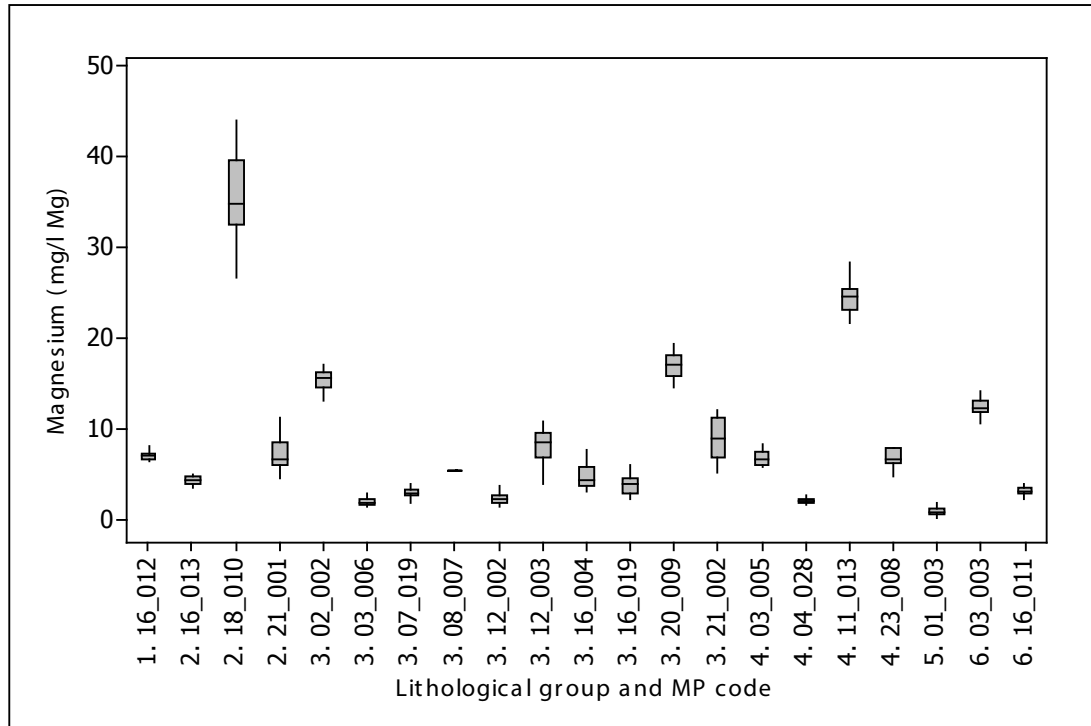


Figure A17. Box and whisker plot summarising magnesium data from each monitoring point used to establish natural background levels for magnesium in Irish groundwater. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

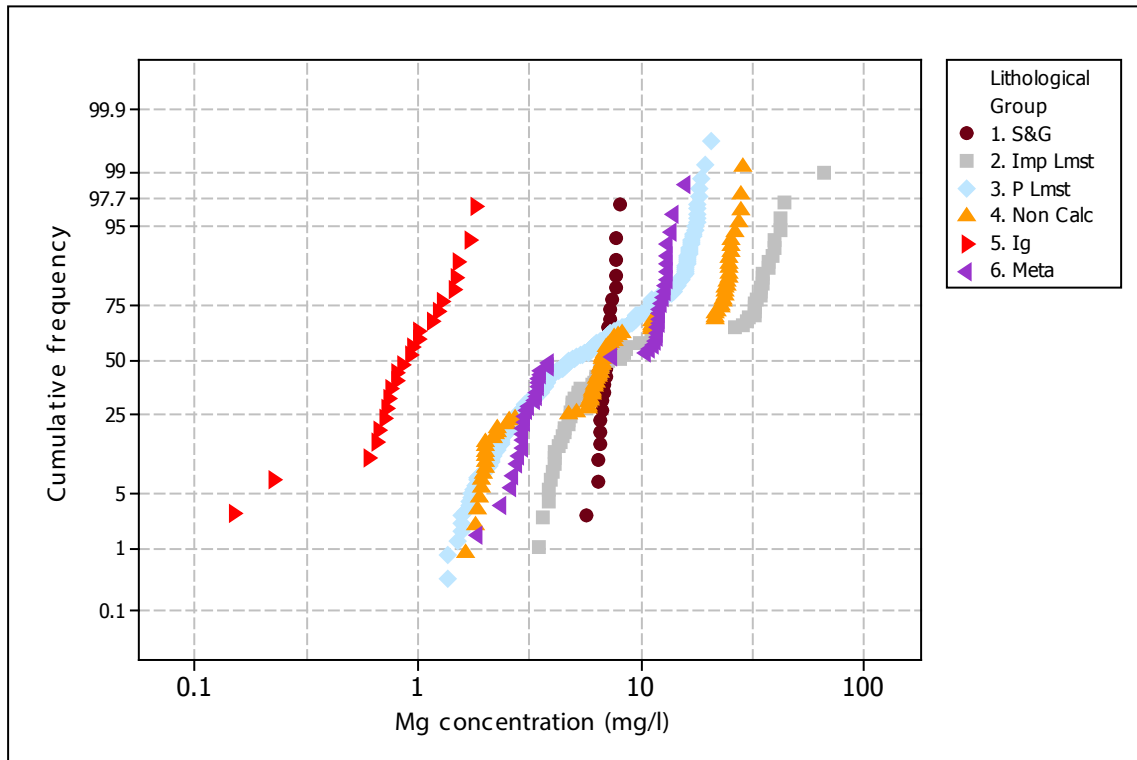


Figure A18. Cumulative frequency diagram showing the distribution of magnesium data used to establish natural background levels for magnesium in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Total Hardness

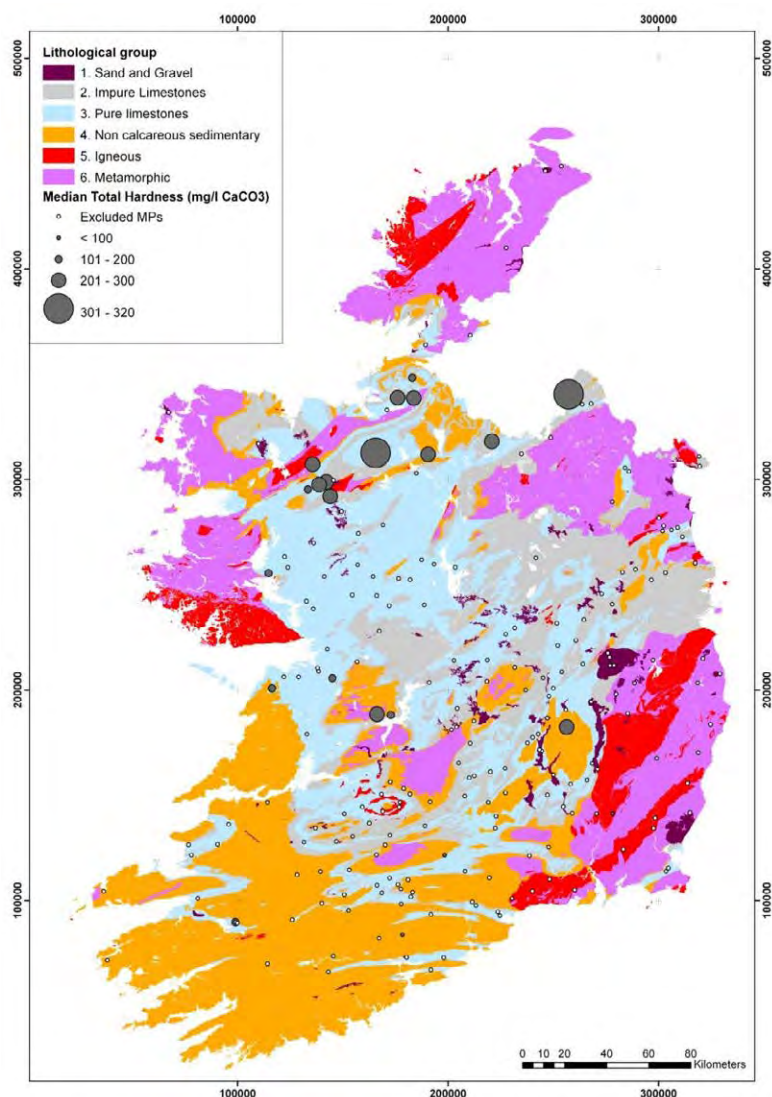


Figure A19. Location and median total hardness values of the monitoring points used to establish natural background levels for total hardness in Irish groundwater.

Table A7. Descriptive statistics of total hardness for monitoring points used to establish natural background levels for total hardness in Irish groundwater presented for all unconfined monitoring points and by lithological group

Total hardness (mg/l CaCO ₃)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	510	83	25	65	279	70	24	47
5th percentile	27.98	206.20	175.40	144.39	96.00	25.05	5.84	222.30
Median	218.65	246.00	283.00	250.00	218.00	70.50	13.75	250.00
95th percentile	310.00	434.07	309.92	293.60	328.41	211.97	42.05	303.01

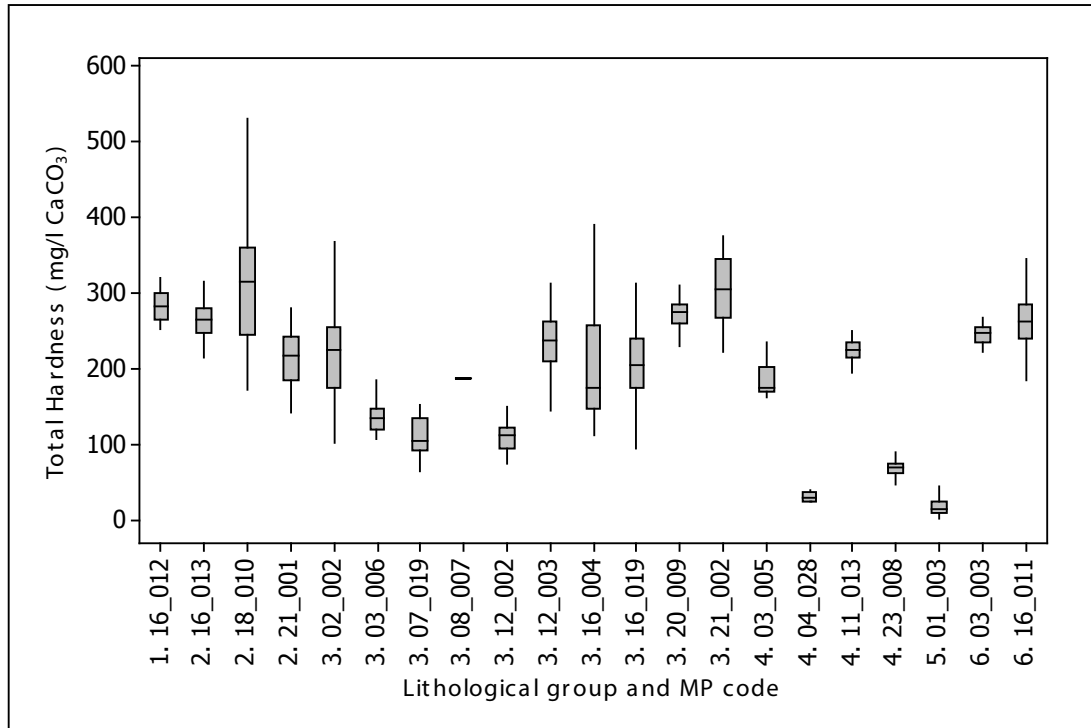


Figure A20. Box and whisker plot summarising total hardness data from each monitoring point used to establish natural background levels for total hardness in Irish groundwater. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

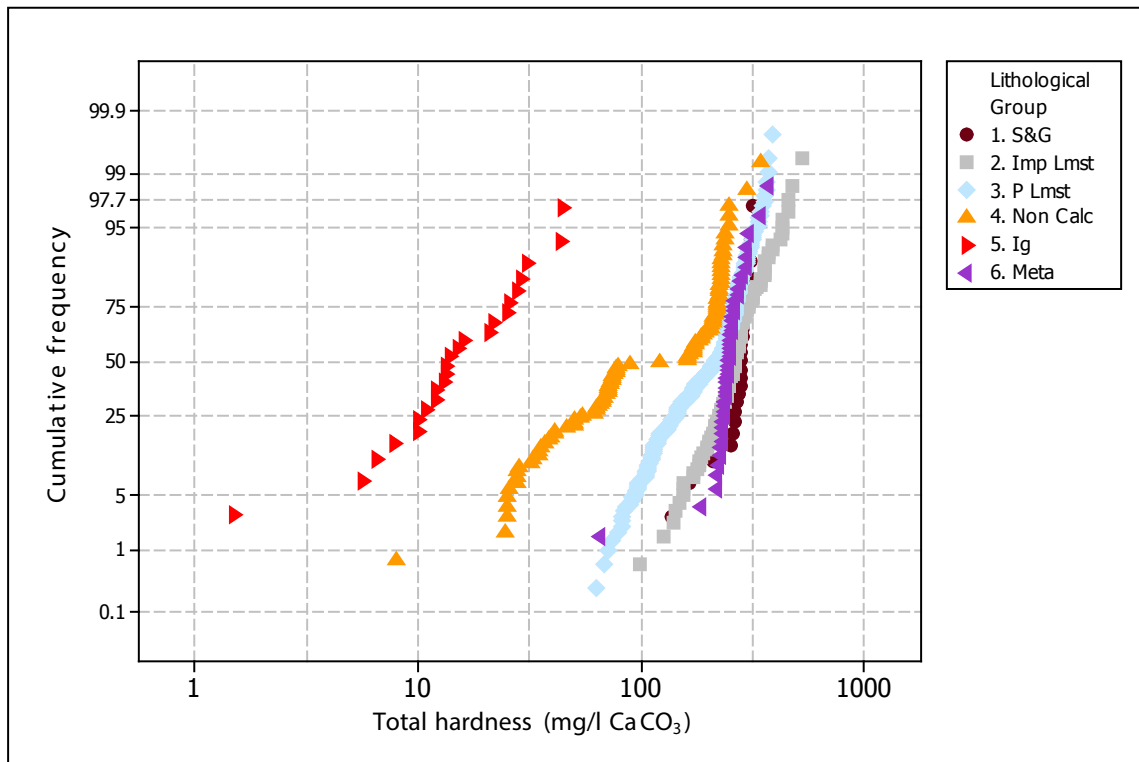


Figure A21. Cumulative frequency diagram showing the distribution of total hardness data used to establish natural background levels for total hardness in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Sodium

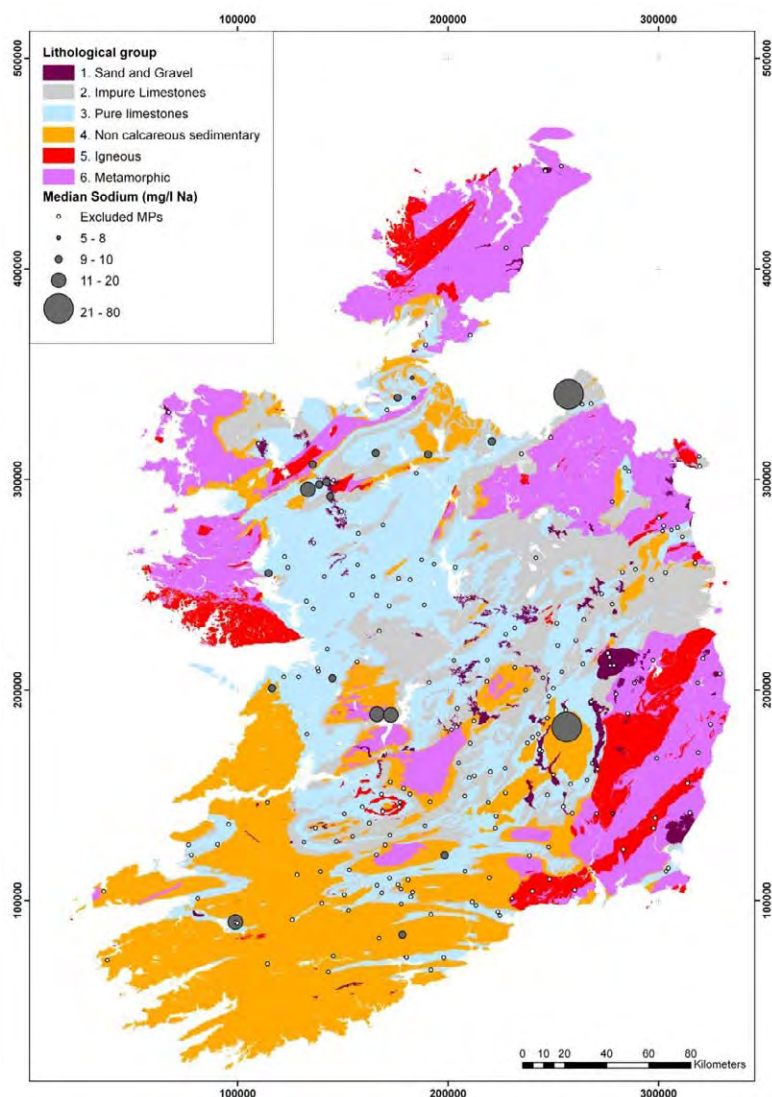


Figure A22. Location and median sodium values of the monitoring points used to establish natural background levels for sodium in Irish groundwater.

Table A8. Descriptive statistics of sodium for monitoring points used to establish natural background levels for sodium in Irish groundwater presented for all monitoring points and by lithological group

Sodium (mg/l Na)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	416	48	25	44	216	59	24	48
5th percentile	5.60	20.91	8.36	6.82	6.03	8.25	2.79	7.61
Median	9.00	46.00	9.00	8.50	8.95	10.00	5.60	9.60
95th percentile	13.07	105.44	10.21	10.55	13.84	12.51	6.95	12.17

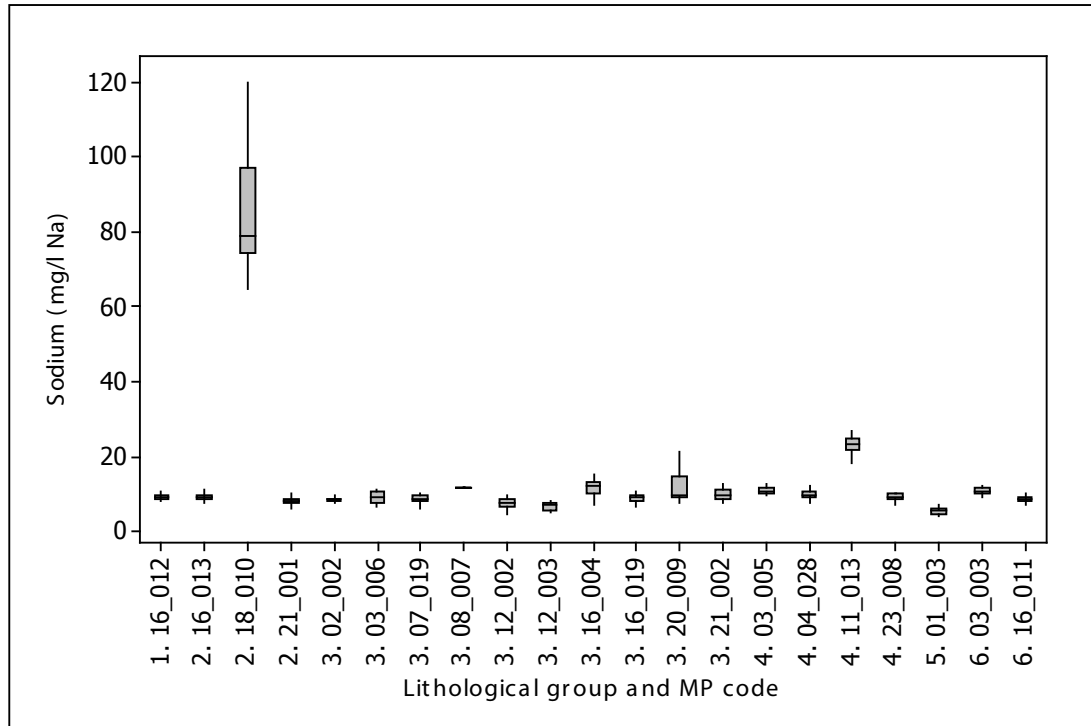


Figure A23. Box and whisker plot summarising sodium data from each monitoring point used to establish natural background levels for sodium in Irish groundwater. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

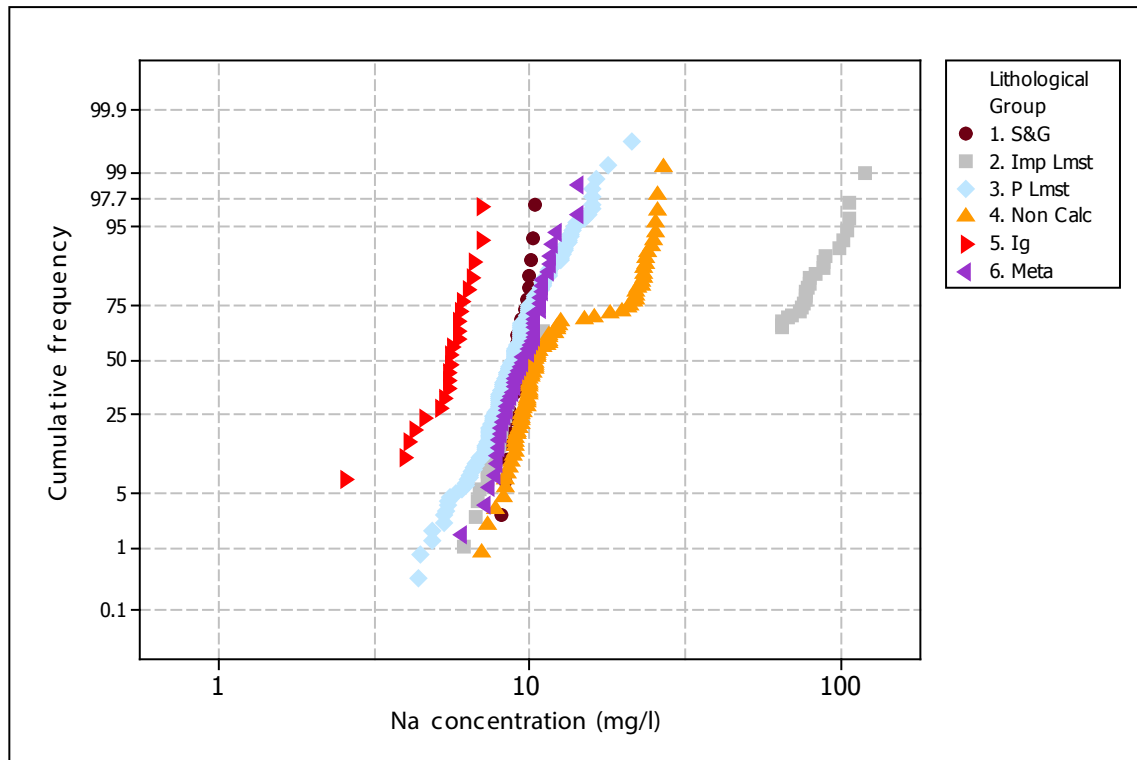


Figure A24. Cumulative frequency diagram showing the distribution of sodium data used to establish natural background levels for sodium in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Potassium

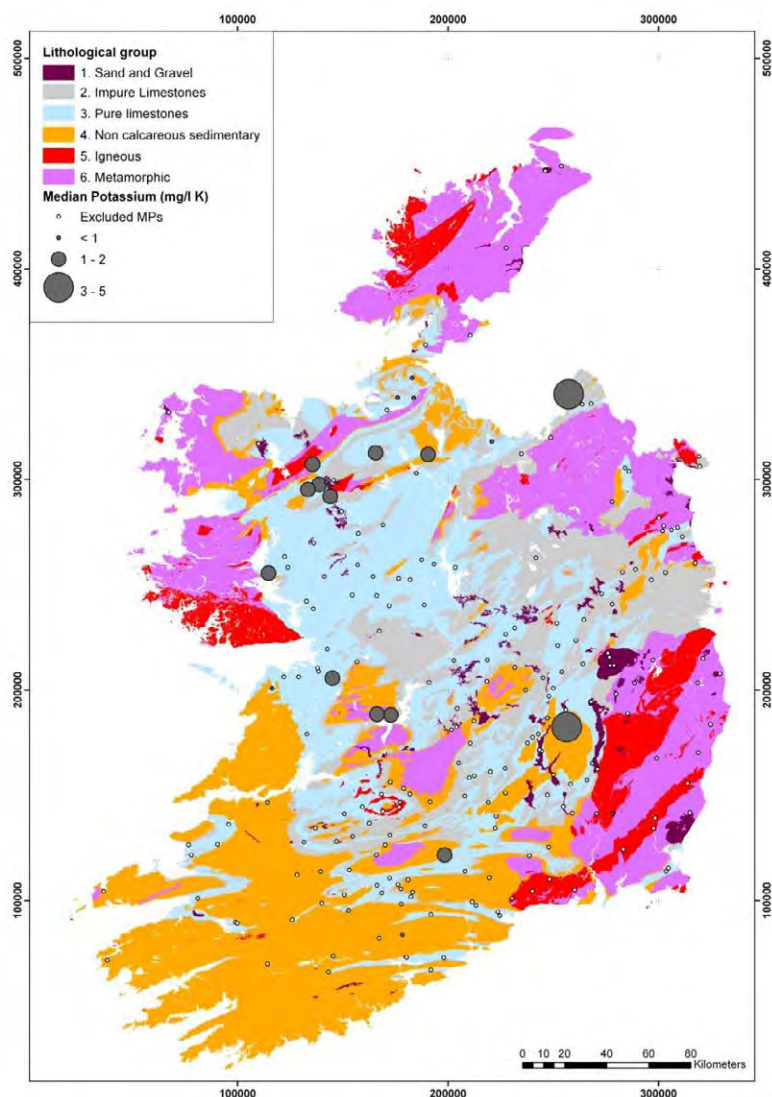


Figure A25. Location and median potassium values of the monitoring points used to establish natural background levels for potassium in Irish groundwater.

Table A9. Descriptive statistics of potassium for monitoring points used to establish natural background levels for potassium in Irish groundwater presented for all monitoring points and by lithological group

Potassium (mg/l K)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	416	48	25	44	216	59	24	48
5th percentile	0.23	3.46	0.75	0.41	0.30	0.48	0.10	1.03
Median	1.12	3.97	0.89	0.95	1.28	1.09	0.20	1.50
95th percentile	2.10	5.86	1.10	1.80	2.22	2.12	0.45	1.80

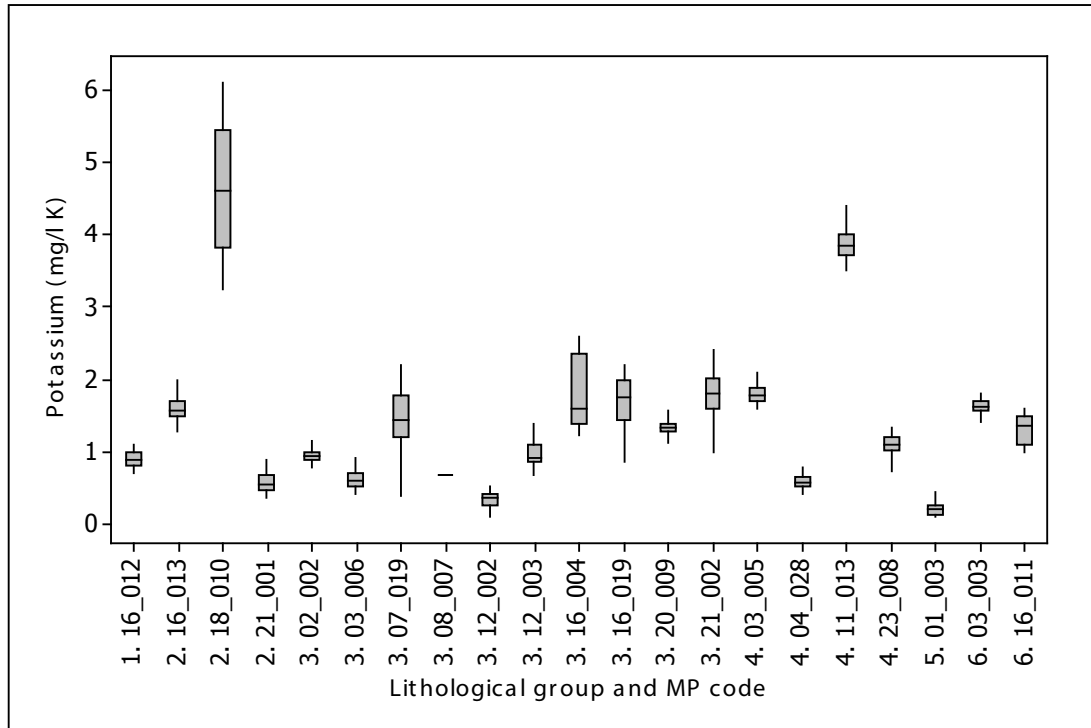


Figure A26. Box and whisker plot summarising potassium data from each monitoring point used to establish natural background levels for potassium in Irish groundwater. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

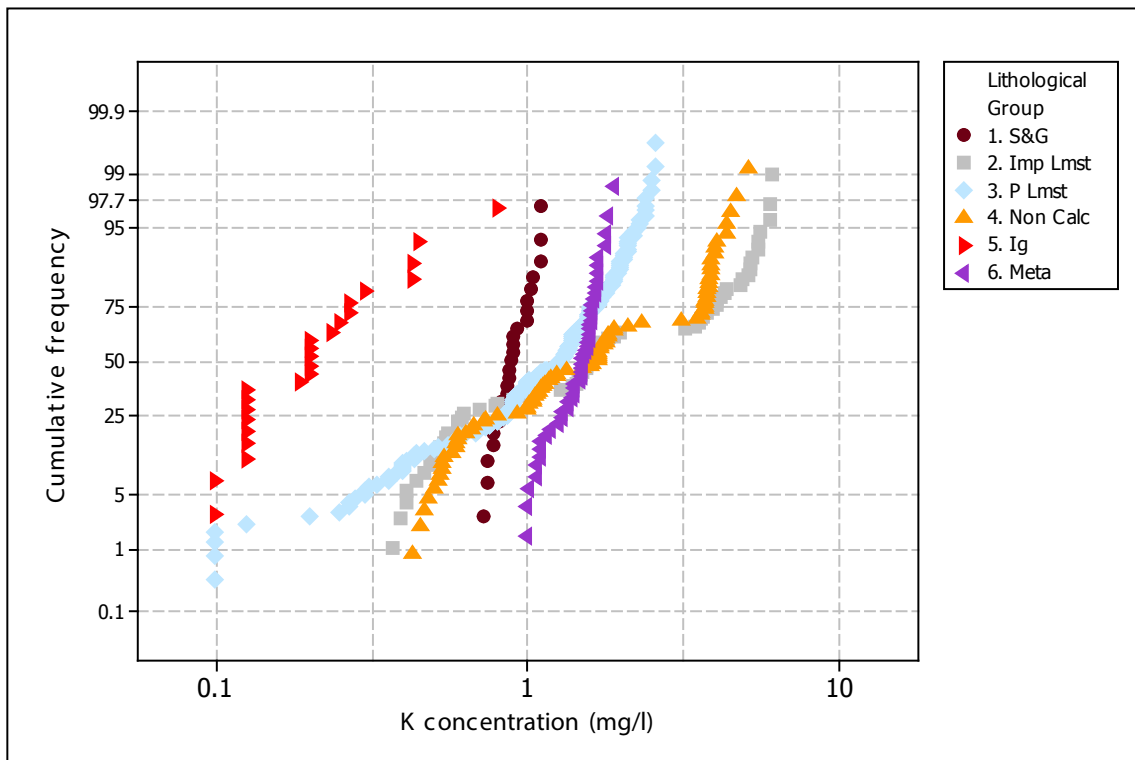


Figure A27. Cumulative frequency diagram showing the distribution of potassium data used to establish natural background levels for potassium in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Bicarbonate (Alkalinity)

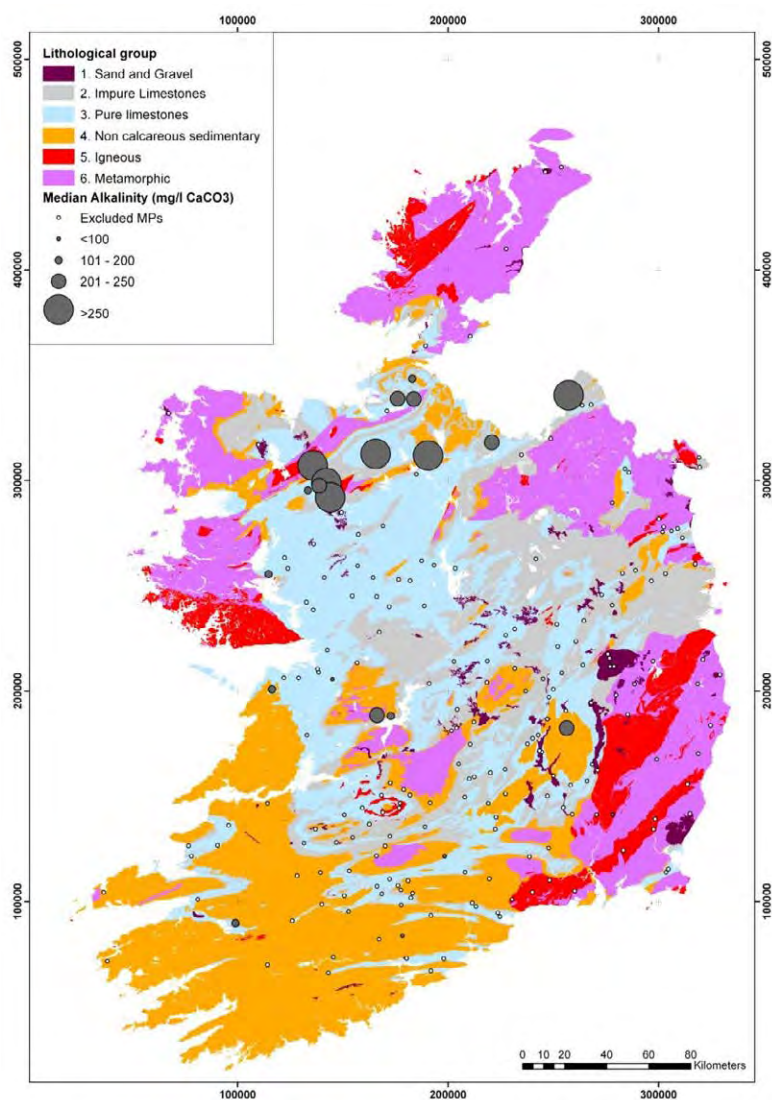


Figure A28. Location and median bicarbonate (alkalinity) values of the monitoring points used to establish natural background levels for bicarbonate (alkalinity) in Irish groundwater.

Table A10. Descriptive statistics of bicarbonate (alkalinity) for monitoring points used to establish natural background levels for bicarbonate (alkalinity) in Irish groundwater presented for all monitoring points and by lithological group

Bicarbonate (alkalinity) (mg/l CaCO ₃)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	513	93	25	65	278	73	24	48
5th percentile	20.00	219.20	227.40	144.40	95.70	16.80	6.00	227.03
Median	220.00	284.00	266.00	246.00	216.00	60.00	14.50	251.00
95th percentile	318.80	387.20	350.00	290.00	322.00	215.80	43.40	310.00

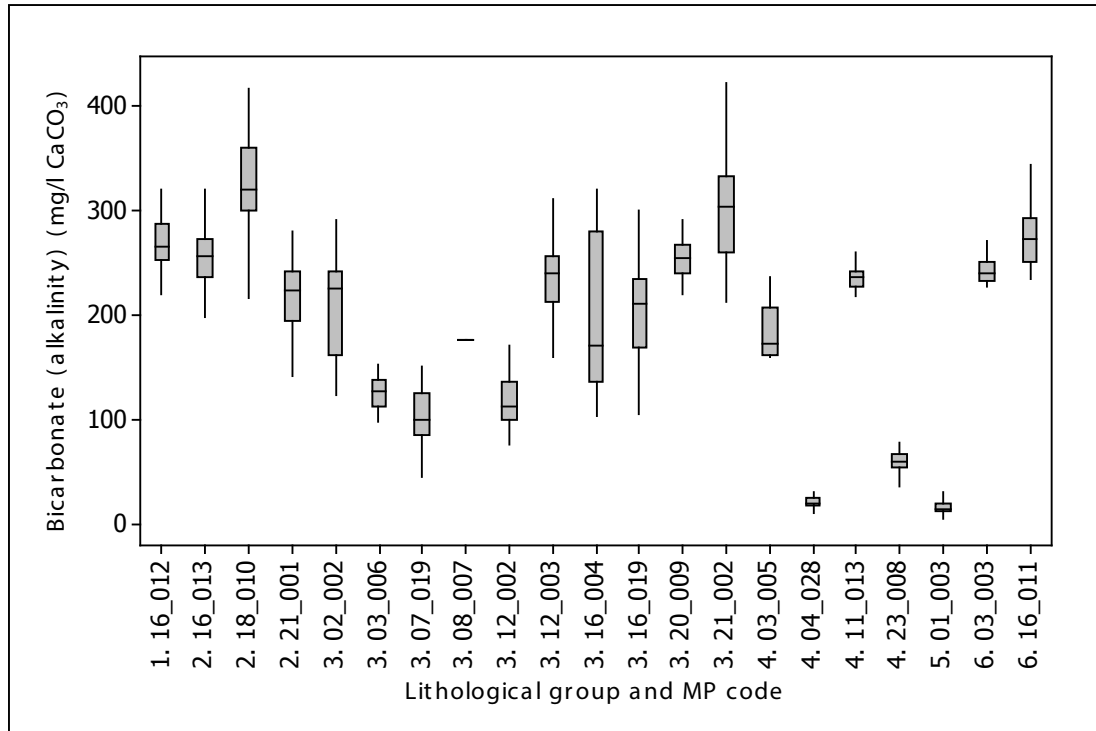


Figure A29. Box and whisker plot summarising bicarbonate (alkalinity) data from each monitoring point used to establish natural background levels for bicarbonate (alkalinity) in Irish groundwater. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

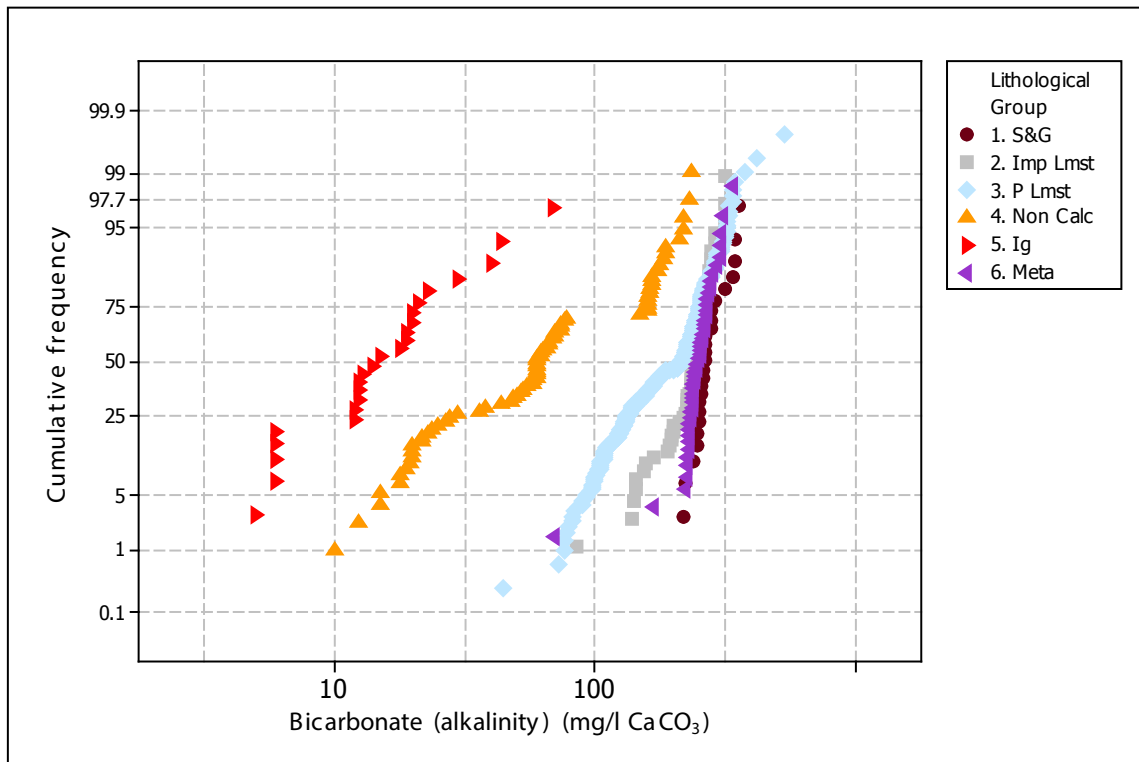


Figure A30. Cumulative frequency diagram showing the distribution of bicarbonate (alkalinity) data used to establish natural background levels for bicarbonate (alkalinity) in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, Non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Chloride

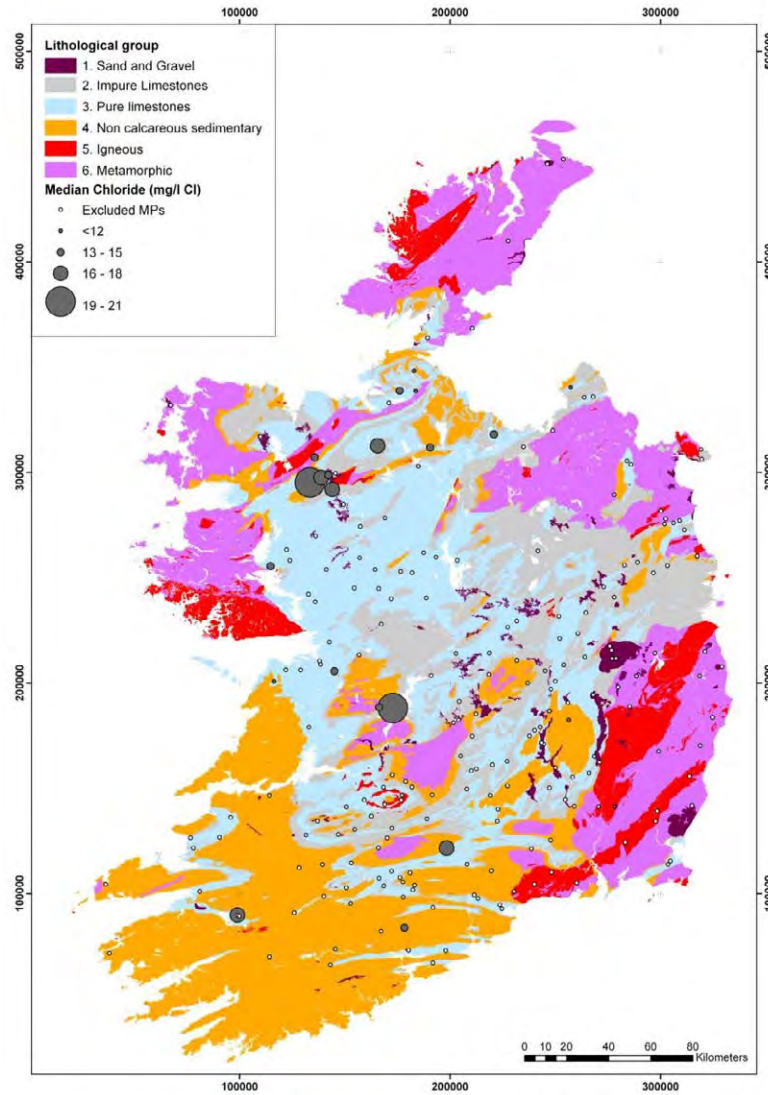


Figure A31. Location and median chloride values of the monitoring points used to establish natural background levels for chloride in Irish groundwater.

Table A11. Descriptive statistics of chloride for monitoring points used to establish natural background levels for chloride in Irish groundwater presented for all monitoring points and by lithological group

Chloride (mg/l Cl)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	520	93	25	66	283	74	24	48
5th percentile	8.00	6.20	13.00	10.25	8.42	12.72	1.30	11.54
Median	14.30	10.40	15.00	14.65	14.00	17.00	8.00	13.20
95th percentile	21.02	15.40	17.00	19.00	22.36	20.14	10.85	15.76

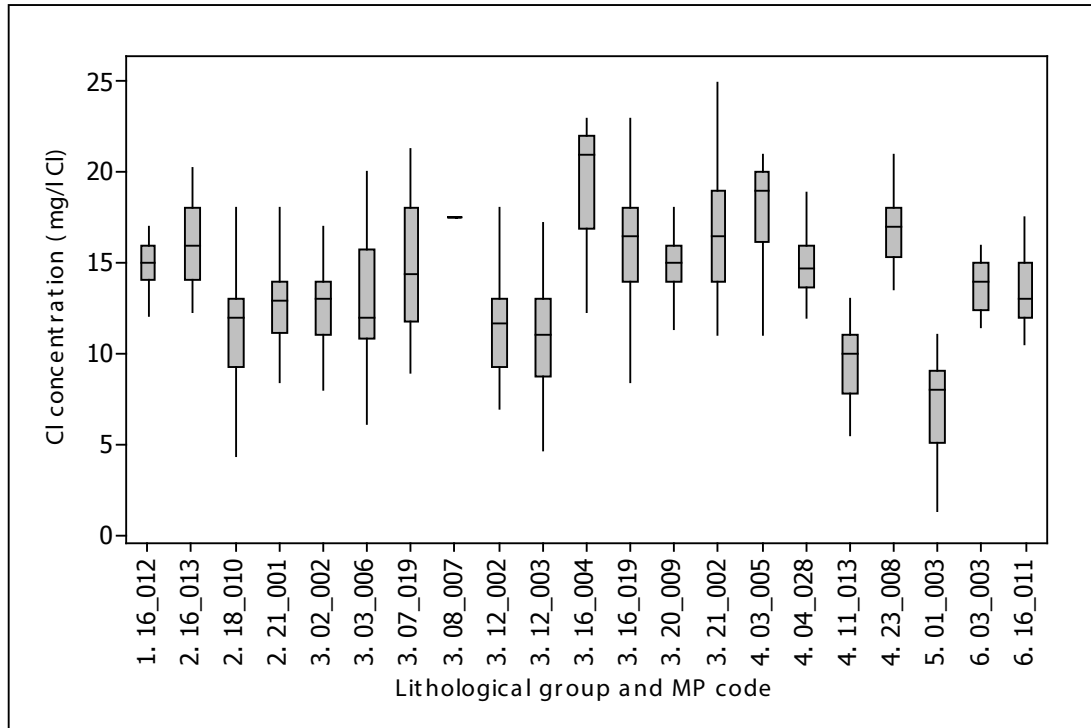


Figure A32. Box and whisker plot summarising chloride data from each monitoring point used to establish natural background levels for chloride in Irish groundwater. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

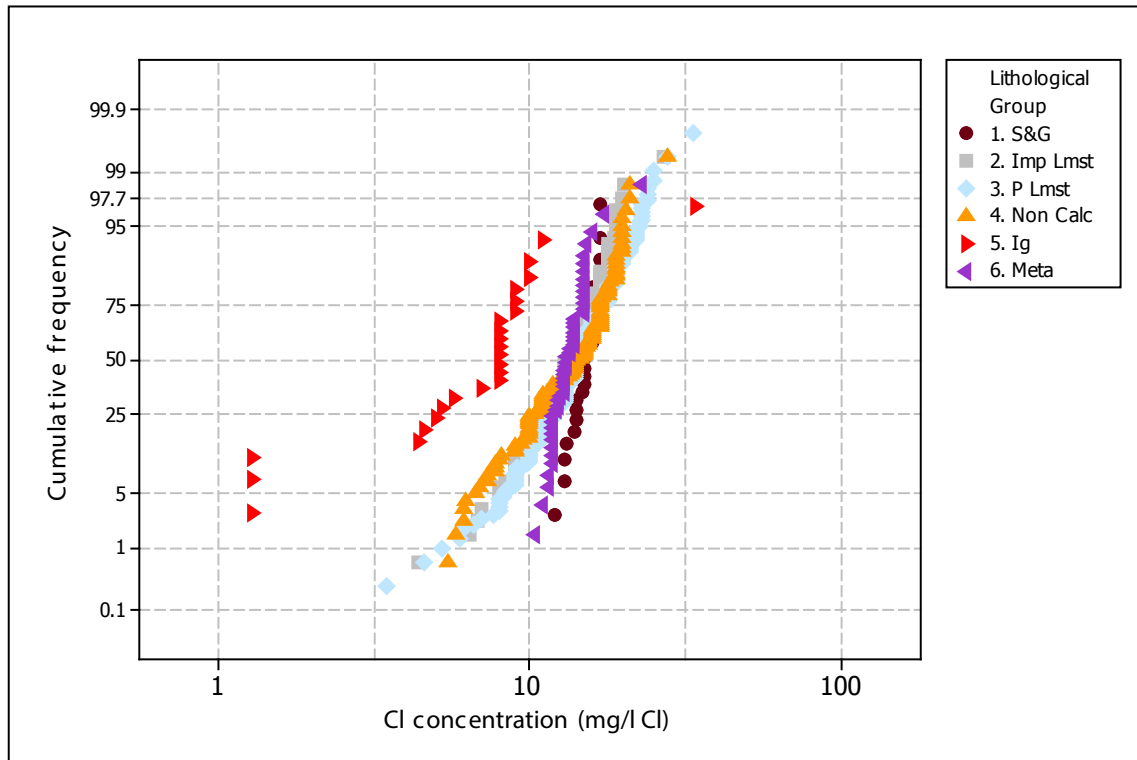


Figure A33. Cumulative frequency diagram showing the distribution of chloride data used to establish natural background levels for chloride in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Sulphate

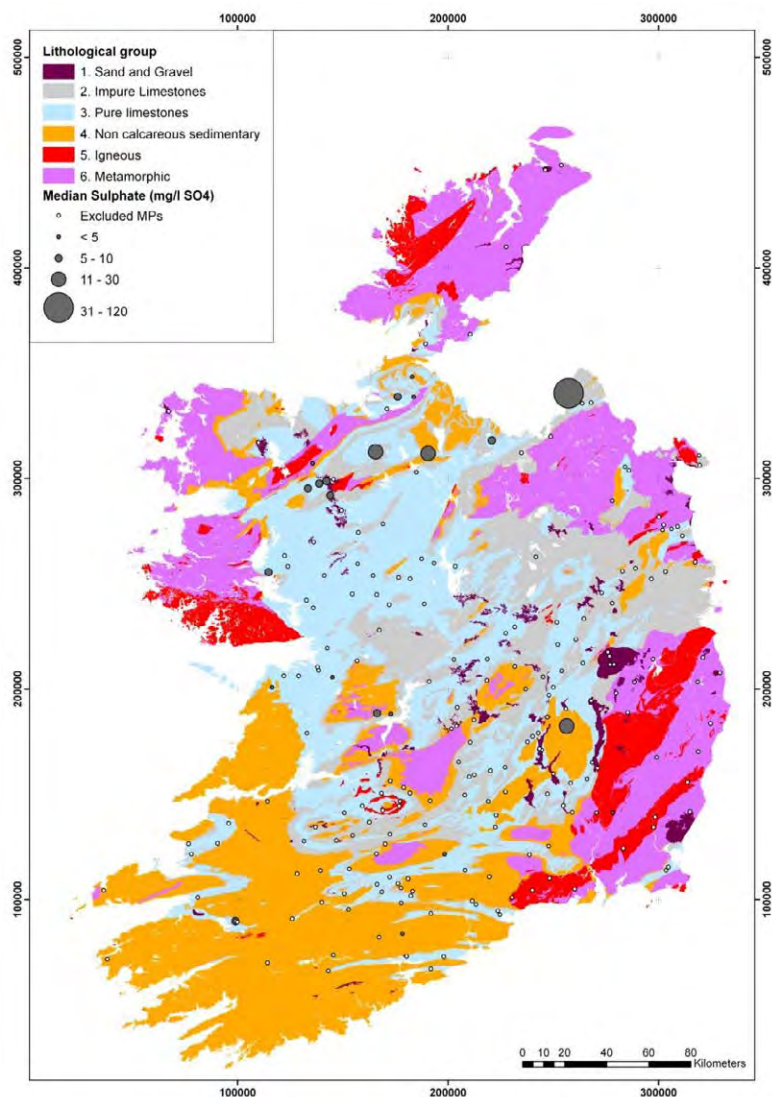


Figure A34. Location and median sulphate values of the monitoring points used to establish natural background levels for sulphate in Irish groundwater.

Table A12. Descriptive statistics of sulphate for monitoring points used to establish natural background levels for sulphate in Irish groundwater presented for all monitoring points and by lithological group

Sulphate (mg/l SO ₄)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	513	91	25	65	280	71	24	48
5th percentile	0.50	25.64	4.44	1.36	0.50	0.50	0.50	0.72
Median	5.80	60.00	8.20	7.40	7.00	4.40	3.00	5.15
95th percentile	13.16	223.00	11.36	10.80	14.62	5.90	4.17	7.38

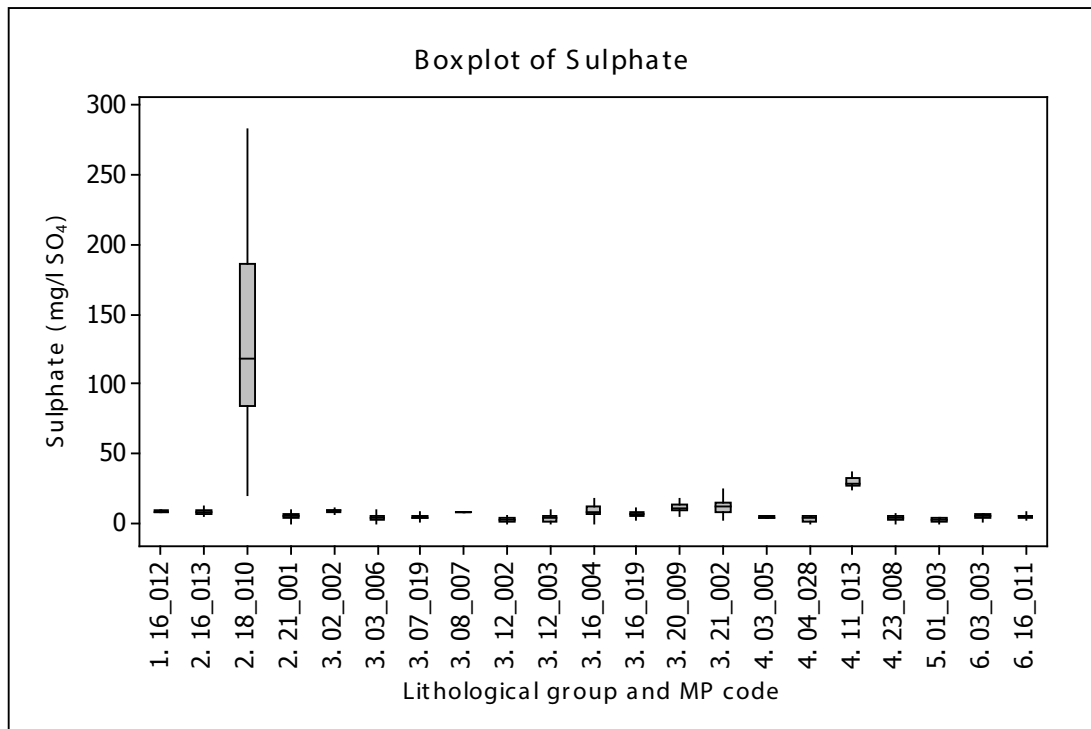


Figure A35. Box and whisker plot summarising sulphate data from each monitoring point used to establish natural background levels for sulphate in Irish groundwater. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

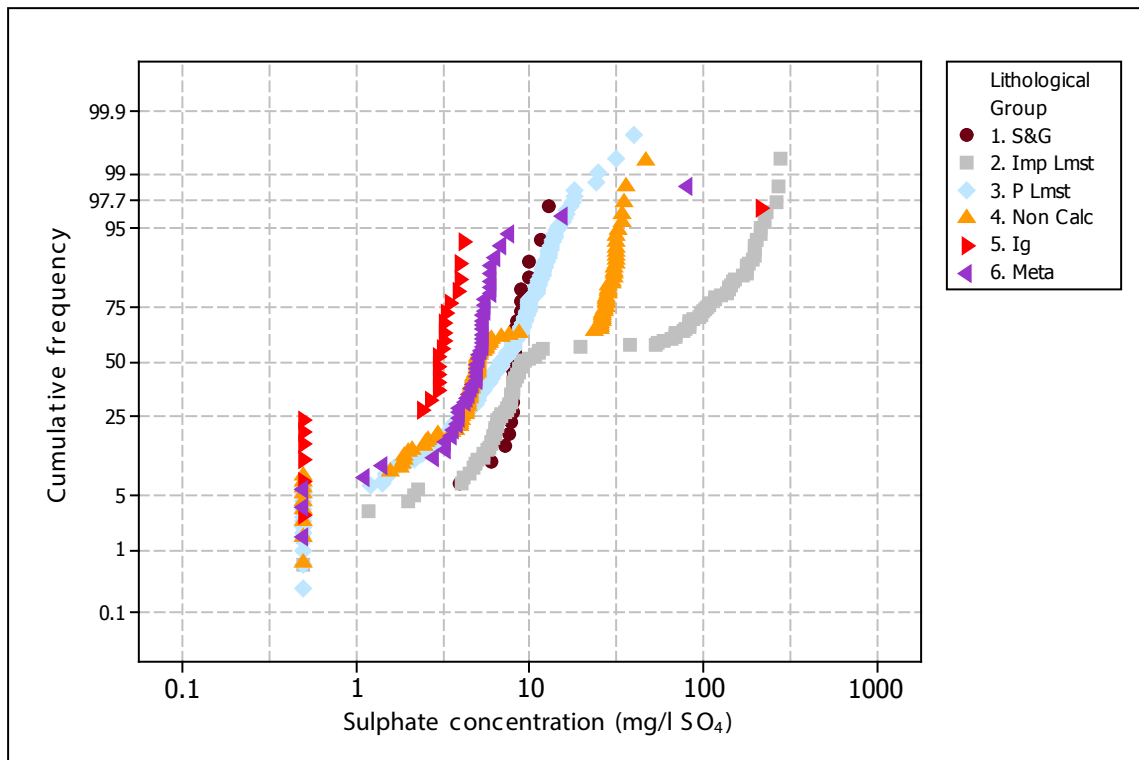


Figure A36. Cumulative frequency diagram showing the distribution of sulphate data used to establish natural background levels for sulphate in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Barium

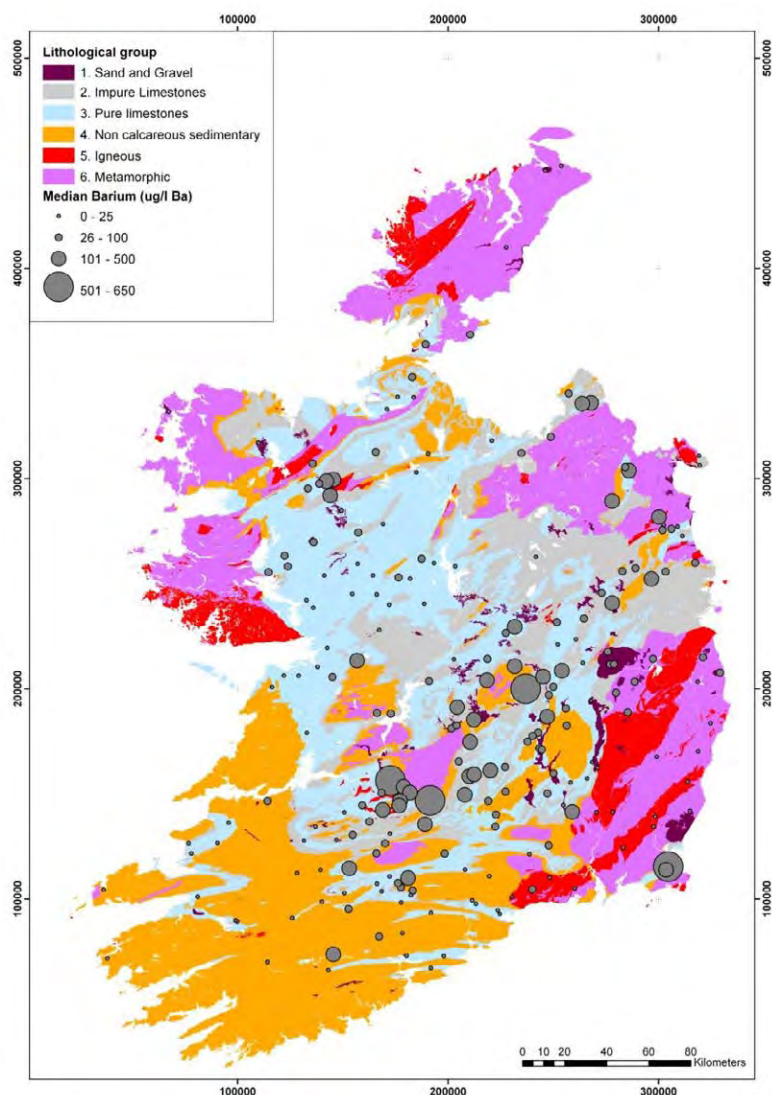


Figure A37. Location and median barium values of the monitoring points used to establish natural background levels for barium in Irish groundwater.

Table A13. Descriptive statistics of barium for monitoring points used to establish natural background levels for barium in Irish groundwater presented for all monitoring points and by lithological group

Barium (µg/l Ba)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	215	2	30	29	96	31	13	16
Number of data points	4861	48	659	605	2230	711	297	359
5th percentile	2.70	46.28	6.68	6.84	3.00	4.80	0.86	0.50
Median	29.30	60.40	54.79	45.70	21.18	45.20	7.00	20.30
95th percentile	223.60	78.60	585.73	195.00	178.64	426.95	179.20	114.10

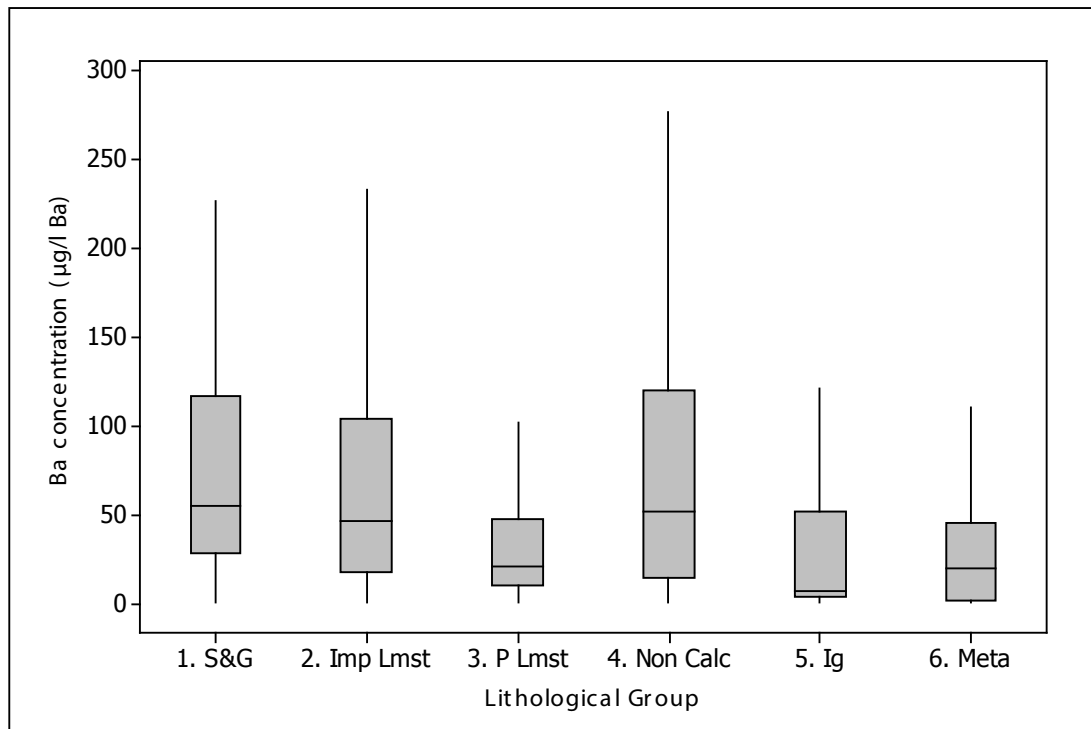


Figure A38. Box and whisker plot summarising barium data from each monitoring point used to establish natural background levels for barium in Irish groundwater presented by lithological group.

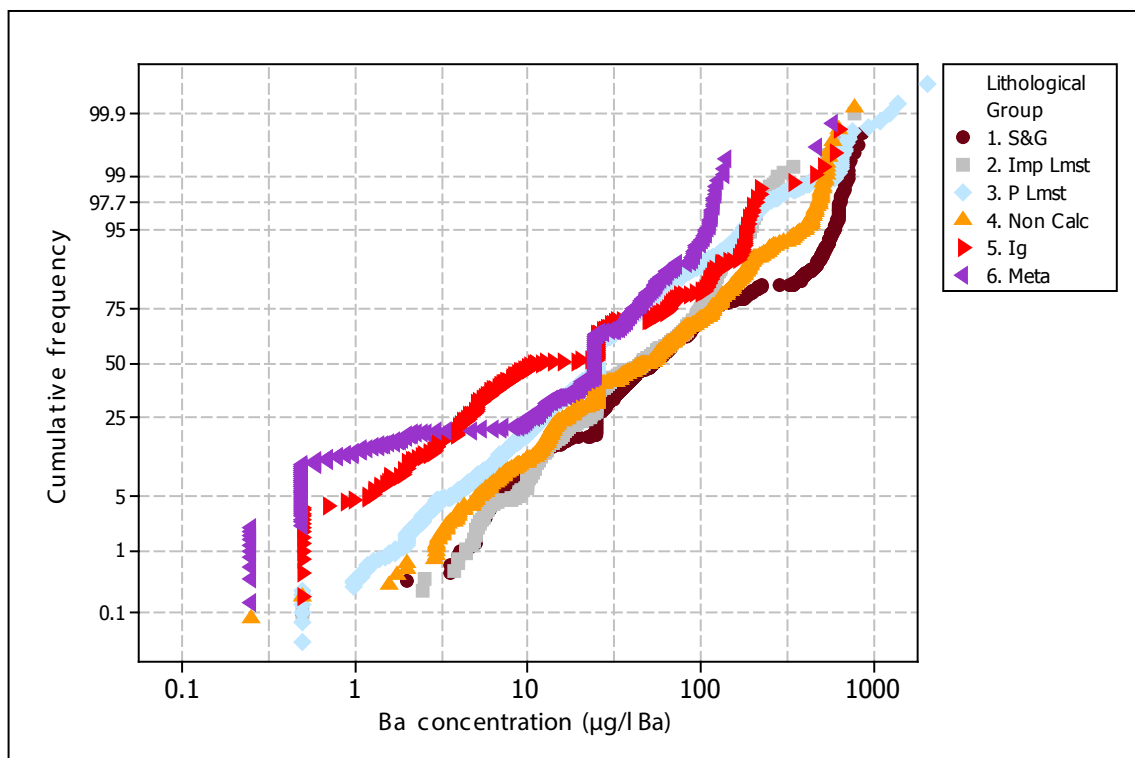


Figure A39. Cumulative frequency diagram showing the distribution of barium data used to establish natural background levels for barium in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Fluoride

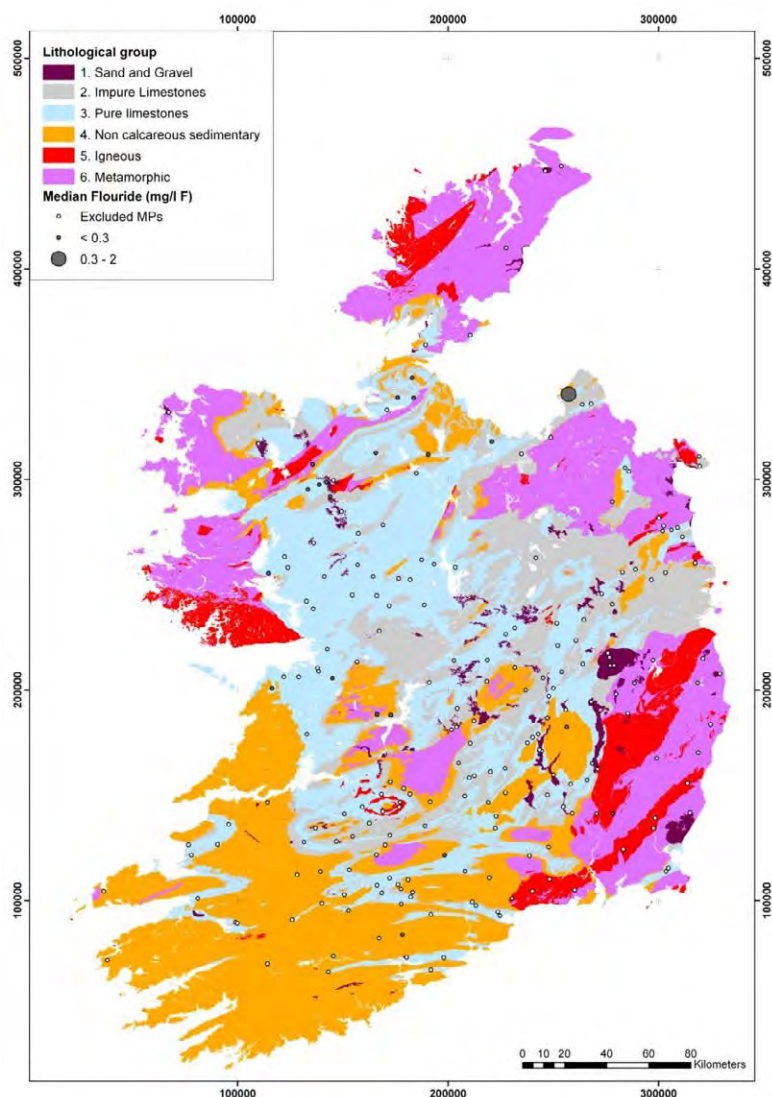


Figure A40. Location and median fluoride values of the monitoring points used to establish natural background levels for fluoride in Irish groundwater.

Table A14. Descriptive statistics of fluoride for monitoring points used to establish natural background levels for fluoride in Irish groundwater presented for all monitoring points and by lithological group

Fluoride (mg/l F)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	502	76	25	65	275	66	23	48
5th percentile	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Median	0.08	1.10	0.08	0.08	0.08	0.05	0.05	0.08
95th percentile	0.20	2.61	0.20	0.20	0.20	0.08	0.08	0.20

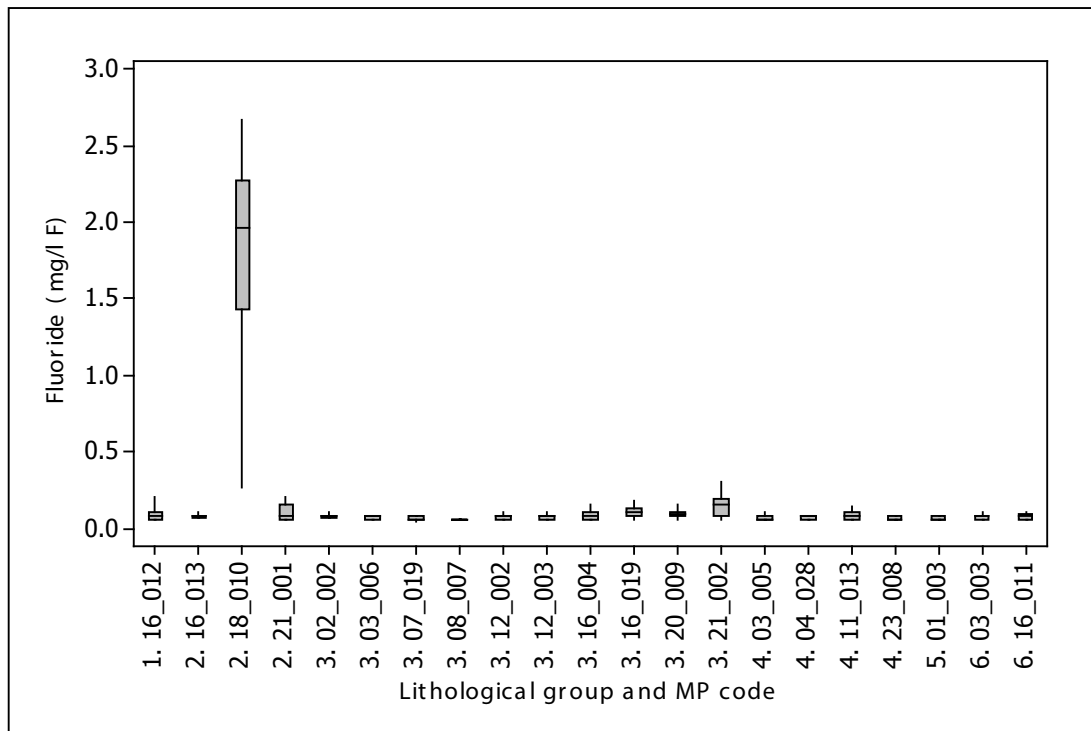


Figure A41. Box and whisker plot summarising fluoride data from each monitoring point used to establish natural background levels for fluoride in Irish groundwater. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

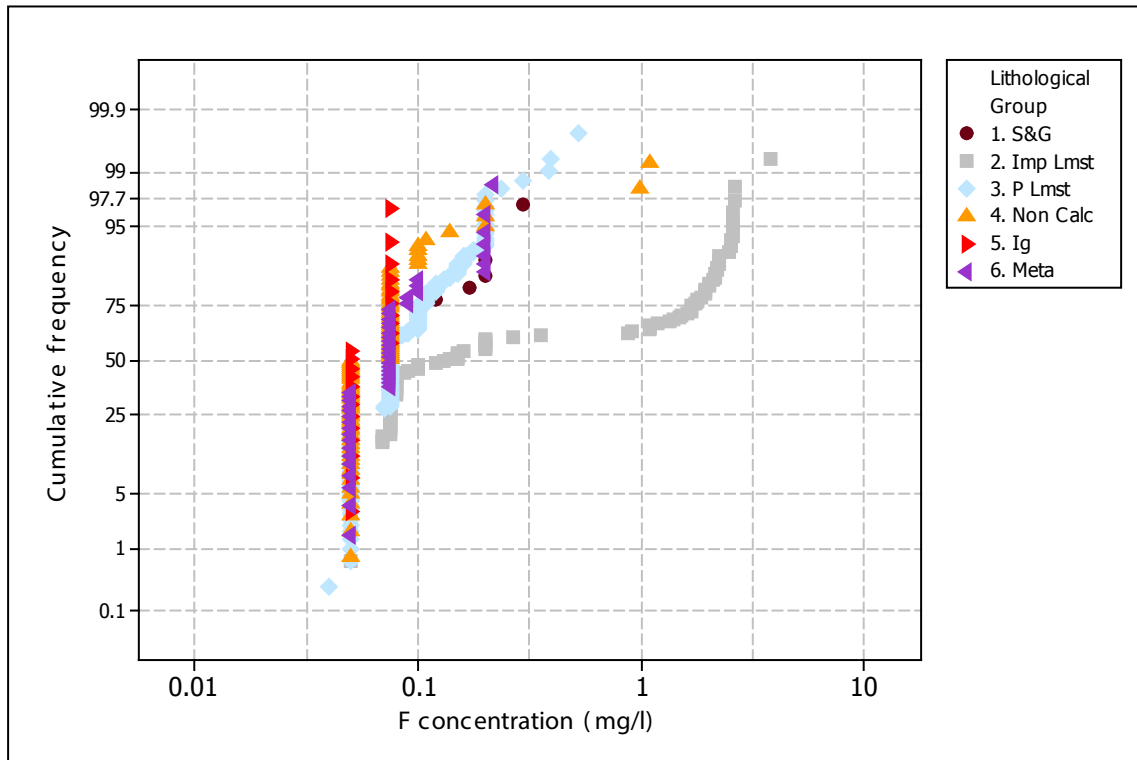


Figure A42. Cumulative frequency diagram showing the distribution of fluoride data used to establish natural background levels for fluoride in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Iron

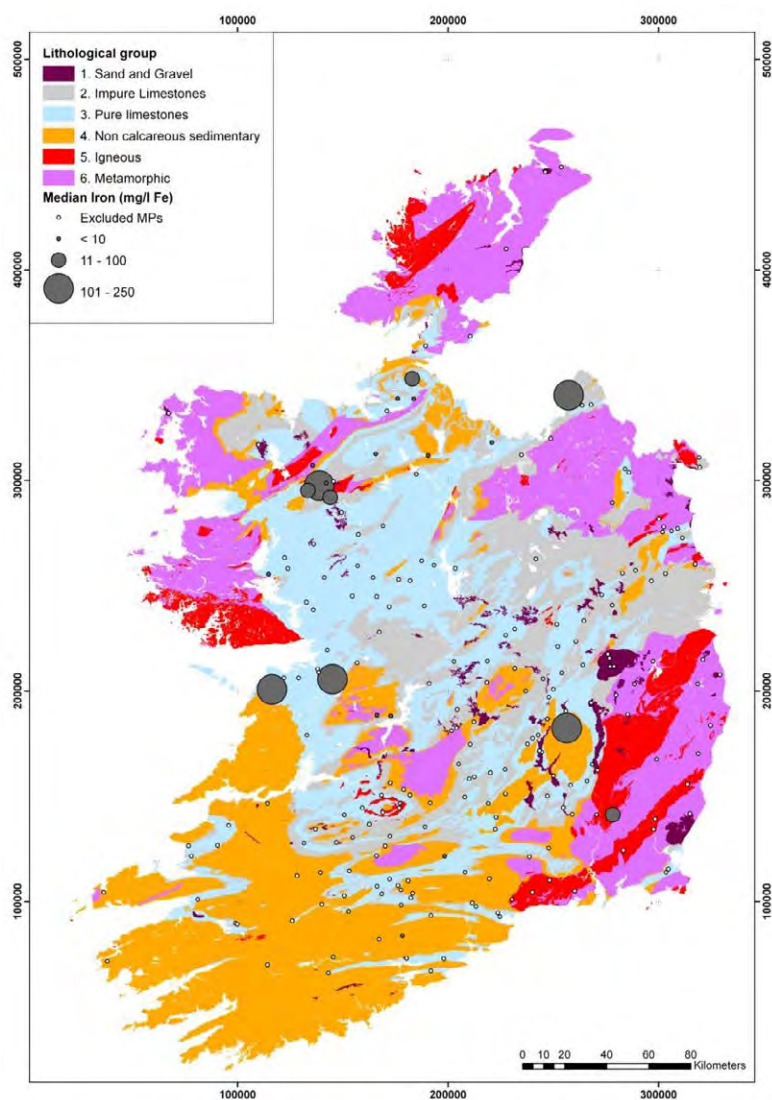


Figure A43. Location and median iron values of the monitoring points used to establish natural background levels for iron in Irish groundwater.

Table A15. Descriptive statistics of iron for monitoring points used to establish natural background levels for iron in Irish groundwater presented for all monitoring points and by lithological group

Iron ($\mu\text{g/l Fe}$)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	416	48	25	44	216	59	24	48
5th percentile	2.00	16.45	1.20	1.23	2.50	2.50	1.23	1.53
Median	11.00	159.85	5.00	9.50	28.00	5.00	24.36	5.00
95th percentile	268.43	762.20	37.57	62.65	346.90	16.10	71.20	89.85

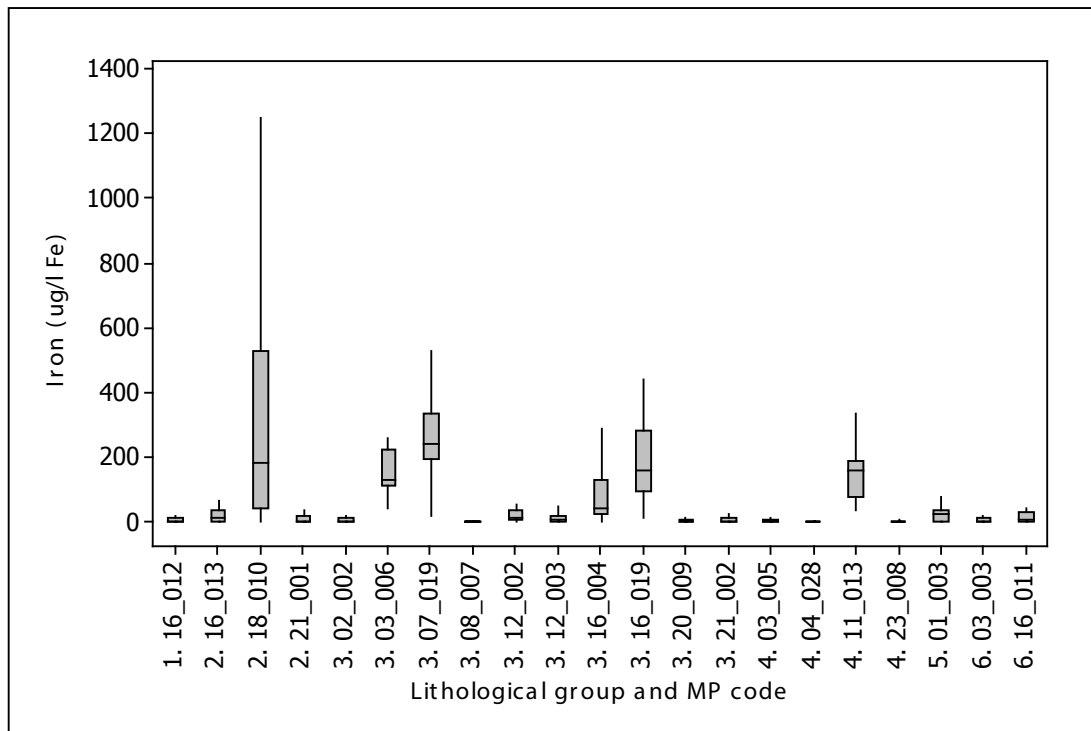


Figure A44. Box and whisker plot summarising iron data from each monitoring point used to establish natural background levels for iron in Irish groundwater. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

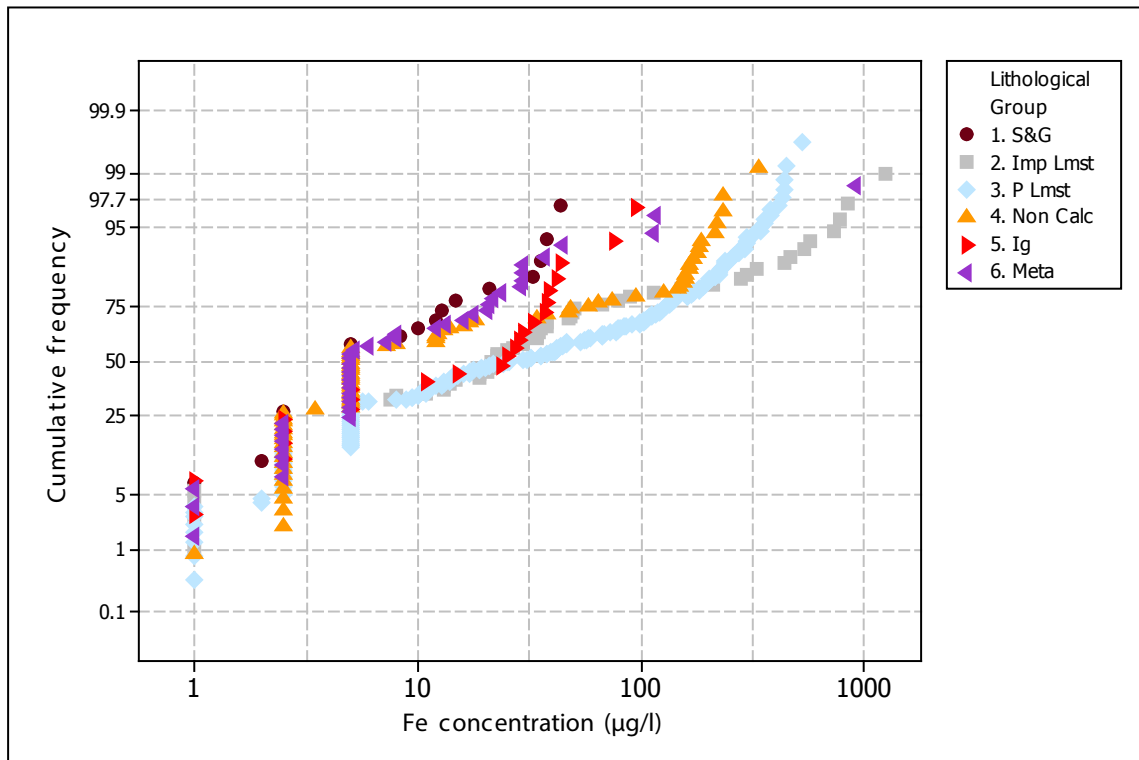


Figure A45. Cumulative frequency diagram showing the distribution of iron data used to establish natural background levels for iron in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Manganese

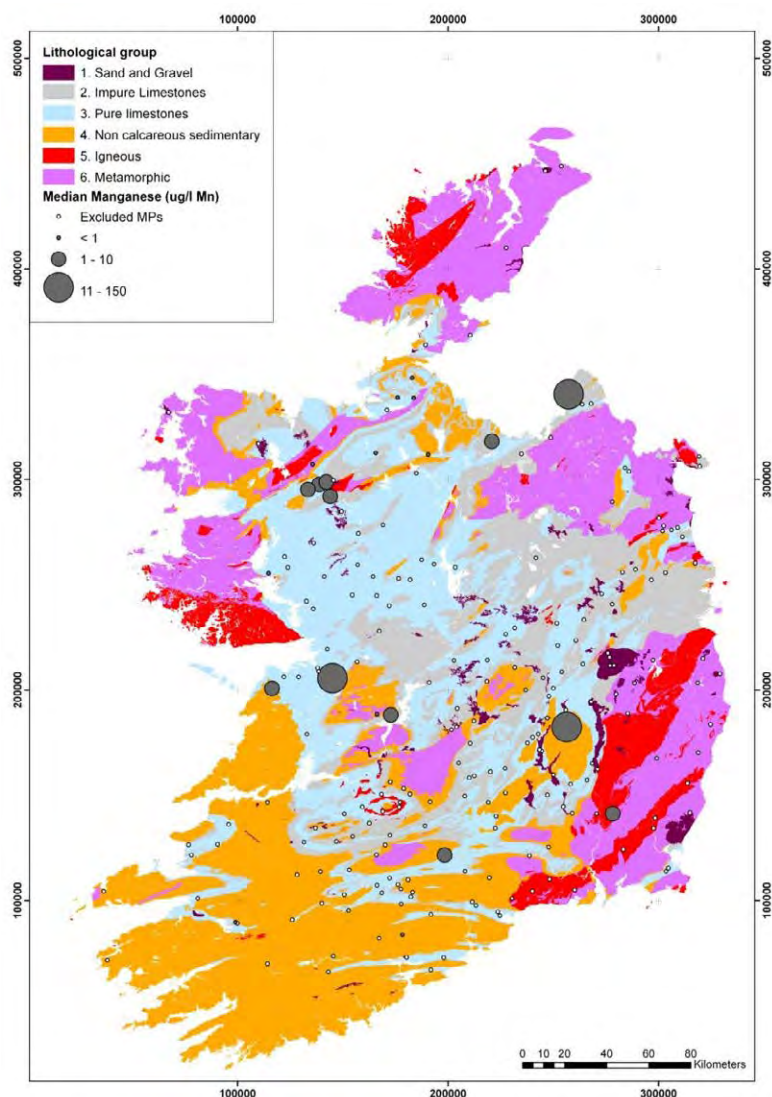


Figure A46. Location and median manganese values of the monitoring points used to establish natural background levels for manganese in Irish groundwater.

Table A16. Descriptive statistics of manganese for monitoring points used to establish natural background levels for manganese in Irish groundwater presented for all monitoring points and by lithological group

Manganese (µg/l Mn)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	416	47	25	44	216	59	24	48
5th percentile	0.50	36.10	0.50	0.50	0.50	0.50	3.00	0.50
Median	2.00	103.00	1.30	0.50	2.00	3.00	5.00	0.50
95th percentile	23.25	176.10	4.60	12.94	33.09	13.51	9.90	8.76

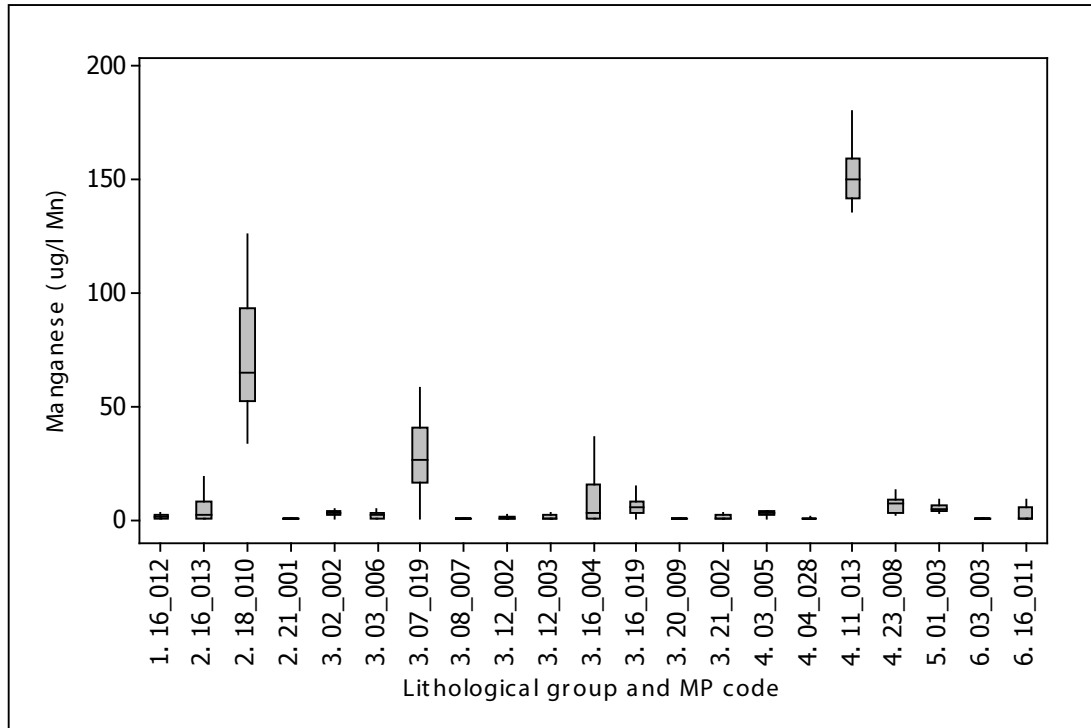


Figure A47. Box and whisker plot summarising manganese data from each monitoring point used to establish natural background levels for manganese in Irish groundwater. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

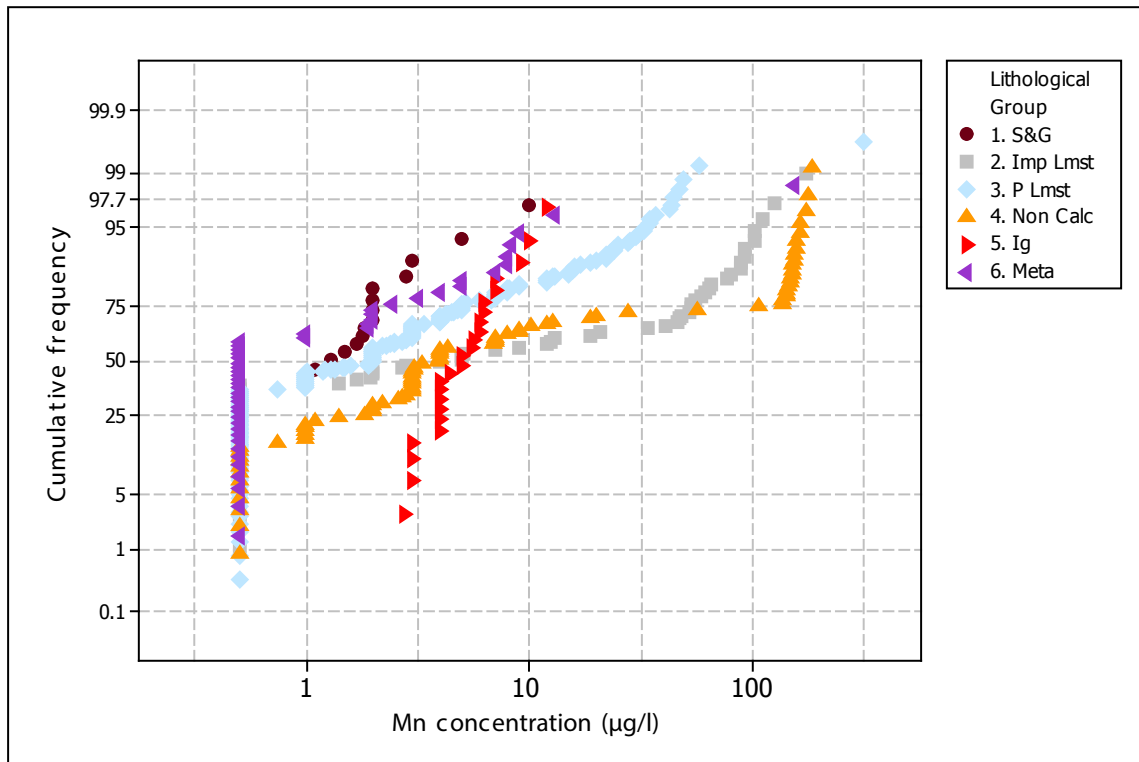


Figure A48. Cumulative frequency diagram showing the distribution of manganese data used to establish natural background levels for manganese in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Silica

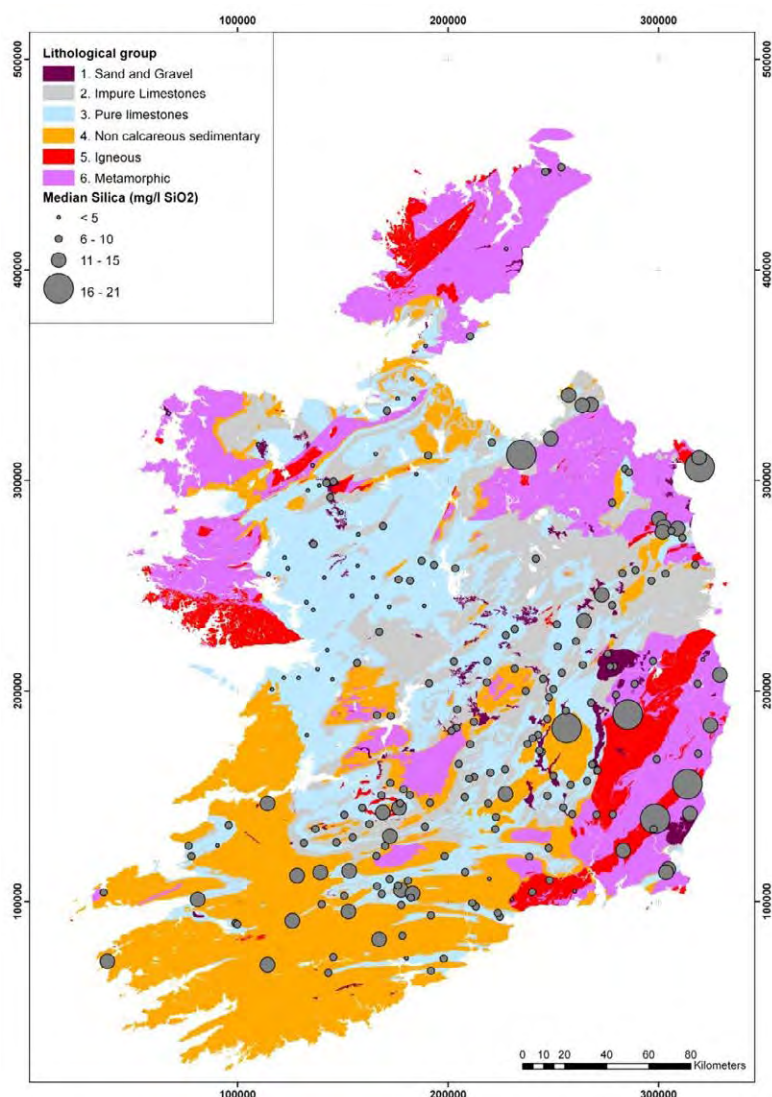


Figure A49. Location and median silica values of the monitoring points used to establish natural background levels for silica in Irish groundwater.

Table A17. Descriptive statistics of silica for monitoring points used to establish natural background levels for silica in Irish groundwater presented for all monitoring points and by lithological group

Silica (mg/l SiO ₂)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	215	2	30	29	96	31	13	16
Number of data points	2970	30	399	372	1367	442	179	211
5th percentile	3.20	12.26	4.70	4.10	2.19	4.60	3.87	3.81
Median	6.91	15.52	7.23	8.42	5.93	7.91	9.40	9.29
95th percentile	13.98	18.60	12.92	17.20	10.14	13.74	19.33	16.03

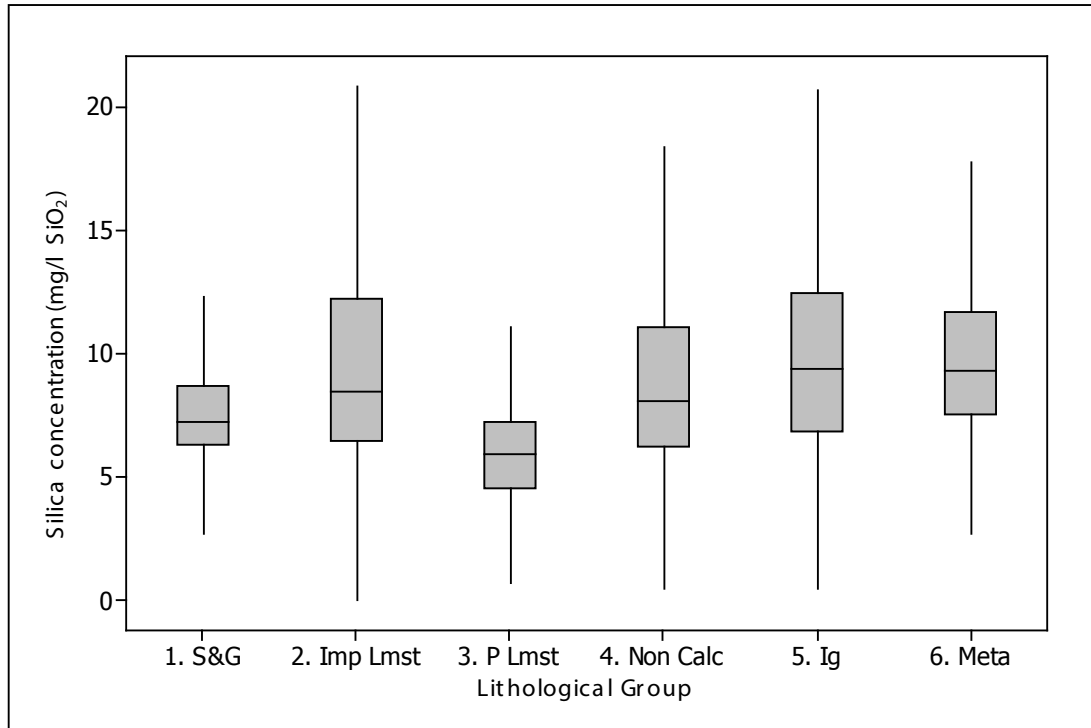


Figure A50. Box and whisker plot summarising silica data from each monitoring point used to establish natural background levels for silica in Irish groundwater presented by lithological group.

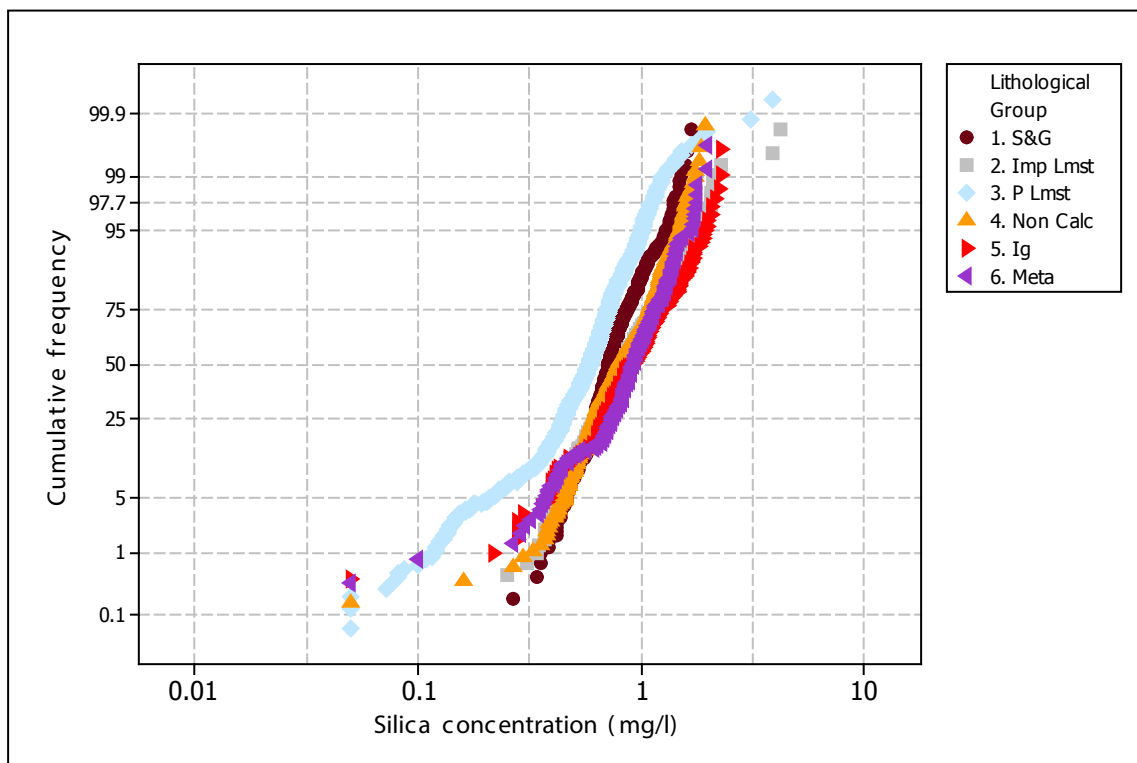


Figure A51. Cumulative frequency diagram showing the distribution of manganese data used to establish natural background levels for manganese in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Strontium

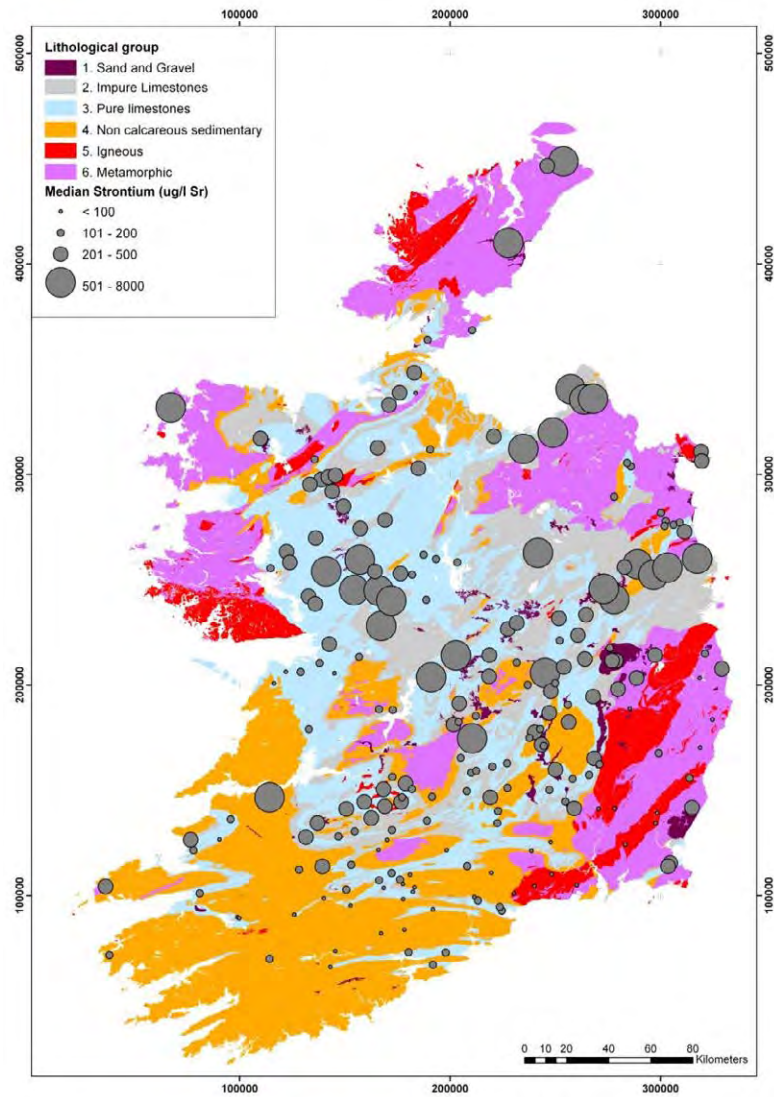


Figure A52. Location and median strontium values of the monitoring points used to establish natural background levels for strontium in Irish groundwater.

Table A18. Descriptive statistics of strontium for monitoring points used to establish natural background levels for strontium in Irish groundwater presented for all monitoring points and by lithological group

Strontium (µg/l Sr)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	215	2	30	29	96	31	13	16
Number of data points	4856	48	659	605	2227	708	297	360
5th percentile	44.48	319.95	83.93	84.47	81.76	29.06	8.95	50.20
Median	187.00	524.00	203.00	486.50	190.90	101.00	56.00	163.50
95th percentile	763.10	7026.20	651.30	2899.60	575.00	320.00	498.00	772.25

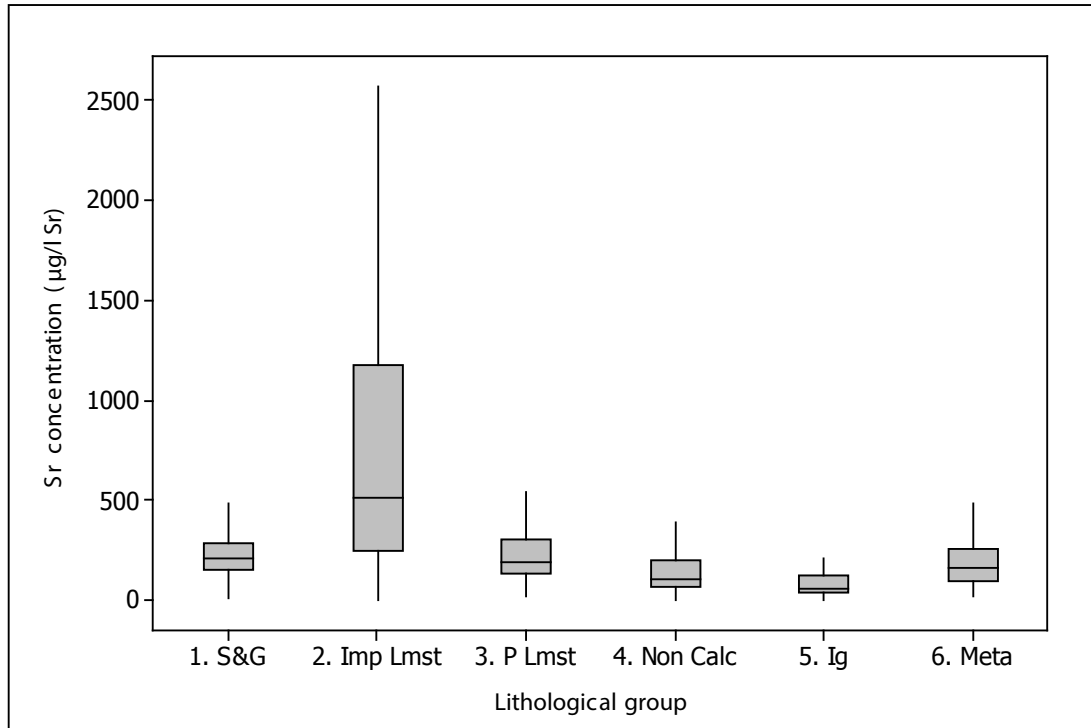


Figure A53. Box and whisker plot summarising strontium data from each monitoring point used to establish natural background levels for strontium in Irish groundwater presented by lithological group.

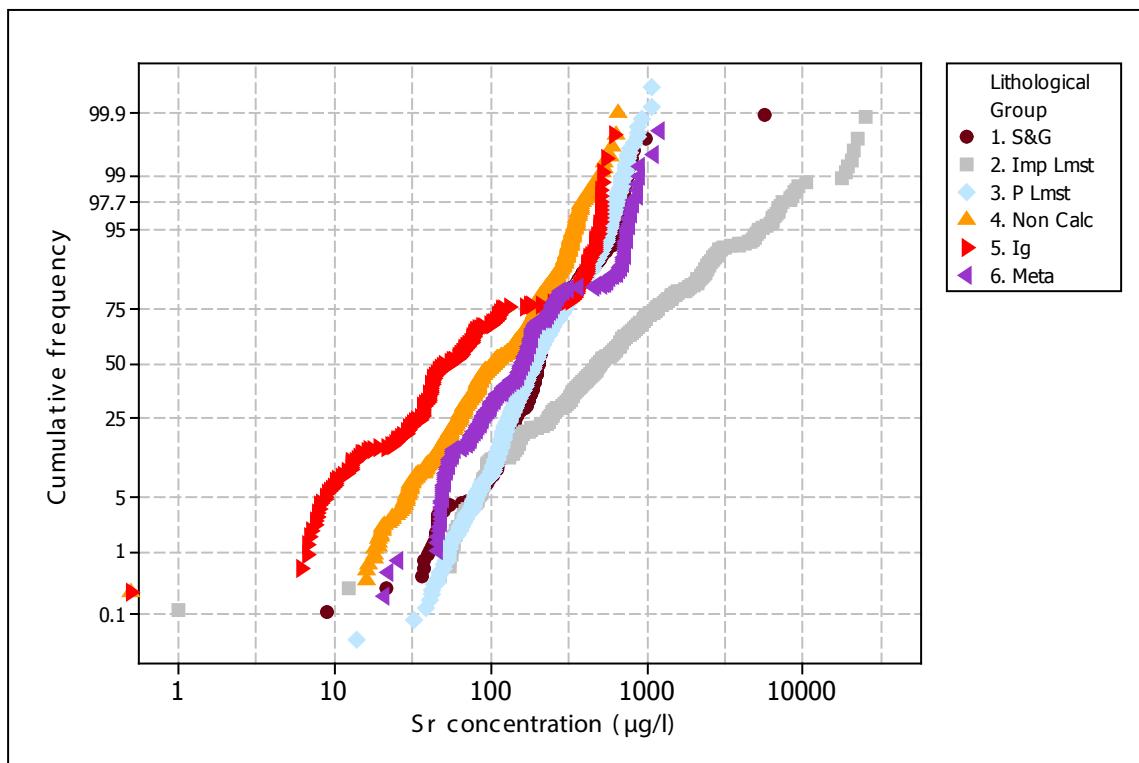


Figure A54. Cumulative frequency diagram showing the distribution of strontium data used to establish natural background levels for strontium in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Nitrate

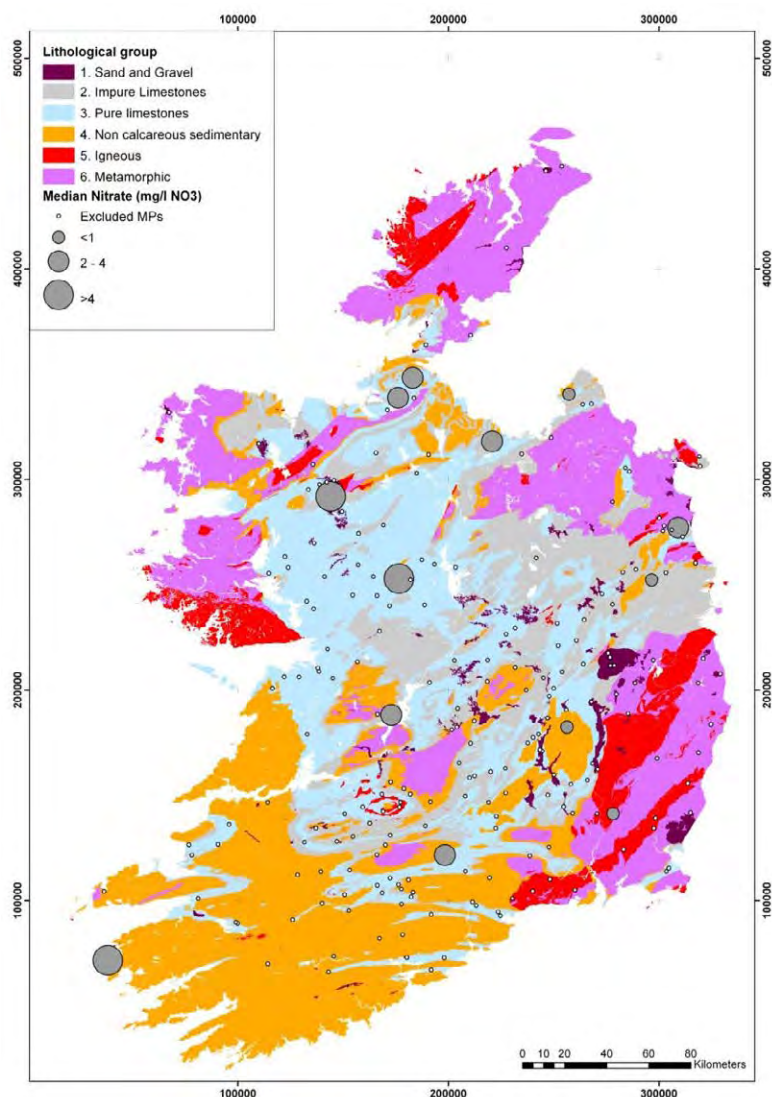


Figure A55. Location and median nitrate values of the monitoring points used to establish natural background levels for nitrate in Irish groundwater.

Table A19. Descriptive statistics of nitrate for monitoring points used to establish natural background levels for nitrate in Irish groundwater presented for all monitoring points and by lithological group

Nitrate (mg/l NO ₃)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	10	2	0	2	4	3	1	0
Number of data points	328	93	0	66	165	73	24	0
5th percentile	0.27	0.04	—	1.58	0.26	1.33	0.18	—
Median	3.47	0.27	—	5.10	3.50	3.39	0.62	—
95th percentile	8.73	1.48	—	7.78	10.15	8.00	1.23	—

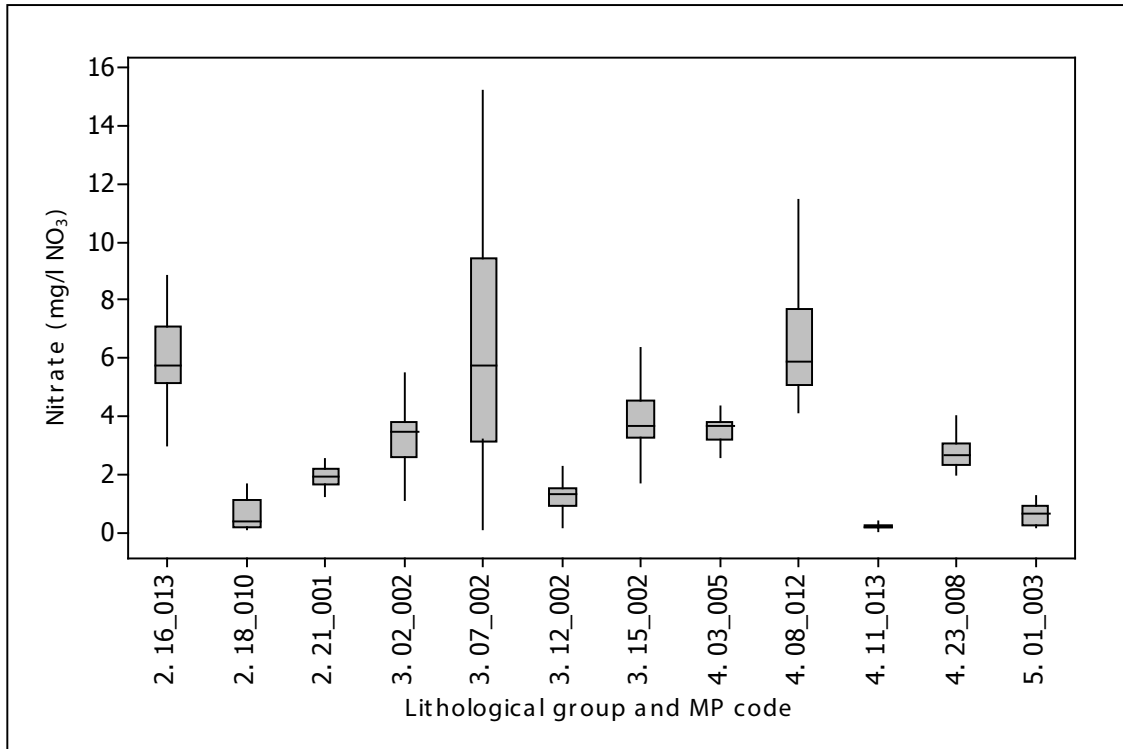


Figure A56. Box and whisker plot summarising nitrate data from each monitoring point used to establish natural background levels for nitrate in Irish groundwater. 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous.

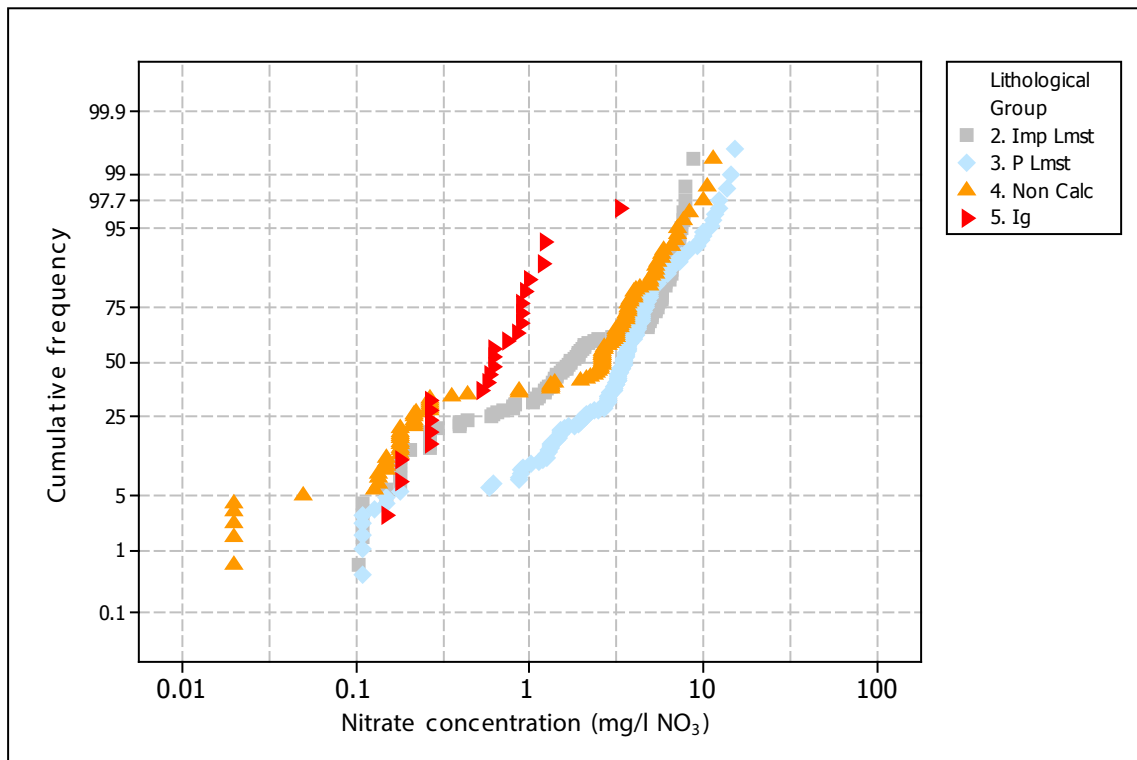


Figure A57. Cumulative frequency diagram showing the distribution of nitrate data used to establish natural background levels for nitrate in Irish groundwater presented by lithological group. Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous.

Nitrite

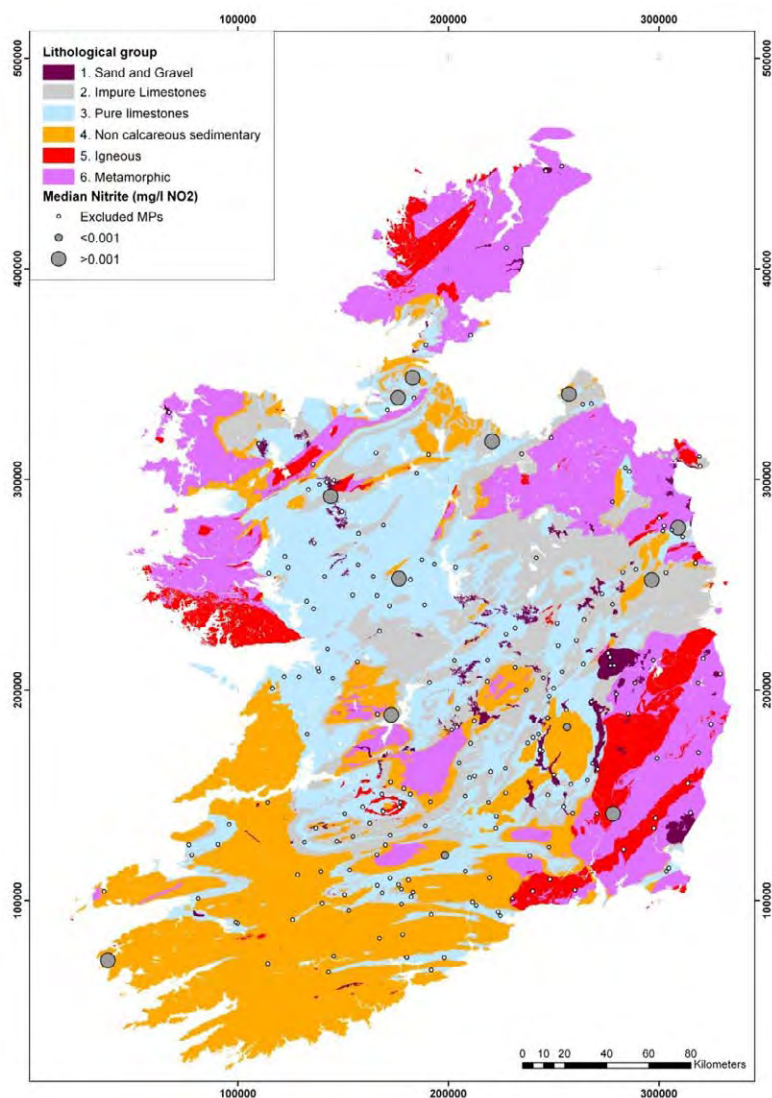


Figure A58. Location and median nitrite values of the monitoring points used to establish natural background levels for nitrite in Irish groundwater.

Table A20. Descriptive statistics of nitrite for monitoring points used to establish natural background levels for nitrite in Irish groundwater presented for all monitoring points and by lithological group

Nitrite (mg/l NO ₂)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	10	2	0	2	4	3	1	0
Number of data points	319	87	0	63	159	73	24	0
5th percentile	0.001	0.001	–	0.001	0.001	0.001	0.001	–
Median	0.003	0.002	–	0.003	0.003	0.001	0.022	–
95th percentile	0.025	0.025	–	0.025	0.025	0.025	0.025	–

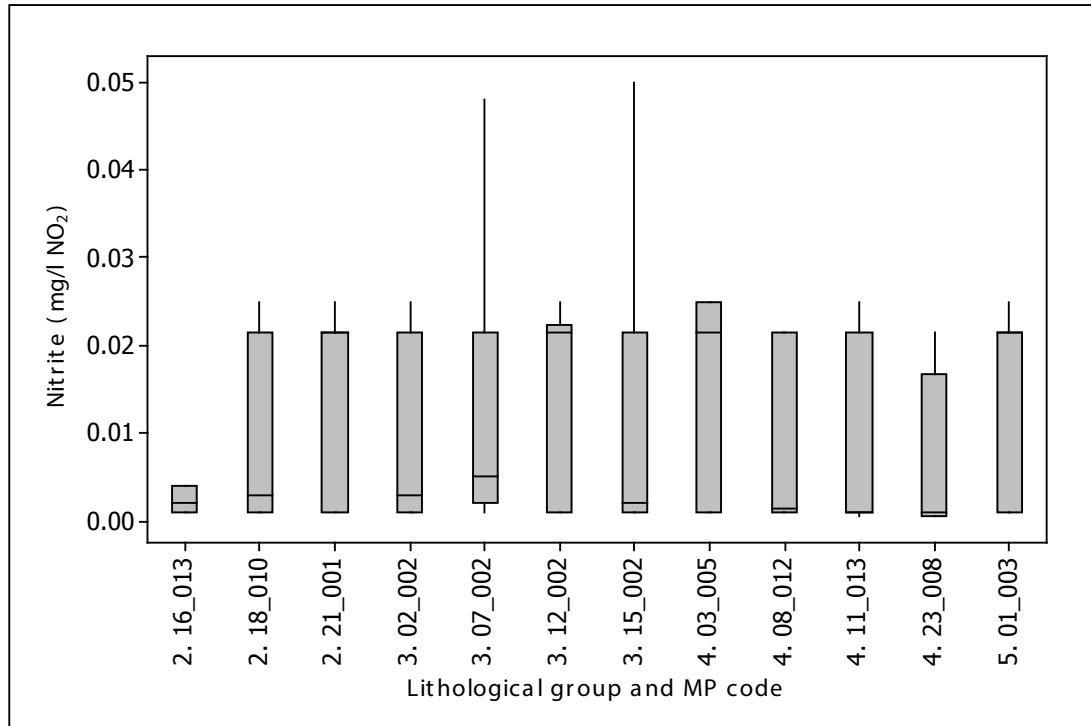


Figure A59. Box and whisker plot summarising nitrite data from each monitoring point used to establish natural background levels for nitrite in Irish groundwater. 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous.

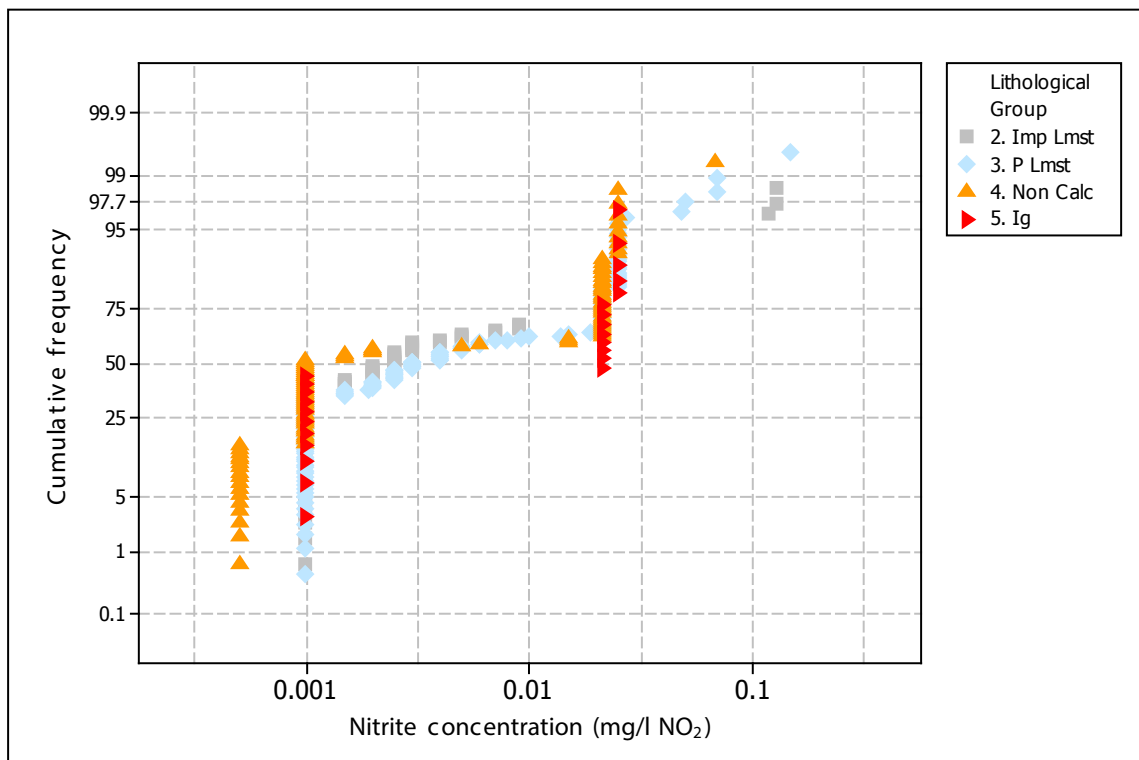


Figure A60. Cumulative frequency diagram showing the distribution of nitrite data used to establish natural background levels for nitrite in Irish groundwater presented by lithological group. Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous.

Ammonium

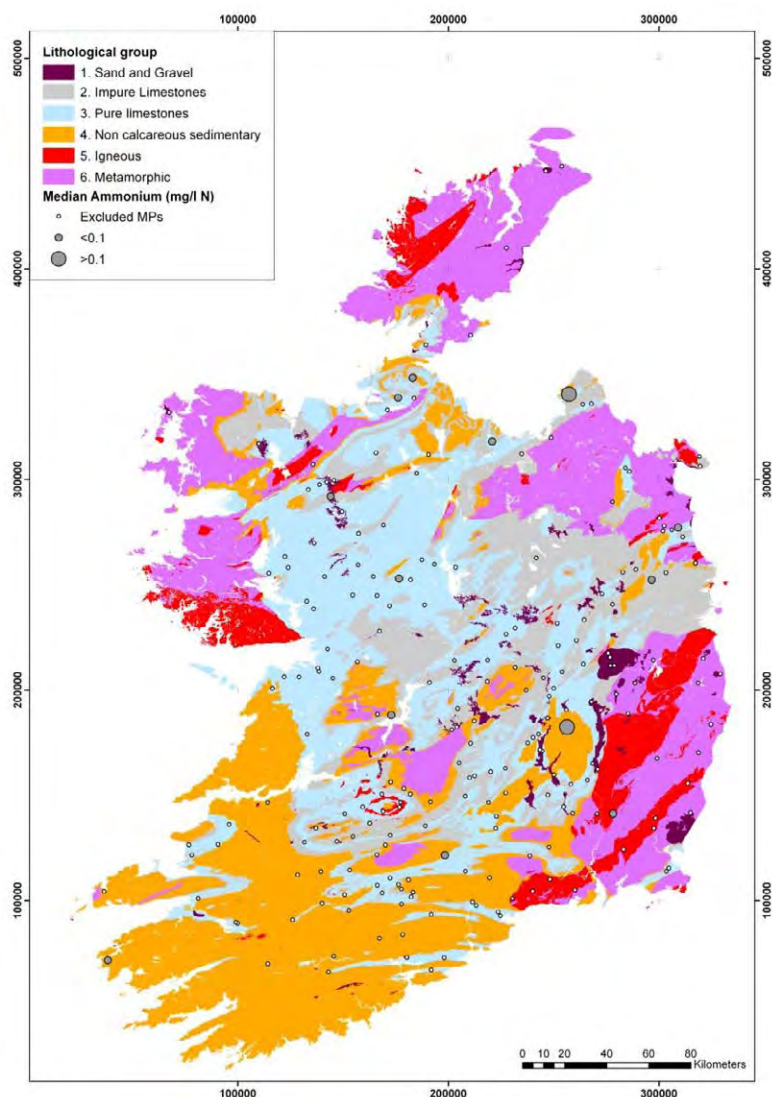


Figure A61. Location and median ammonium values of the monitoring points used to establish natural background levels for ammonium in Irish groundwater.

Table A21. Descriptive statistics of ammonium for monitoring points used to establish natural background levels for ammonium in Irish groundwater presented for all monitoring points and by lithological group

Ammonium (mg/l N)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	10	2	0	2	4	3	1	0
Number of data points	326	92	0	66	163	73	24	0
5th percentile	0.00	0.02	–	0.00	0.00	0.00	0.00	–
Median	0.01	0.12	–	0.01	0.02	0.01	0.01	–
95th percentile	0.09	0.39	–	0.05	0.09	0.05	0.10	–

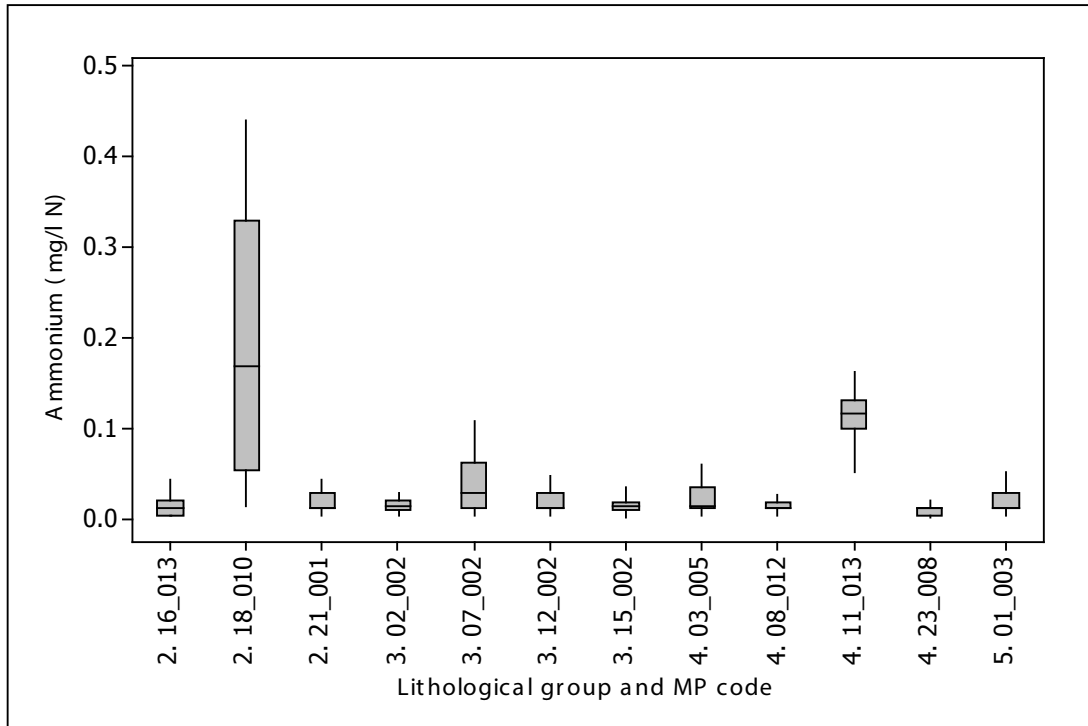


Figure A62. Box and whisker plot summarising ammonium data from each monitoring point used to establish natural background levels for ammonium in Irish groundwater. 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous.

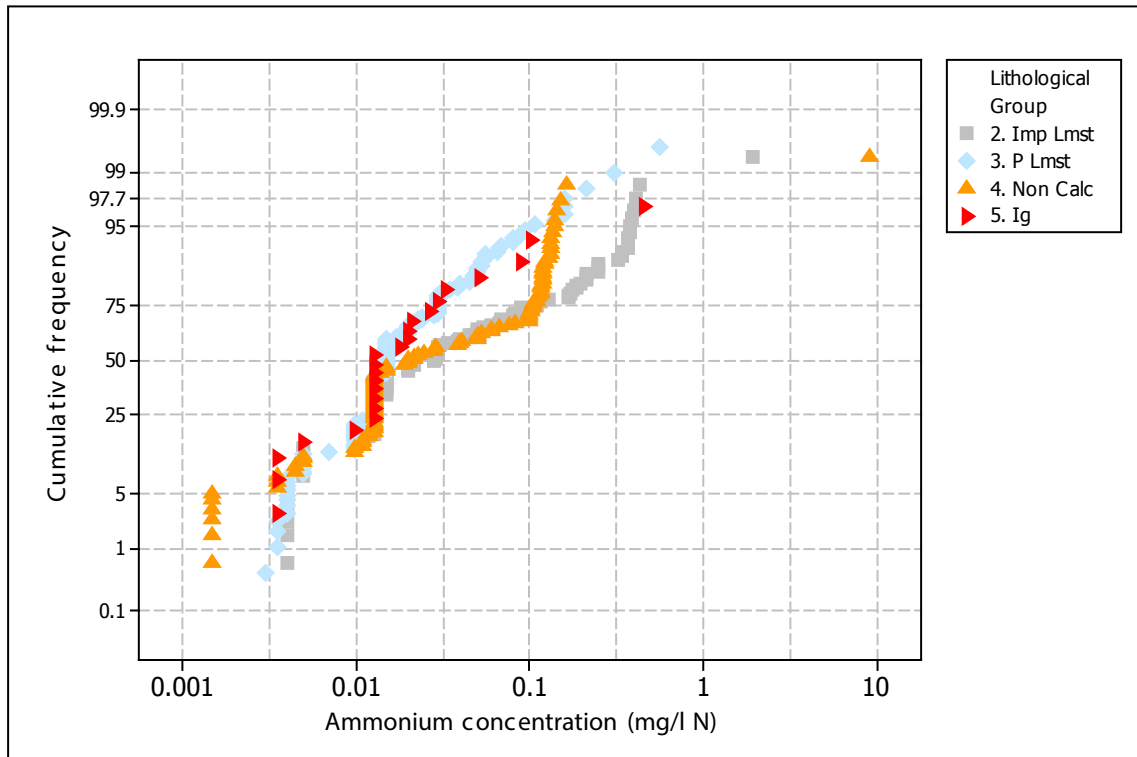


Figure A63. Cumulative frequency diagram showing the distribution of ammonium data used to establish natural background levels for ammonium in Irish groundwater presented by lithological group. Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous.

Total Phosphorus

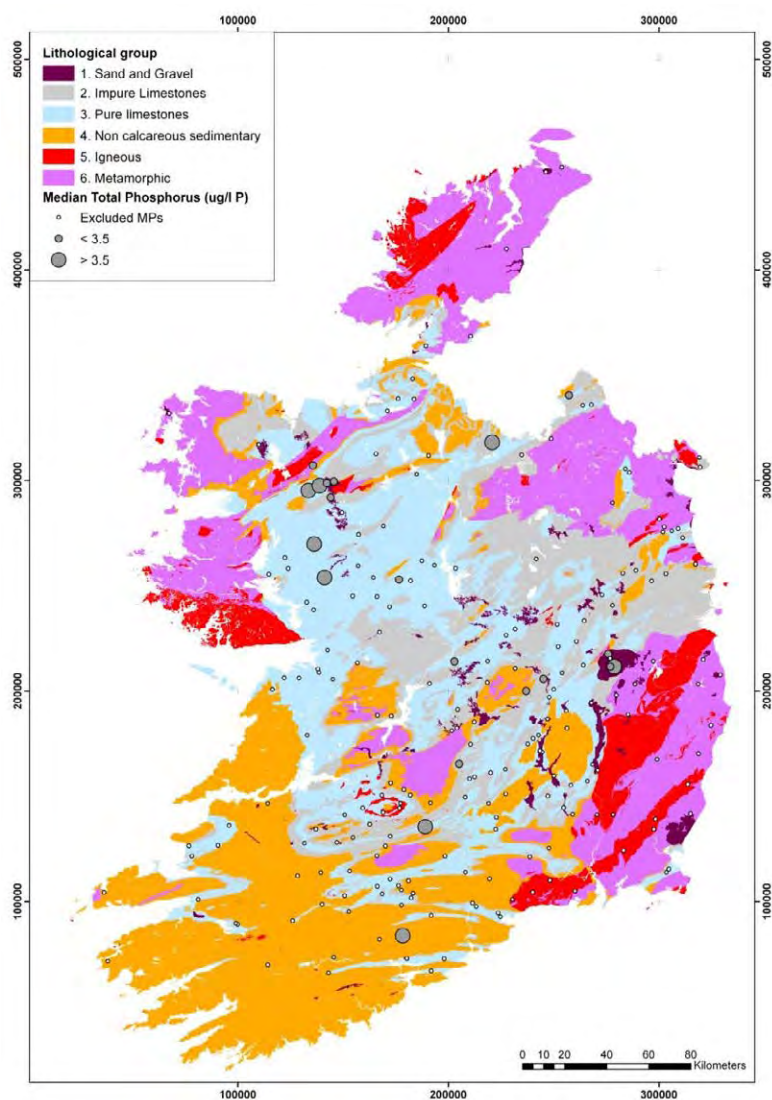


Figure A64. Location and median total phosphorus values of the monitoring points used to establish natural background levels for total phosphorus in Irish groundwater.

Table A22. Descriptive statistics of total phosphorus for monitoring points used to establish natural background levels for total phosphorus in Irish groundwater presented for all monitoring points and by lithological group

Total phosphorus ($\mu\text{g/l P}$)						
Summary statistics	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non calc sedimentary	5. Igneous	6. Metamorphic
Number of MPs	5	4	9	1	0	1
Number of data points	53	40	92	11	0	10
5th percentile	3.50	3.50	3.50	5.75	—	3.50
median	3.50	3.50	9.50	10.00	—	3.50
95th percentile	12.00	13.00	25.45	16.00	—	25.15

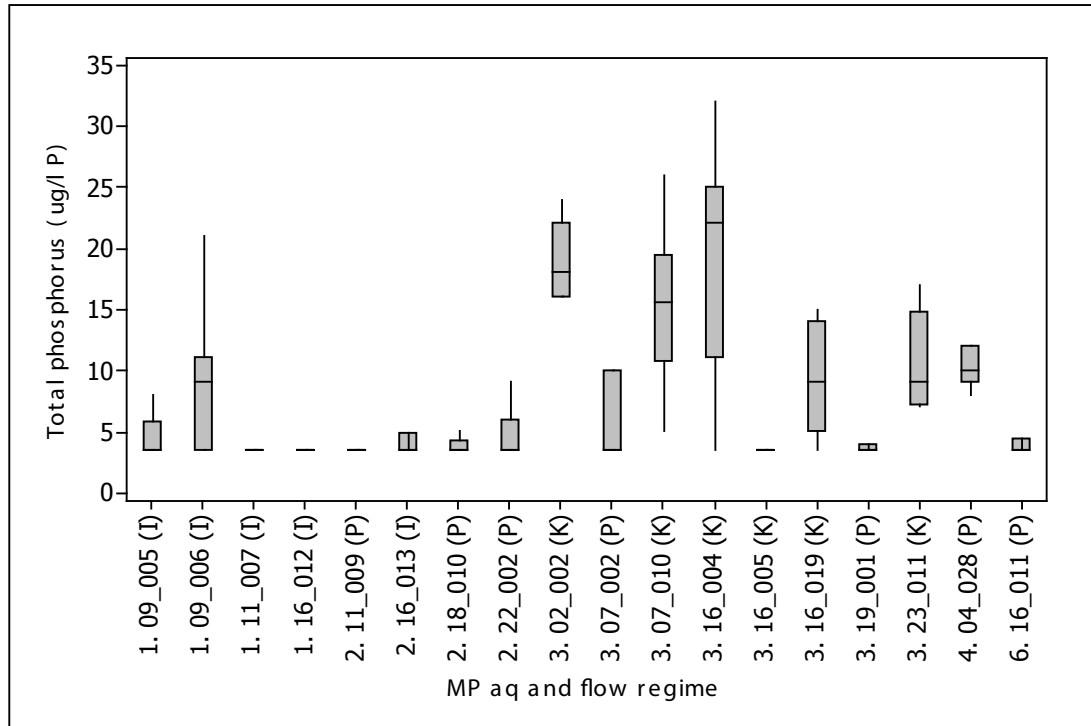


Figure A65. Box and whisker plot summarising total phosphorus data from each monitoring point used to establish natural background levels for total phosphorus in Irish groundwater. Flow regime categories are indicated in parenthesis: (I) intergranular; (K) karstified and (P) poorly productive. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

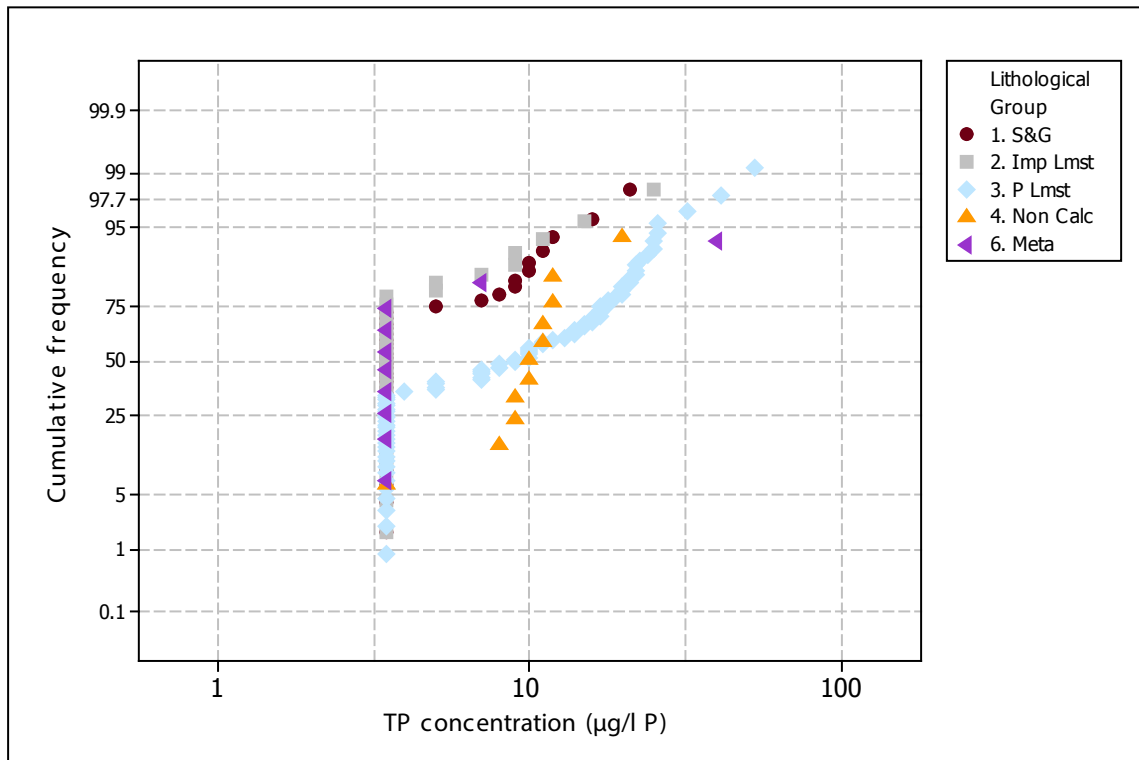


Figure A66. Cumulative frequency diagram showing the distribution of total reactive phosphorus data used to establish natural background levels for total reactive phosphorus in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; lg, igneous; Meta, metamorphic.

Molybdate Reactive Phosphorus

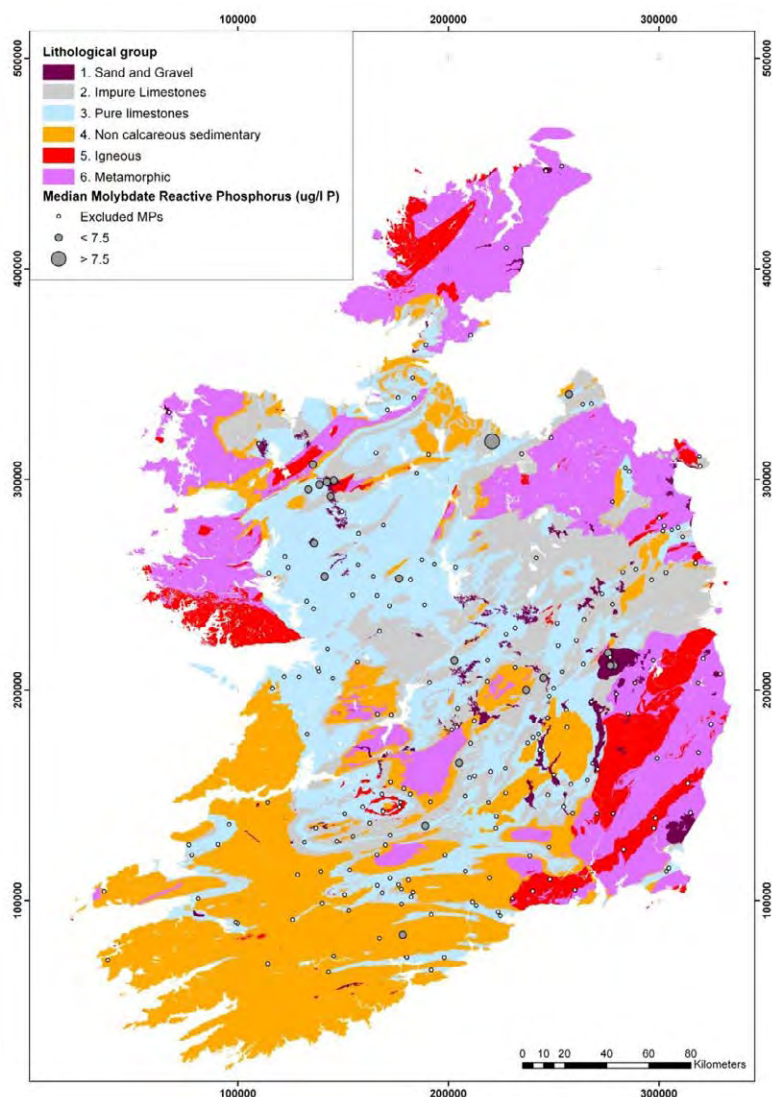


Figure A67. Location and median molybdate reactive phosphorus values of the monitoring points used to establish natural background levels for molybdate reactive phosphorus in Irish groundwater.

Table A23. Descriptive statistics of molybdate reactive phosphorus for monitoring points used to establish natural background levels for molybdate reactive phosphorus in Irish groundwater presented for all monitoring points and by lithological group

Molybdate reactive phosphorus ($\mu\text{g/l P}$)								
	Unconfined MPs	Confined MP's	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MP's	17	1	4	3	8	0	0	1
Number of data points	182	11	43	31	86	11	0	11
5th percentile	7.5	7.5	7.5	7.5	7.5	7.5	—	7.5
Median	7.5	7.5	7.5	7.5	7.5	7.5	—	7.5
95th percentile	17.0	12.8	7.5	7.5	20.0	7.5	—	7.5

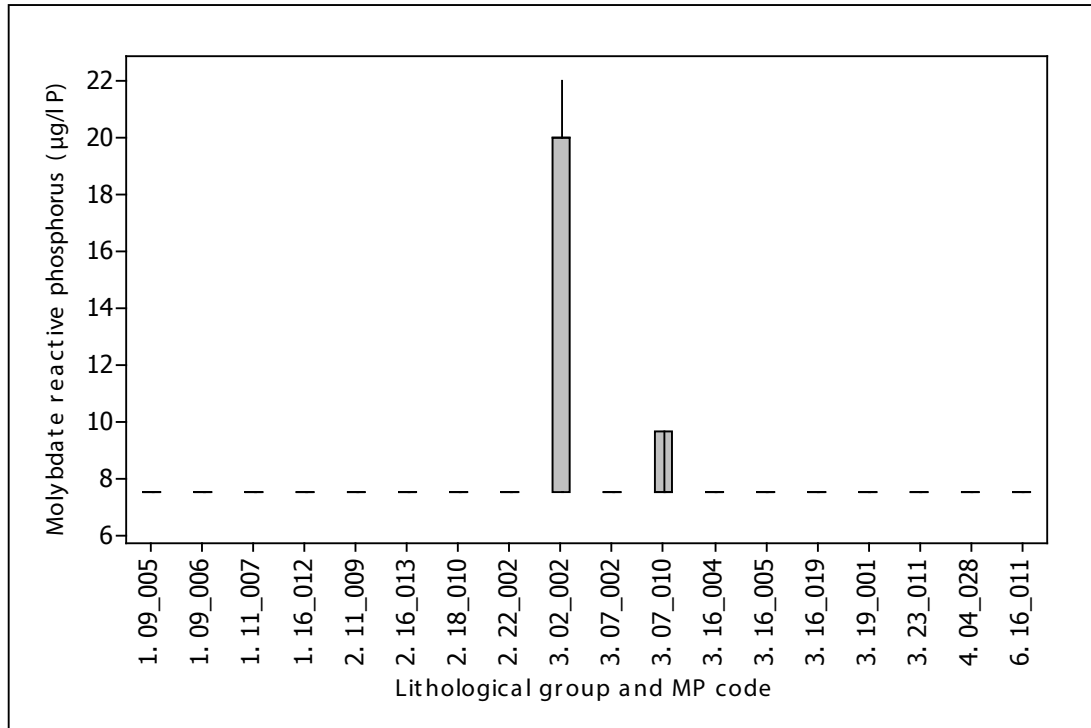


Figure A68. Box and whisker plot summarising molybdate reactive phosphorus data from each monitoring point used to establish natural background levels for molybdate reactive phosphorus in Irish groundwater. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 6, metamorphic.

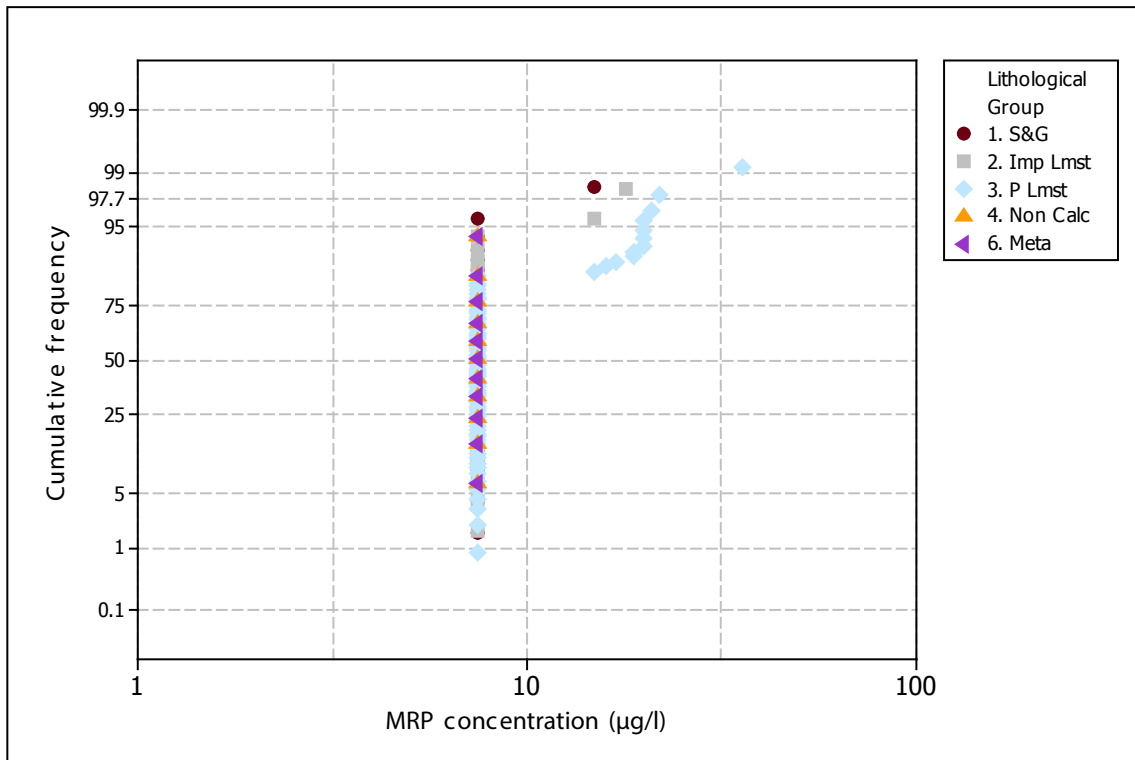


Figure A69. Cumulative frequency diagram showing the distribution of molybdate reactive phosphorus data used to establish natural background levels for molybdate reactive phosphorus in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Total Organic Carbon

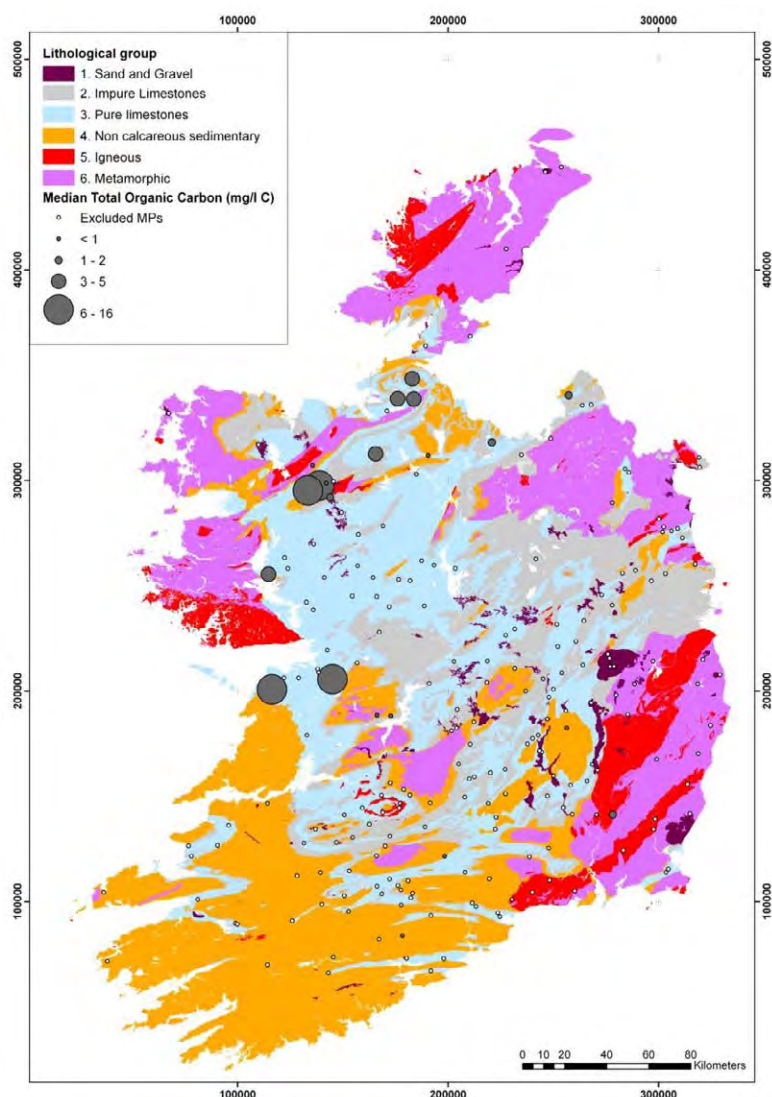


Figure A70. Location and median total organic carbon values of the monitoring points used to establish natural background levels for total organic carbon in Irish groundwater.

Table A24. Descriptive statistics of total organic carbon for monitoring points used to establish natural background levels for total organic carbon in Irish groundwater presented for all monitoring points and by lithological group

Total organic carbon (mg/l C)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	446	71	25	46	234	69	24	48
5th percentile	0.44	0.37	0.74	0.75	0.75	0.13	0.79	0.71
Median	1.80	0.97	1.00	2.05	4.51	0.75	1.78	1.00
95th percentile	26.26	69.55	3.40	46.10	36.04	3.60	9.97	16.00

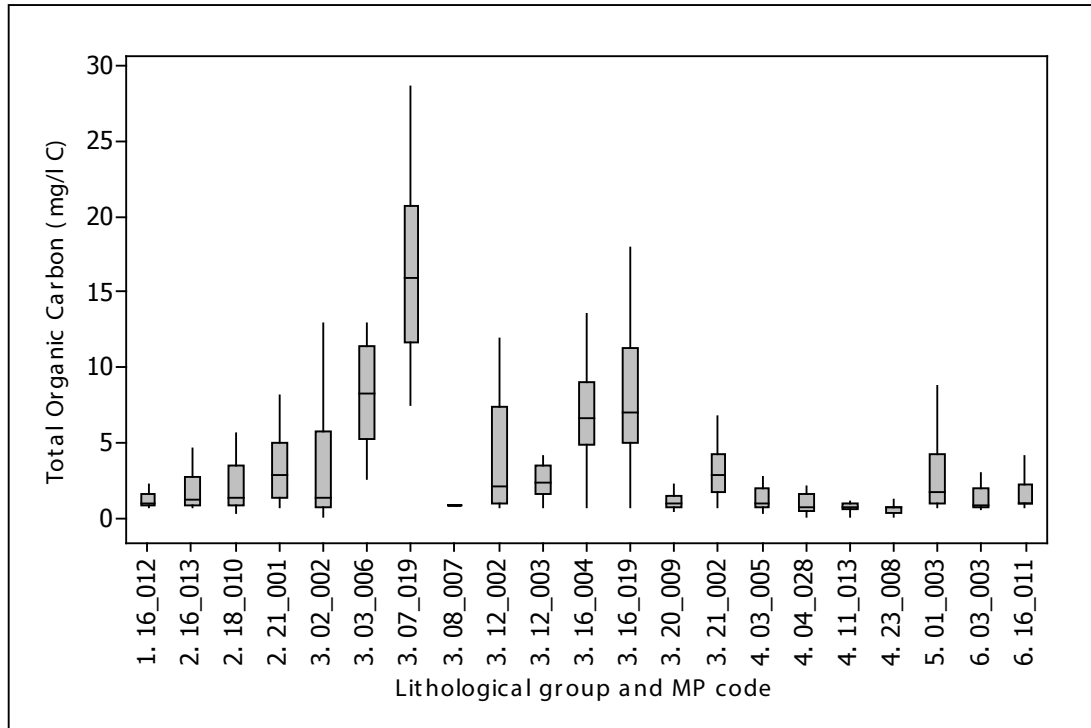


Figure A71. Box and whisker plot summarising total organic carbon data from each monitoring point used to establish natural background levels for total organic carbon in Irish groundwater. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

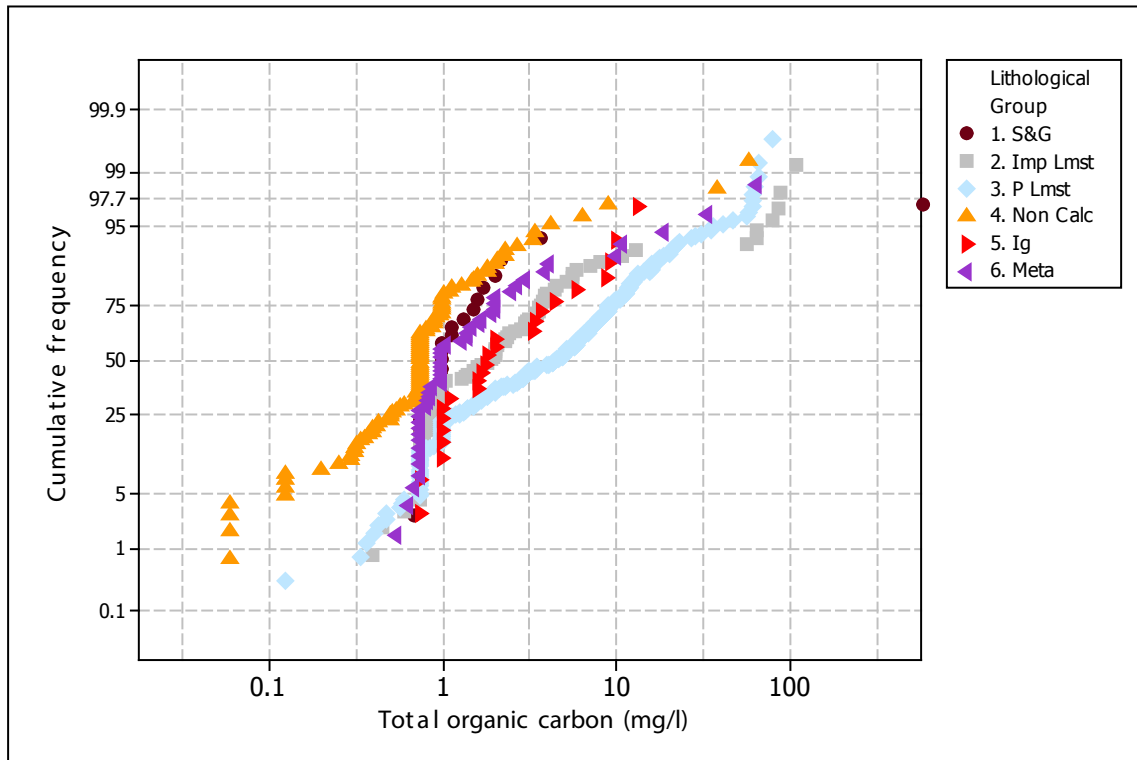


Figure A72. Cumulative frequency diagram showing the distribution of total organic carbon data used to establish natural background levels for total organic carbon in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Aluminium

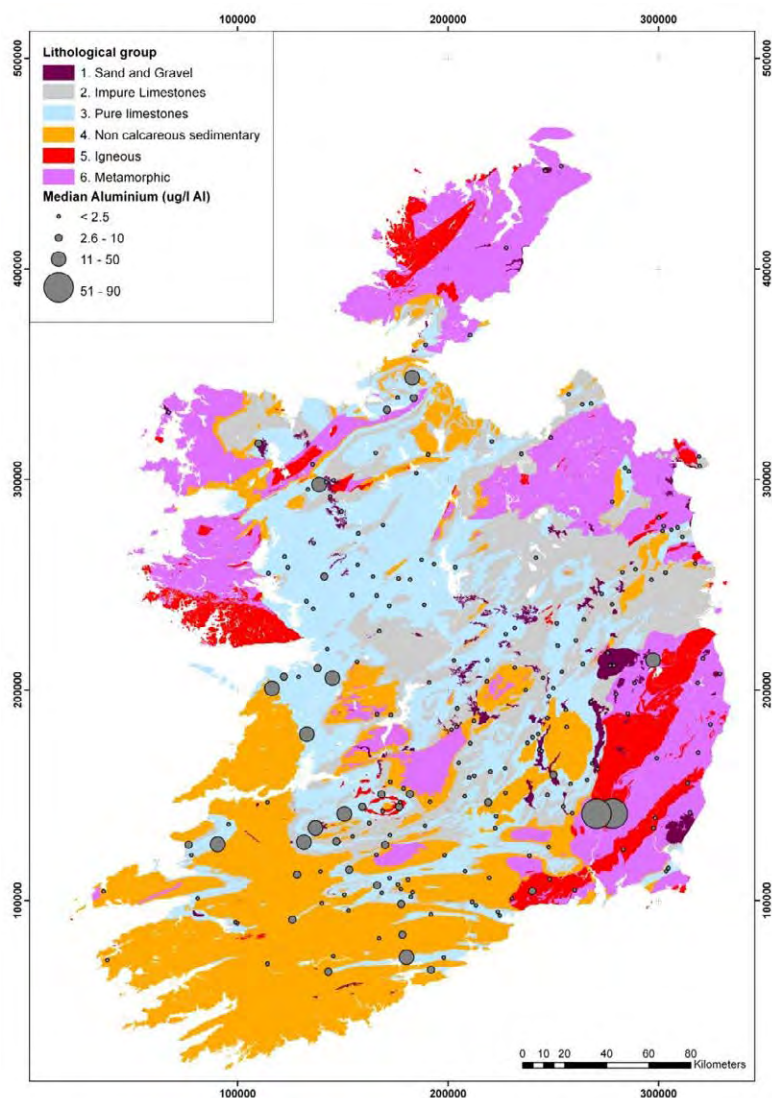


Figure A73. Location and median aluminium values of the monitoring points used to establish natural background levels for aluminium in Irish groundwater.

Table A25. Descriptive statistics of total organic carbon for monitoring points used to establish natural background levels for aluminium in Irish groundwater presented for all monitoring points and by lithological group

Aluminium (µg/l Al)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non - calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	215	2	30	29	96	31	13	16
Number of data points	4682	47	632	583	2145	688	288	346
5th percentile	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Median	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
95th percentile	24.04	14.50	15.18	18.90	26.00	16.00	130.90	18.83

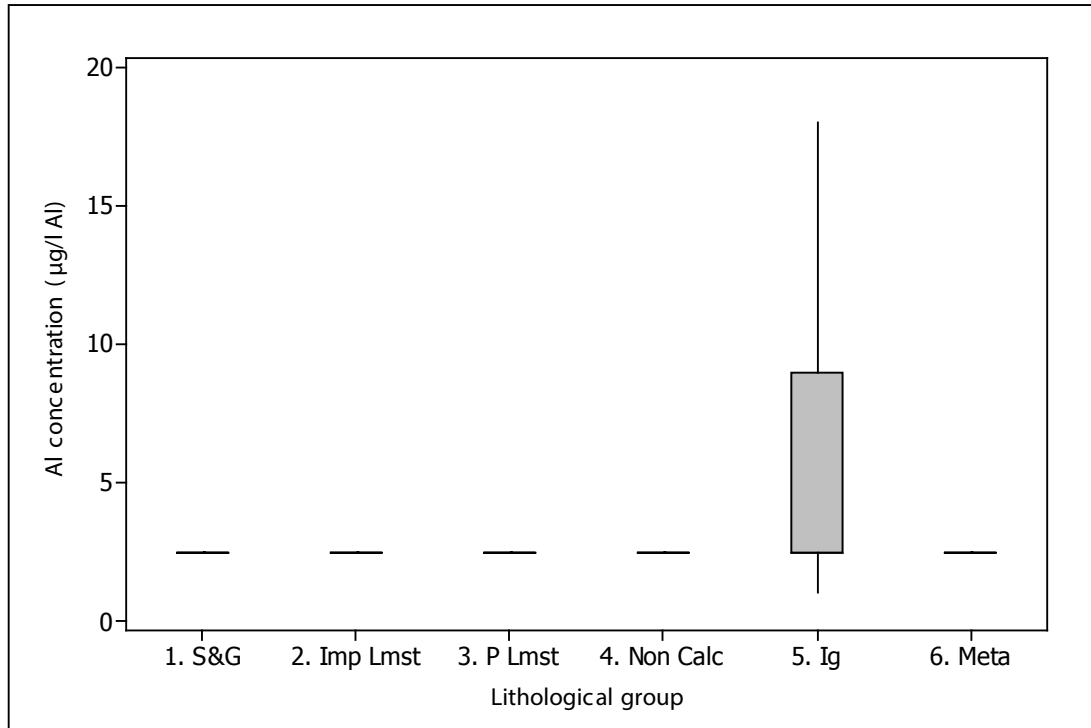


Figure A74. Box and whisker plot summarising total aluminium from each monitoring point used to establish natural background levels for aluminium in Irish groundwater.

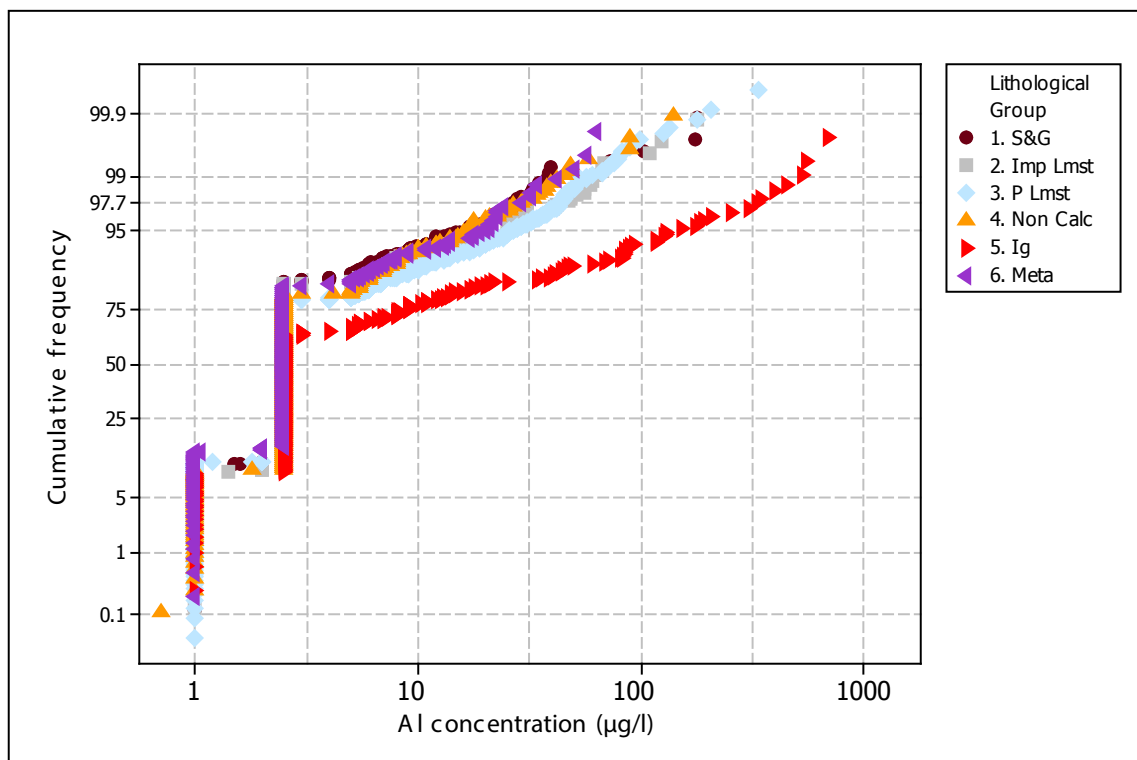


Figure A75. Cumulative frequency diagram showing the distribution of aluminium data used to establish natural background levels for aluminium in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Antimony

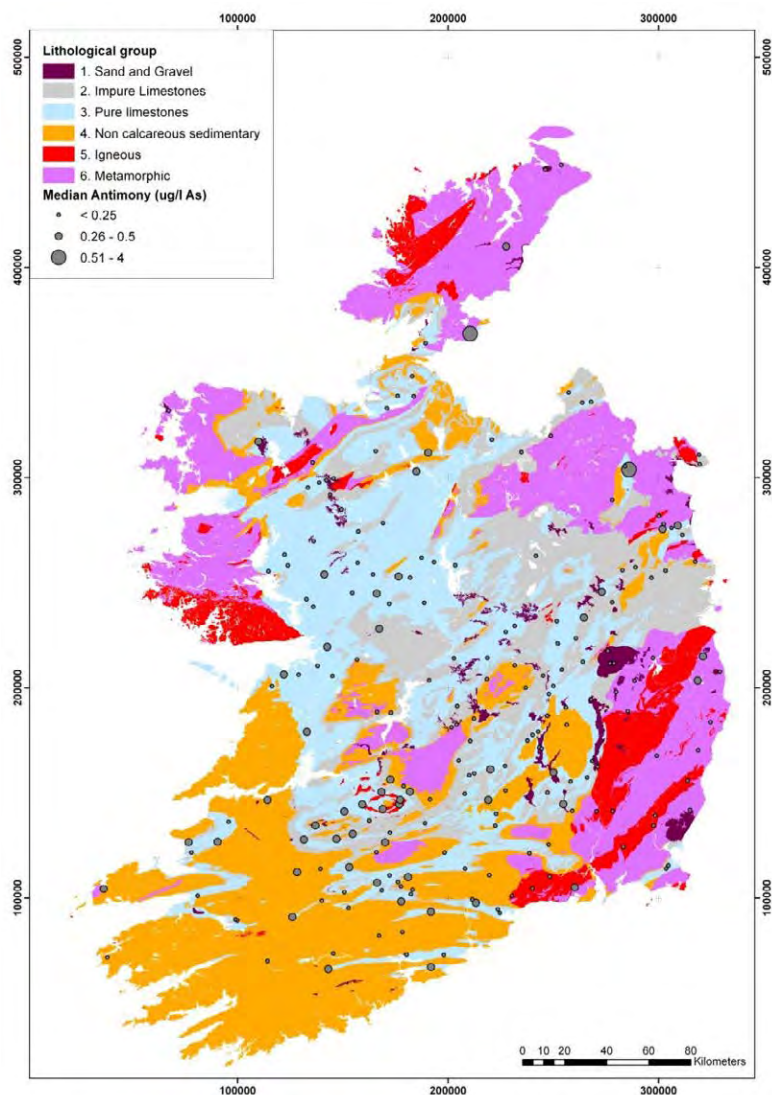


Figure A76. Location and median antimony values of the monitoring points used to establish natural background levels for antimony in Irish groundwater.

Table A26. Descriptive statistics of antimony for monitoring points used to establish natural background levels for antimony in Irish groundwater presented for all monitoring points and by lithological group

Antimony ($\mu\text{g/l Sb}$)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	215	2	30	29	96	31	13	16
Number of data	4857	48	658	605	2227	711	296	360
5th percentile	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Median	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
95th percentile	0.50	0.50	0.50	0.50	0.50	0.50	0.50	3.02

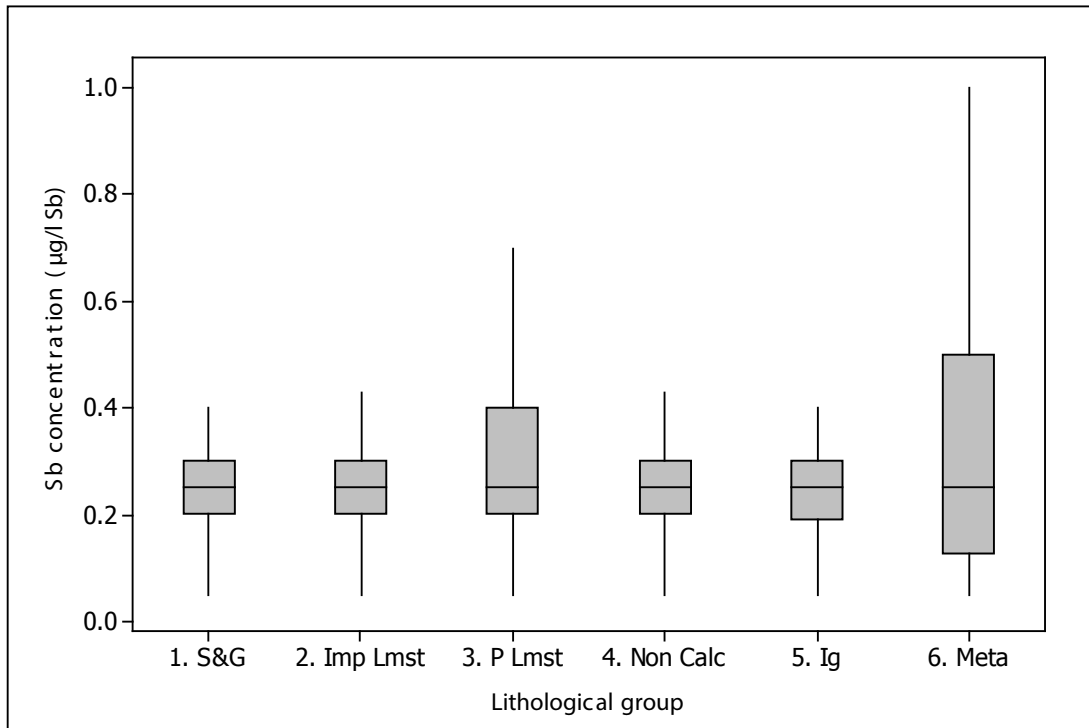


Figure A77. Box and whisker plot summarising total antimony from each monitoring point used to establish natural background levels for antimony in Irish groundwater.

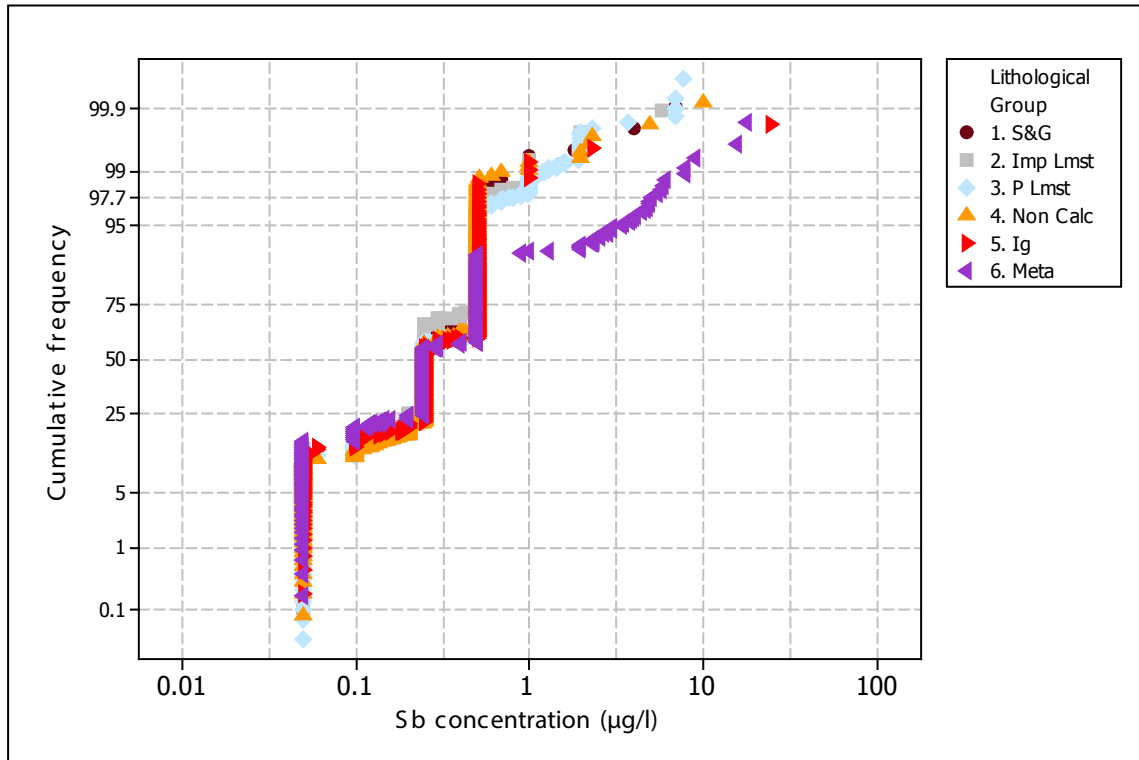


Figure A78. Cumulative frequency diagram showing the distribution of antimony data used to establish natural background levels for antimony in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Arsenic

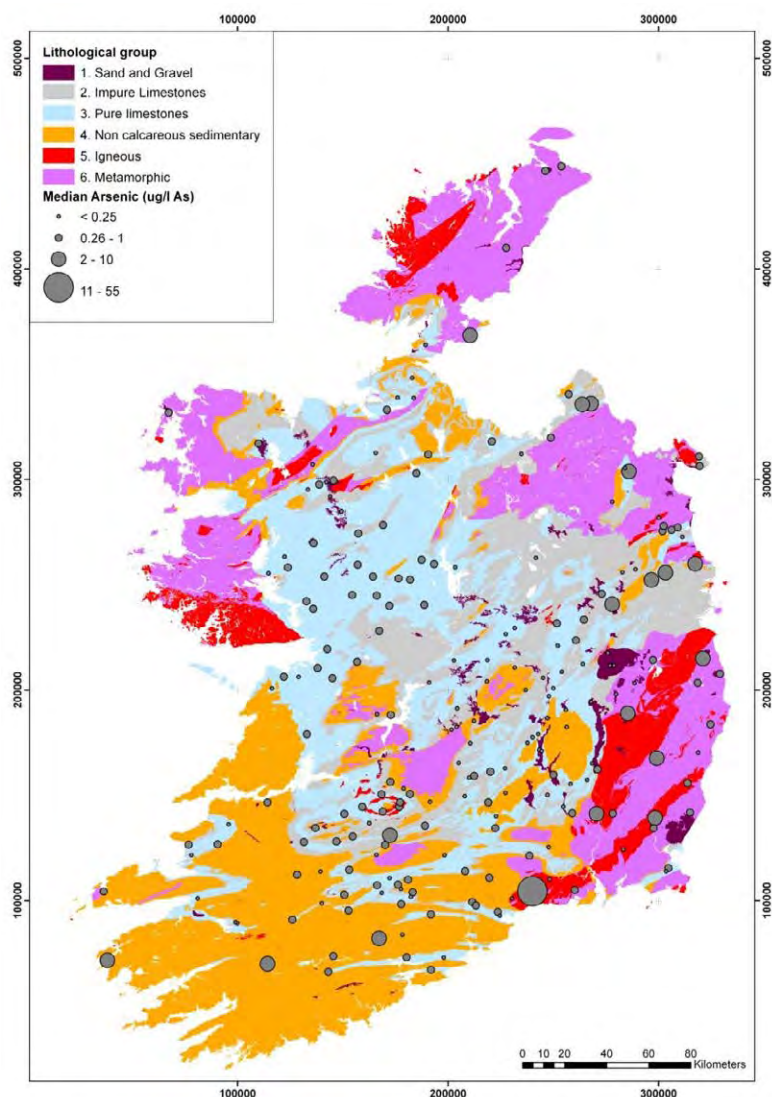


Figure A79. Location and median arsenic values of the monitoring points used to establish natural background levels for arsenic in Irish groundwater.

Table A27. Descriptive statistics of arsenic for monitoring points used to establish natural background levels for arsenic in Irish groundwater presented for all monitoring points and by lithological group

Arsenic ($\mu\text{g/l As}$)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	215	2	30	29	96	31	13	16
Number of data points	4853	48	659	605	2225	707	297	360
5th percentile	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Median	0.25	0.25	0.25	0.30	0.25	0.30	0.50	0.50
95th percentile	2.00	0.50	1.00	3.00	1.00	2.00	52.10	3.14

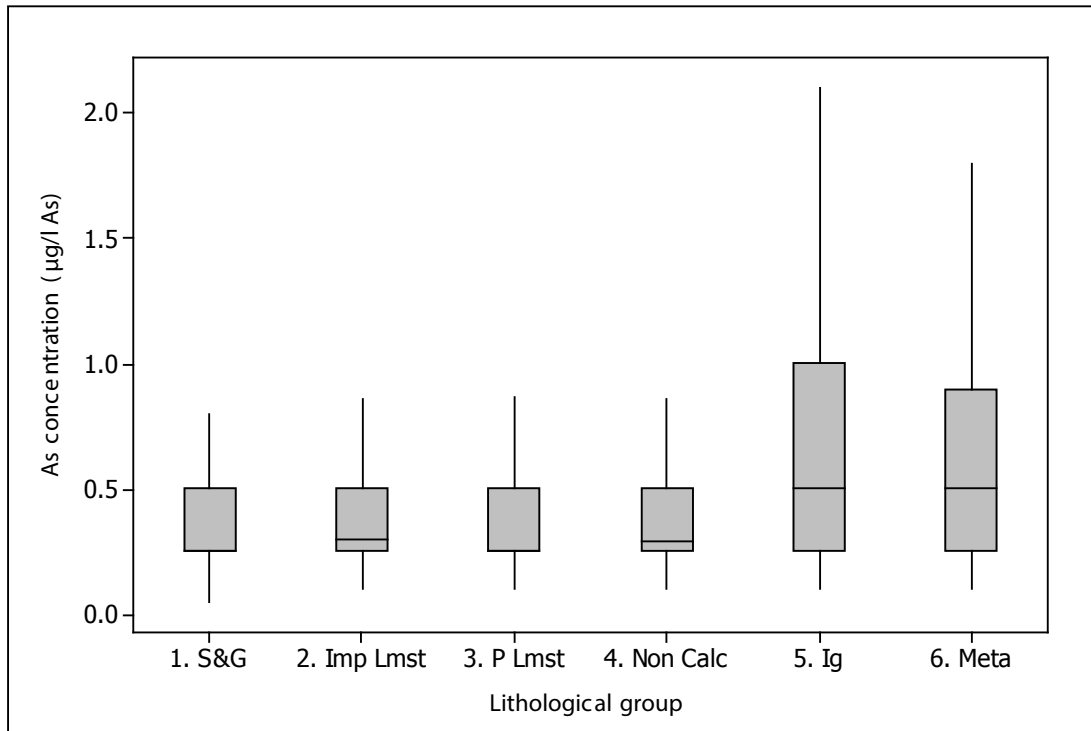


Figure A80. Box and whisker plot summarising total arsenic from each monitoring point used to establish natural background levels for arsenic in Irish groundwater.

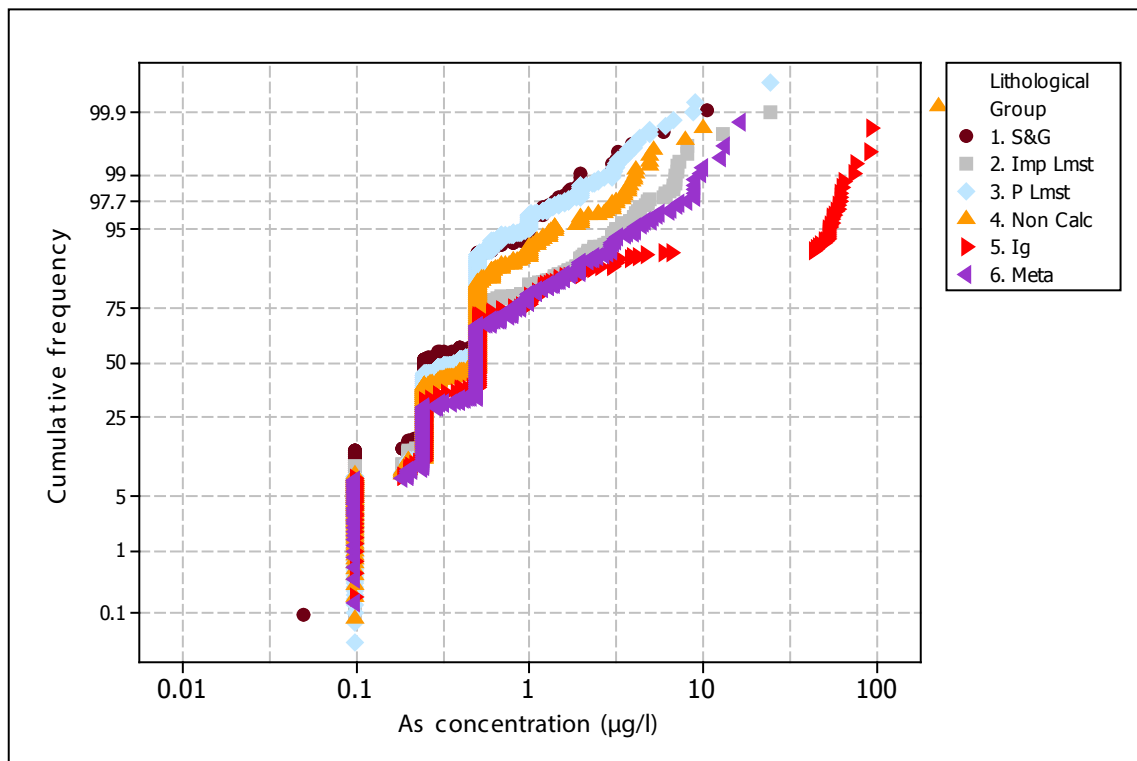


Figure A81. Cumulative frequency diagram showing the distribution of arsenic data used to establish natural background levels for arsenic in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Beryllium

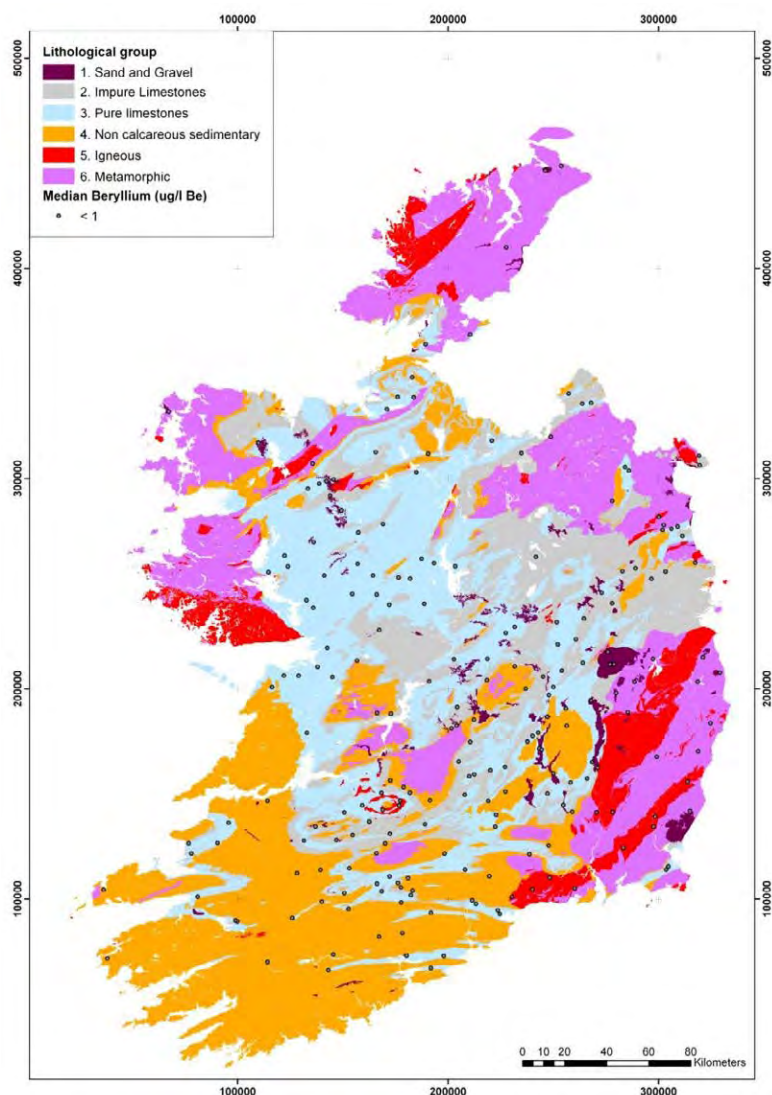


Figure A82. Location and median beryllium values of the monitoring points used to establish natural background levels for beryllium in Irish groundwater.

Table A28. Descriptive statistics of beryllium for monitoring points used to establish natural background levels for beryllium in Irish groundwater presented for all monitoring points and by lithological group

Beryllium (µg/l Be)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	215	2	30	29	96	31	13	16
Number of data	4862	48	659	605	2230	711	297	360
5th percentile	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Median	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
95th percentile	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50

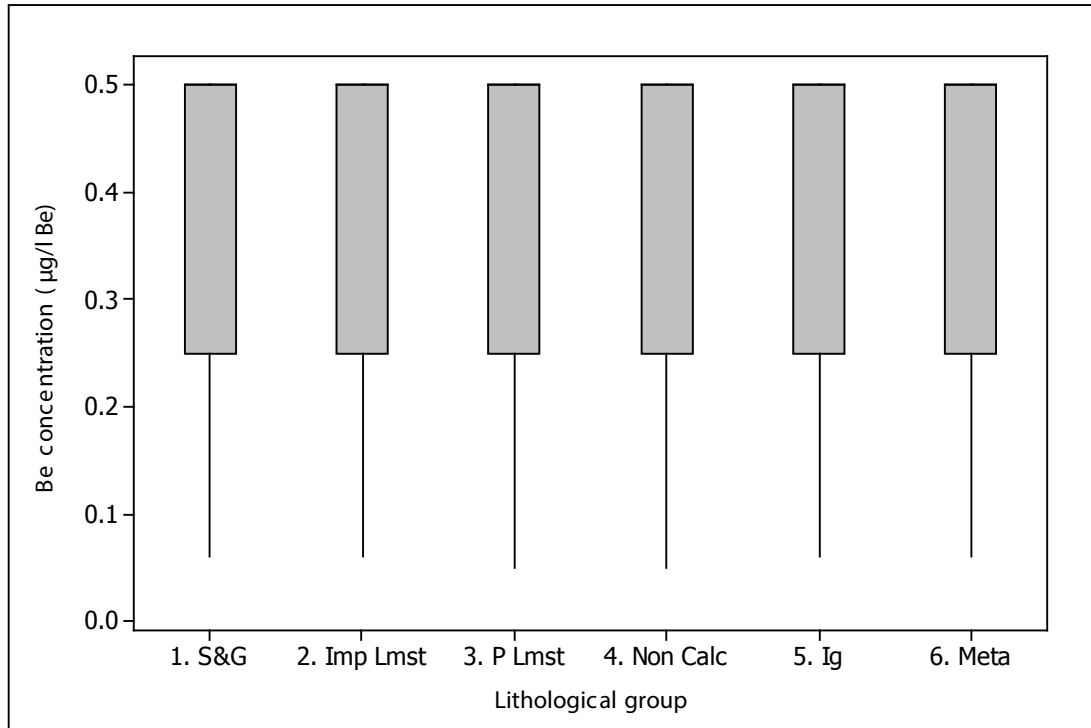


Figure A83. Box and whisker plot summarising total beryllium from each monitoring point used to establish natural background levels for beryllium in Irish groundwater.

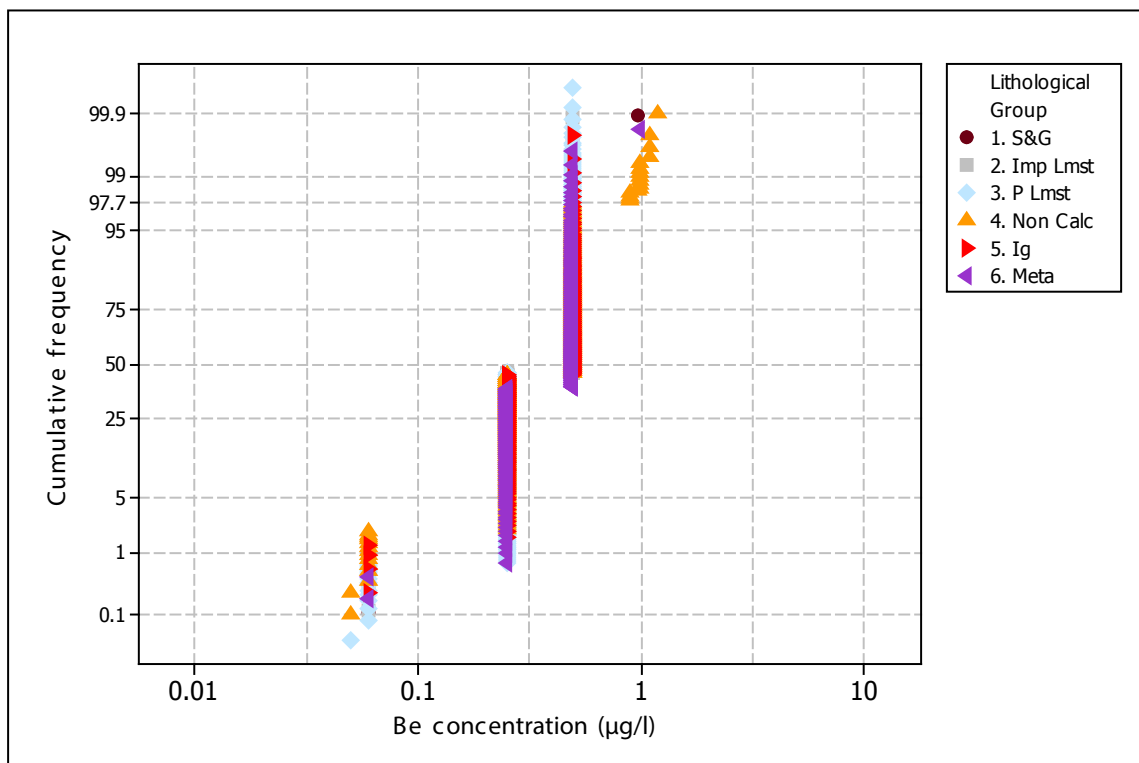


Figure A84. Cumulative frequency diagram showing the distribution of beryllium data used to establish natural background levels for beryllium in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Boron

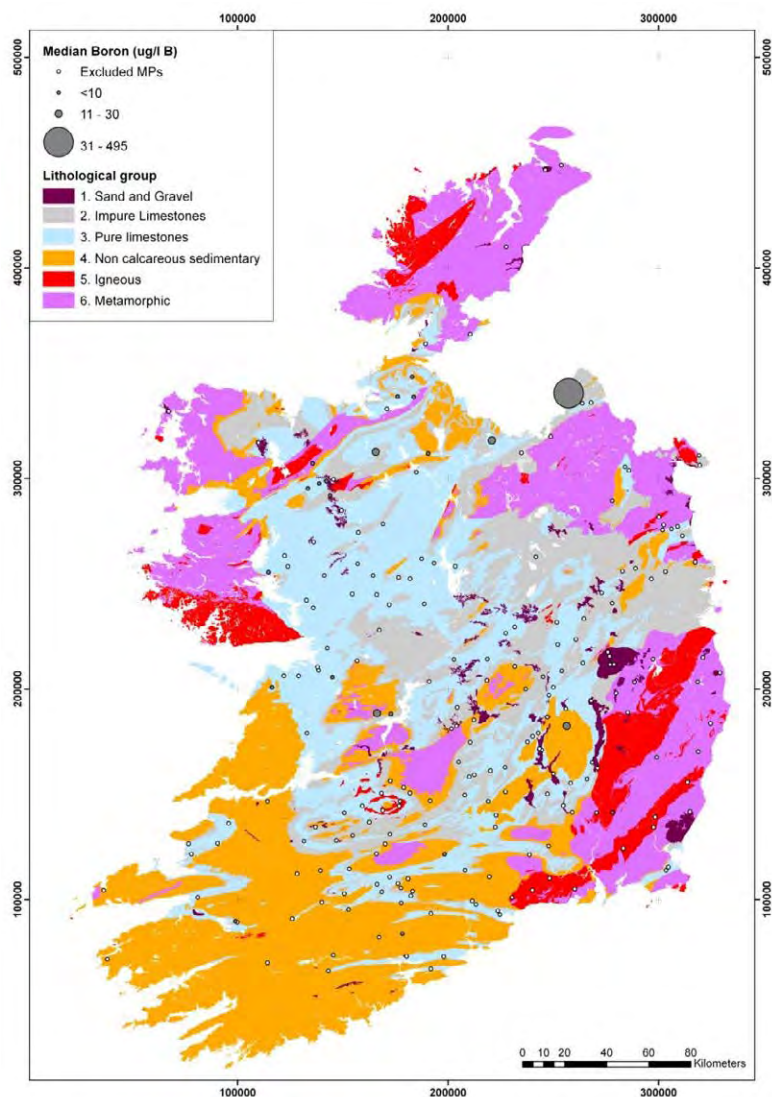


Figure A85. Location and median boron values of the monitoring points used to establish natural background levels for boron in Irish groundwater.

Table A29. Descriptive statistics of boron for monitoring points used to establish natural background levels for boron in Irish groundwater presented for all monitoring points and by lithological group

Boron (µg/l B)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	416	48	25	44	216	59	24	48
5th percentile	1.50	10.00	1.50	1.50	1.50	4.65	1.50	1.50
Median	10.00	32.87	10.00	5.00	10.00	8.50	5.00	10.00
95th percentile	15.00	572.50	11.80	10.85	16.00	11.00	21.85	13.00

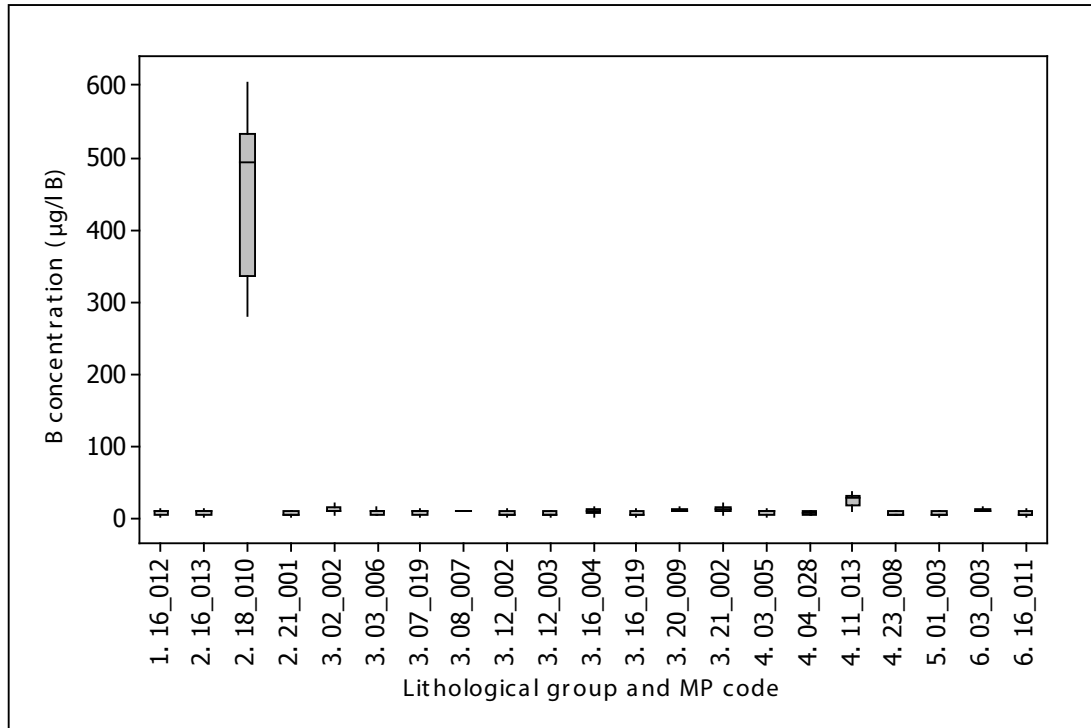


Figure A86. Box and whisker plot summarising total boron from each monitoring point used to establish natural background levels for boron in Irish groundwater. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

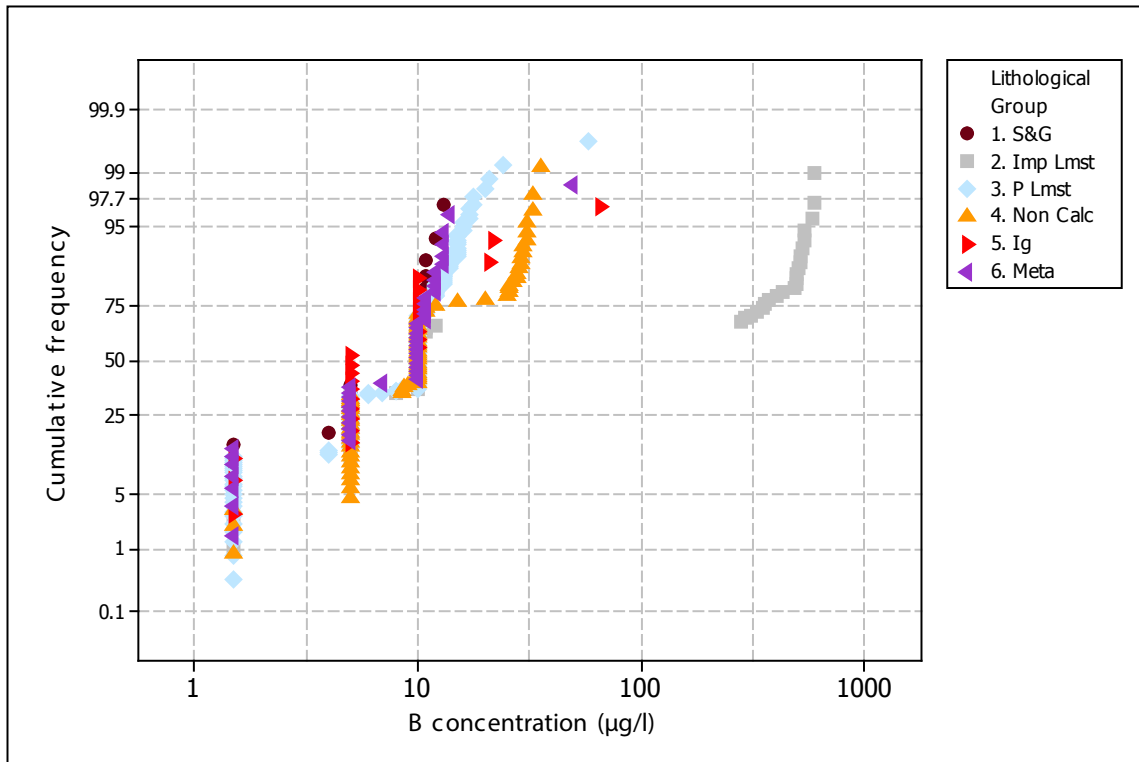


Figure A87. Cumulative frequency diagram showing the distribution of boron data used to establish natural background levels for boron in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Cadmium

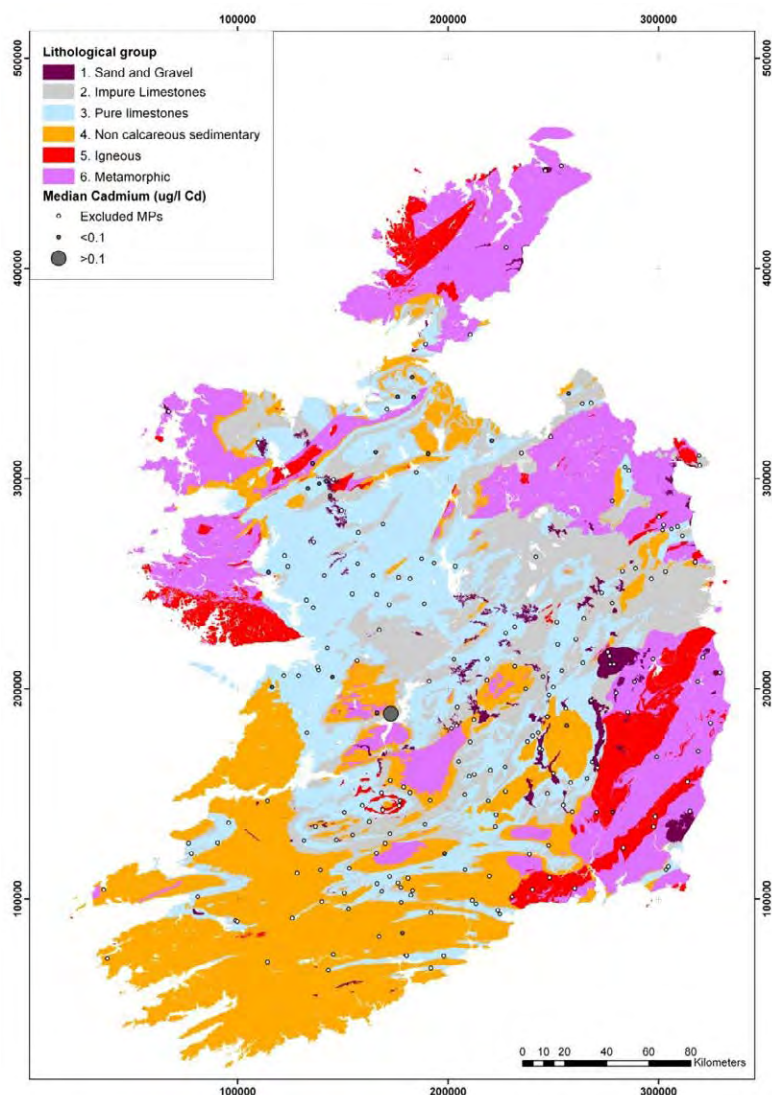


Figure A88. Location and median cadmium values of the monitoring points used to establish natural background levels for cadmium in Irish groundwater.

Table A30. Descriptive statistics of cadmium for monitoring points used to establish natural background levels for cadmium in Irish groundwater presented for all monitoring points and by lithological group

Cadmium ($\mu\text{g/l Cd}$)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	416	48	25	44	216	59	24	48
5th percentile	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Median	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
95th percentile	0.20	0.20	0.20	0.20	0.20	0.50	0.20	0.20

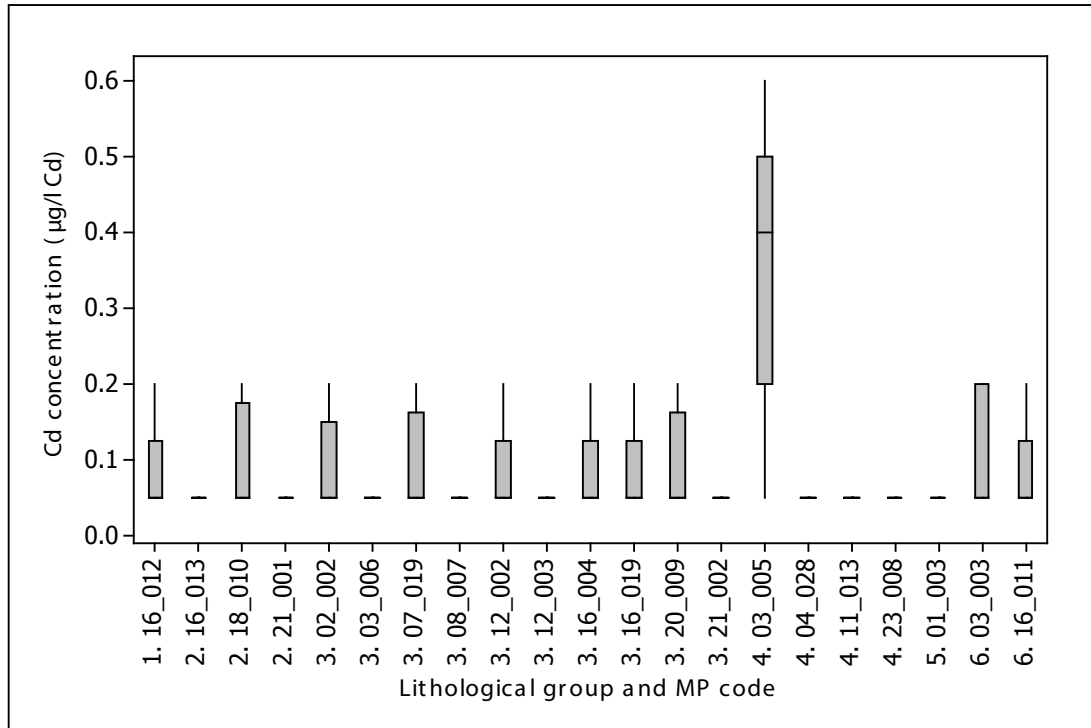


Figure A89. Box and whisker plot summarising total cadmium from each monitoring point used to establish natural background levels for cadmium in Irish groundwater. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

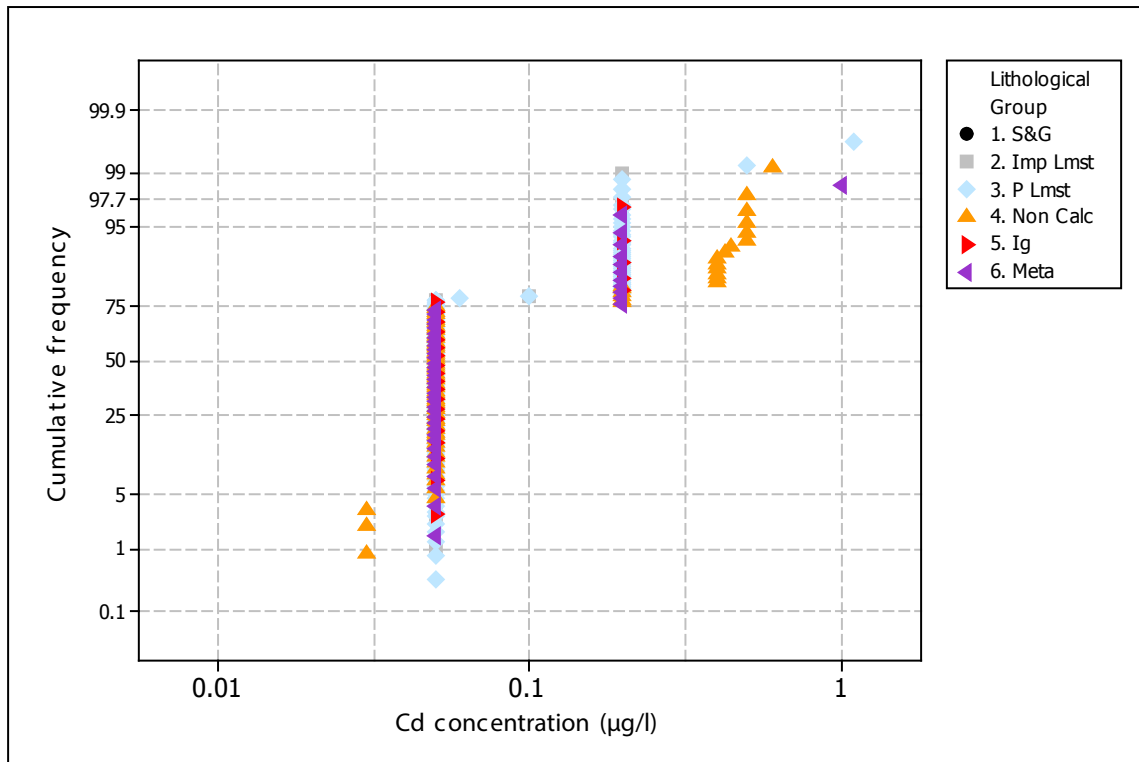


Figure A90. Cumulative frequency diagram showing the distribution of cadmium data used to establish natural background levels for cadmium in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Chromium

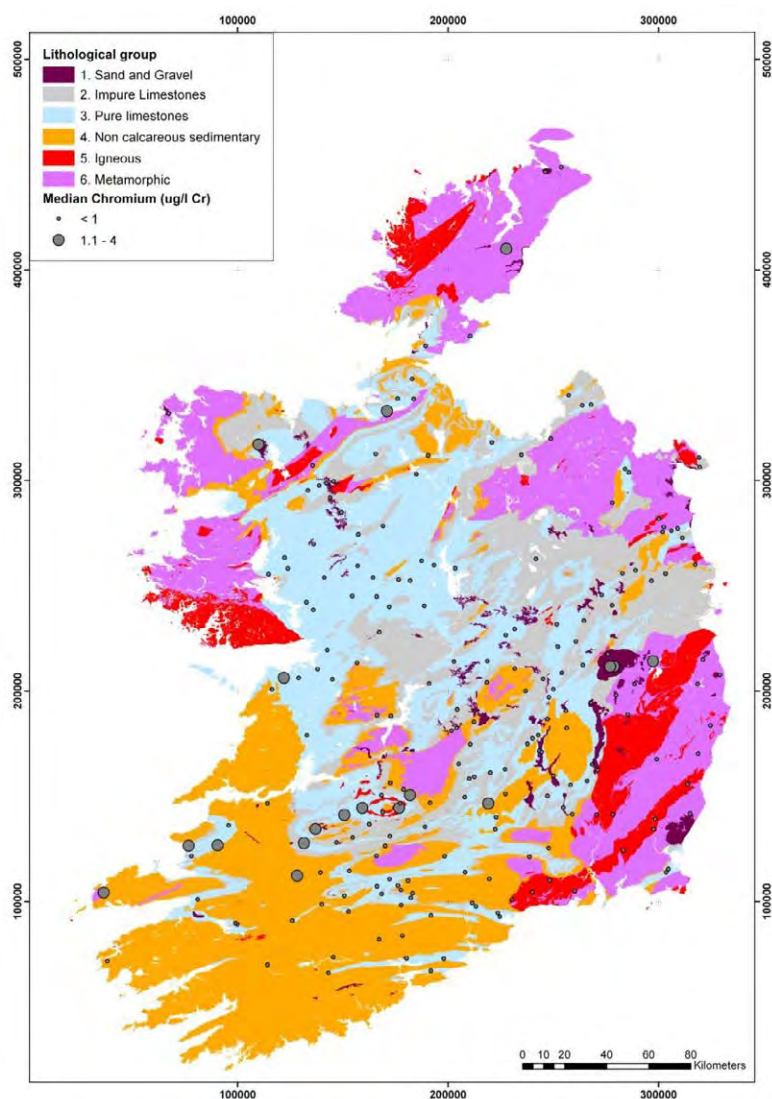


Figure A91. Location and median chromium values of the monitoring points used to establish natural background levels for chromium in Irish groundwater.

Table A31. Descriptive statistics of cadmium for monitoring points used to establish natural background levels for cadmium in Irish groundwater presented for all monitoring points and by lithological group

Chromium (µg/l Cr)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	214	2	30	29	95	31	13	16
Number of data points	4862	48	659	605	2230	711	297	360
5th percentile	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Median	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
95th percentile	10.00	8.30	10.82	11.00	11.00	9.00	4.20	8.00

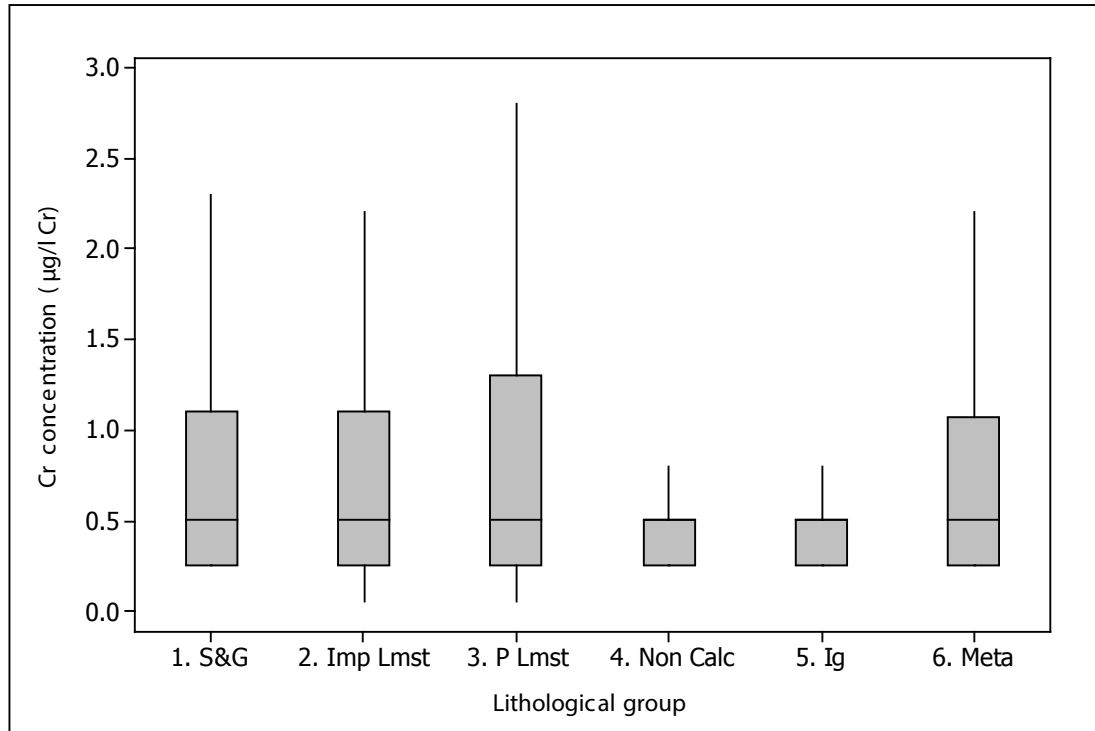


Figure A92. Box and whisker plot summarising total chromium from each monitoring point used to establish natural background levels for chromium in Irish groundwater.

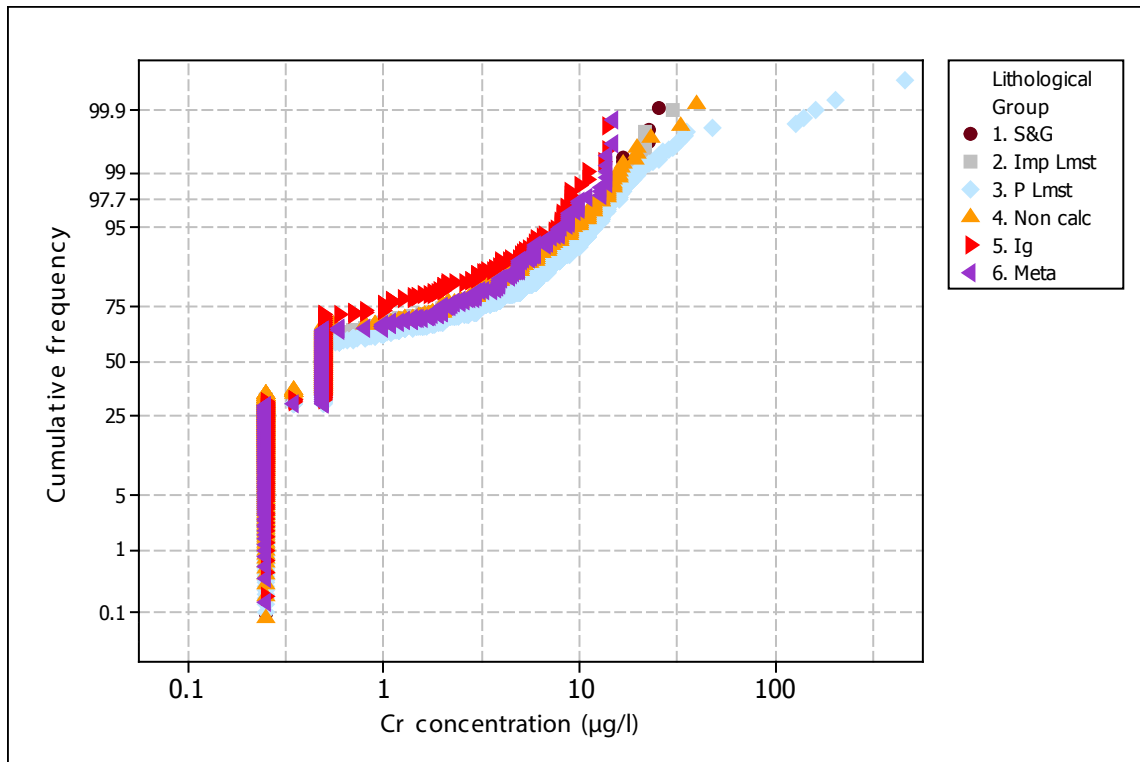


Figure A93. Cumulative frequency diagram showing the distribution of chromium data used to establish natural background levels for chromium in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Cobalt

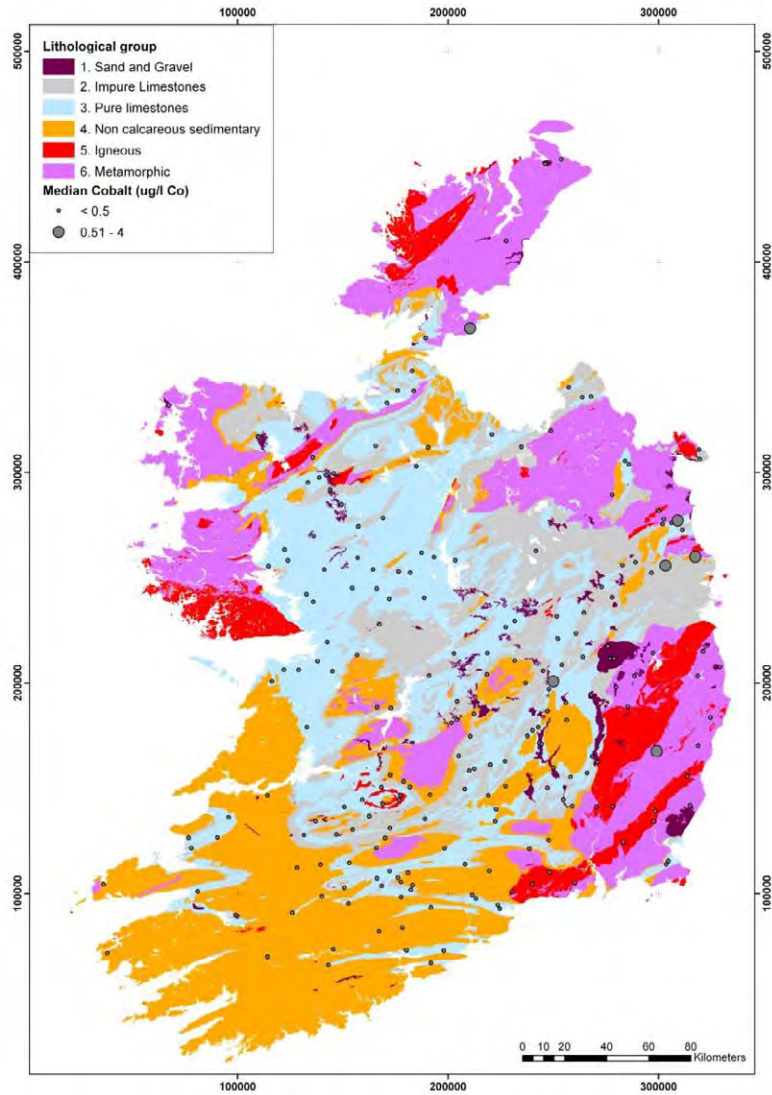


Figure A94. Location and median cobalt values of the monitoring points used to establish natural background levels for cobalt in Irish groundwater.

Table A32. Descriptive statistics of cobalt for monitoring points used to establish natural background levels for cobalt in Irish groundwater presented for all monitoring points and by lithological group

Cobalt (µg/l Co)								
	All lithologies	Unconfined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	217	215	30	29	96	31	13	16
Number of data points	4910	4862	659	605	2230	711	297	360
5th percentile	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Median	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
95th percentile	0.80	0.80	0.50	1.24	0.50	0.60	0.50	3.10

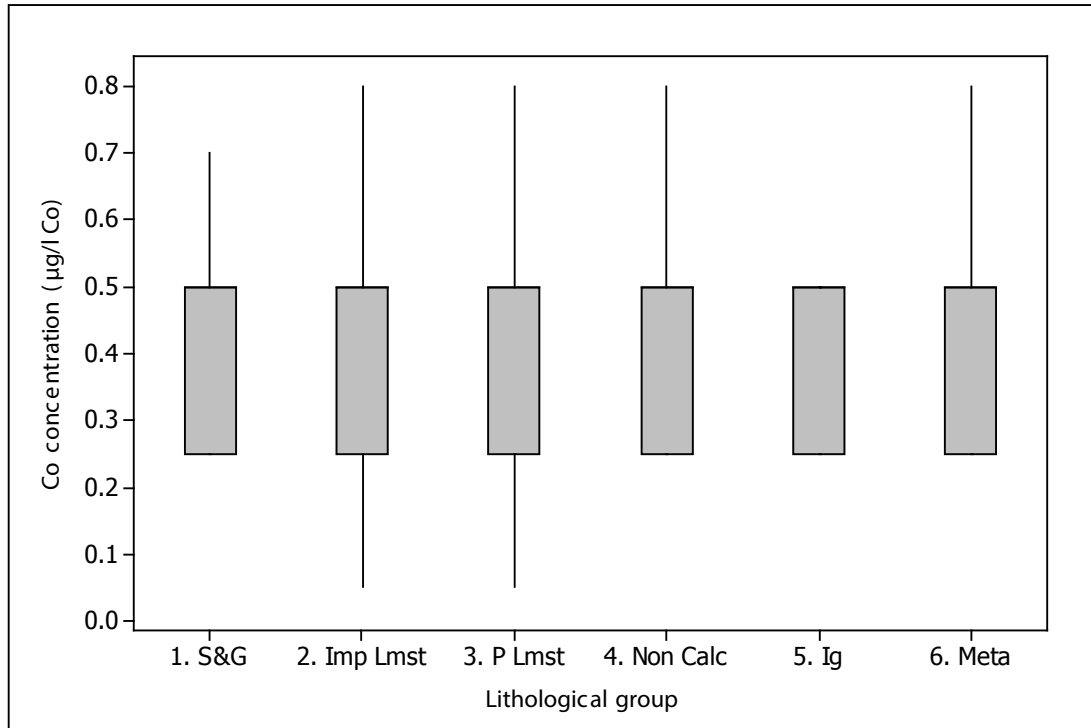


Figure A95. Box and whisker plot summarising total cobalt from each monitoring point used to establish natural background levels for cobalt in Irish groundwater.

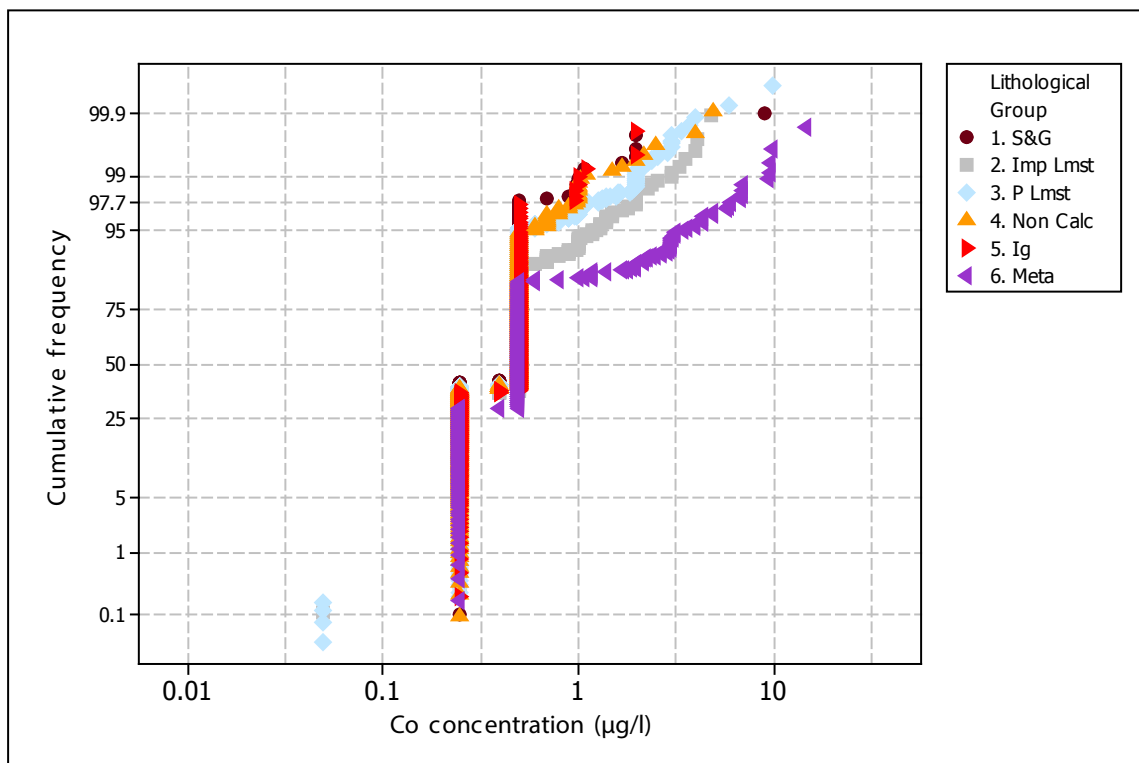


Figure A96. Cumulative frequency diagram showing the distribution of cobalt data used to establish natural background levels for cobalt in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Copper

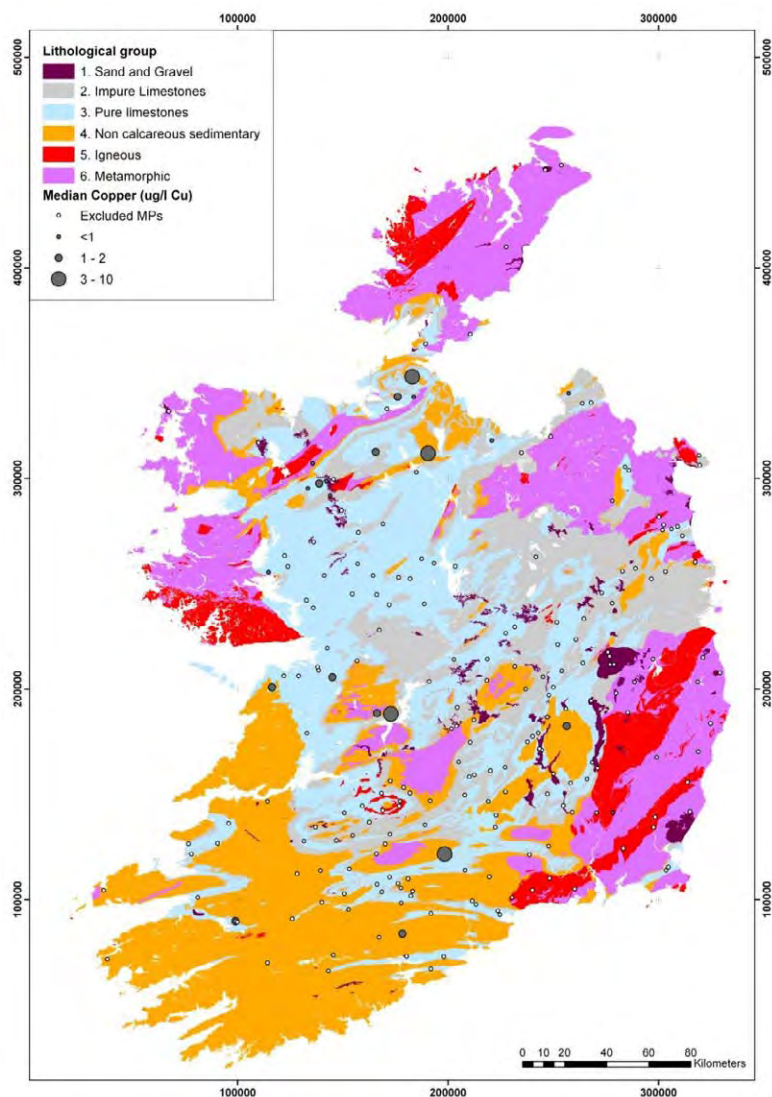


Figure A97. Location and median copper values of the monitoring points used to establish natural background levels for copper in Irish groundwater.

Table A33. Descriptive statistics of copper for monitoring points used to establish natural background levels for copper in Irish groundwater presented for all monitoring points and by lithological group

Copper (µg/l Cu)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	416	48	25	44	216	59	24	48
5th percentile	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Median	1.50	1.50	0.80	0.75	1.45	2.00	0.90	1.10
95th percentile	16.00	8.70	8.53	18.14	8.25	44.20	2.93	7.26

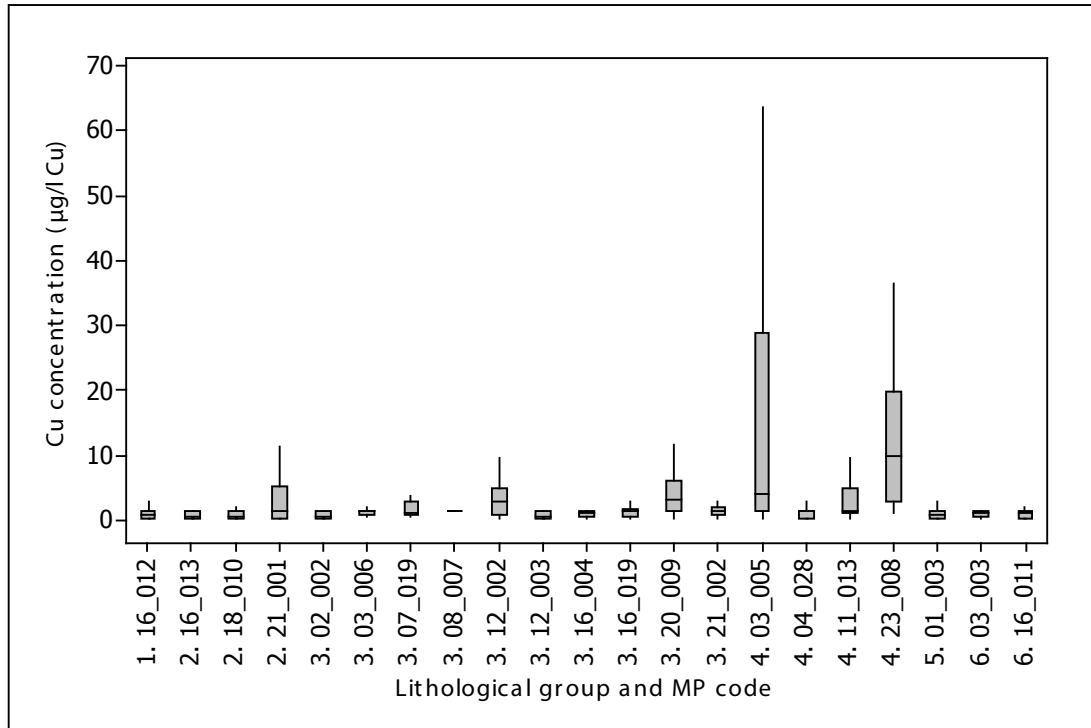


Figure A98. Box and whisker plot summarising total copper from each monitoring point used to establish natural background levels for copper in Irish groundwater. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

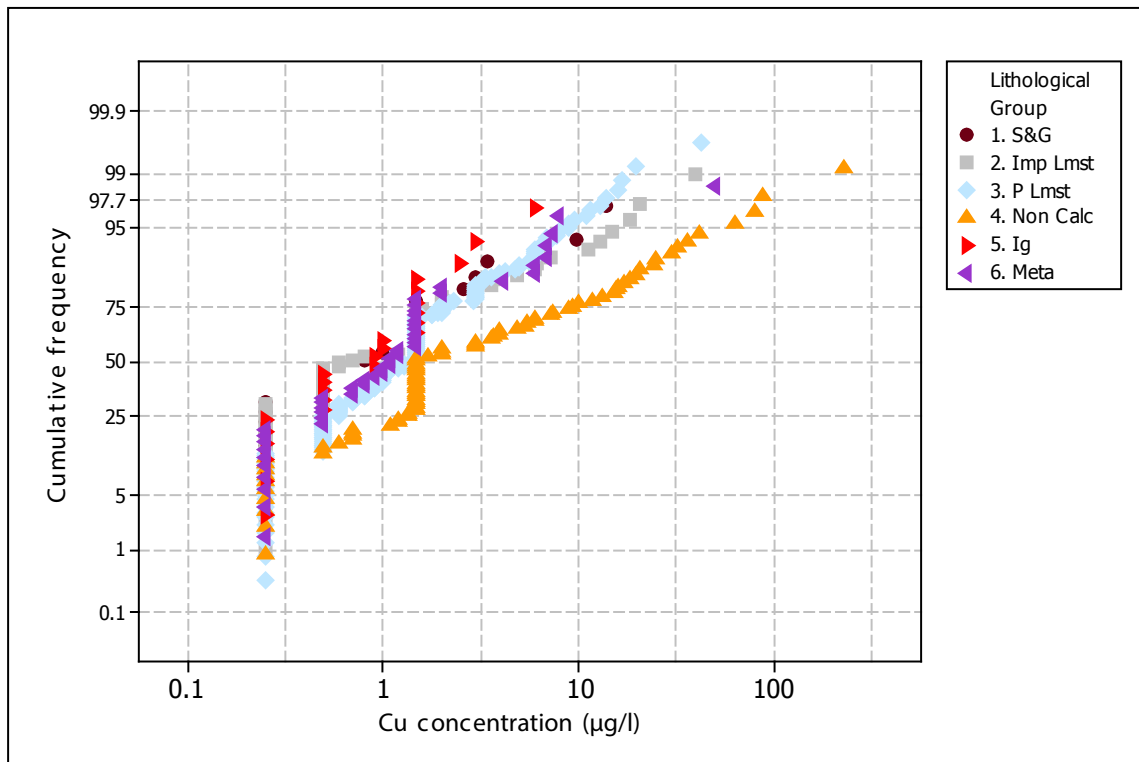


Figure A99. Cumulative frequency diagram showing the distribution of copper data used to establish natural background levels for copper in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Lead

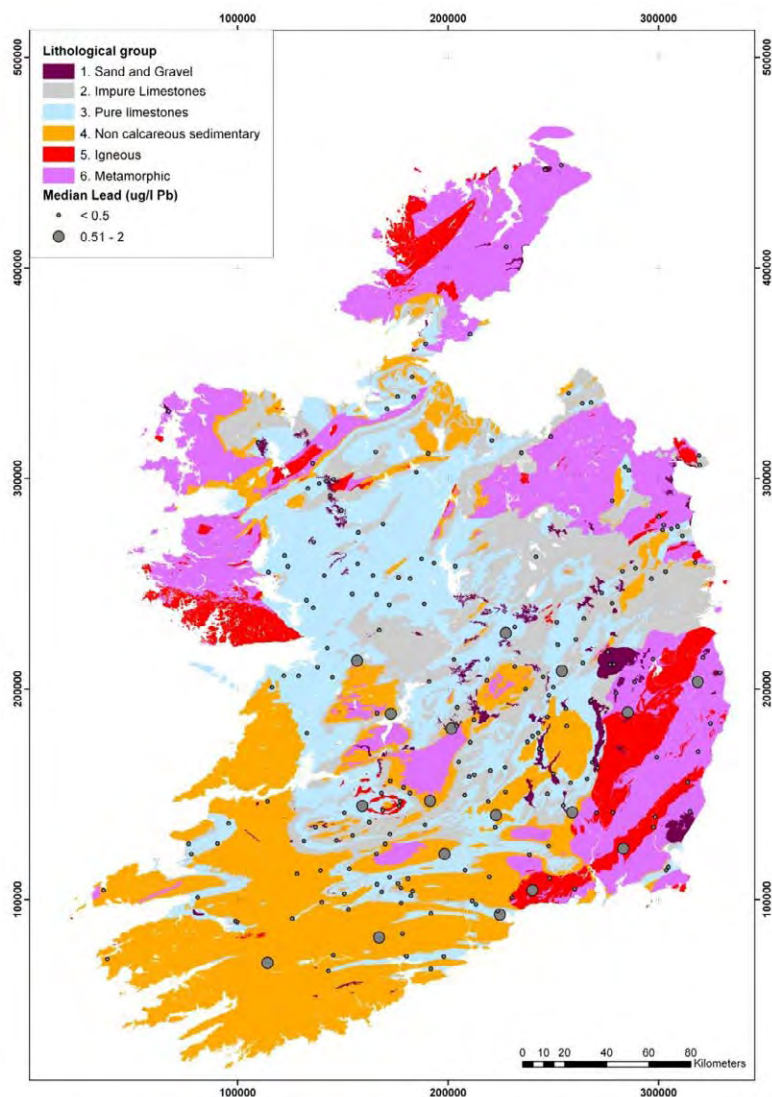


Figure A100. Location and median lead values of the monitoring points used to establish natural background levels for lead in Irish groundwater.

Table A34. Descriptive statistics of lead for monitoring points used to establish natural background levels for lead in Irish groundwater presented for all monitoring points and by lithological group

Lead (µg/l Pb)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	215	2	30	29	96	31	13	16
Number of data points	4861	48	659	605	2230	710	297	360
5th percentile	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Median	0.25	0.25	0.25	0.25	0.25	0.25	0.40	0.25
95th percentile	2.81	2.56	2.41	2.08	2.92	3.00	3.00	2.20

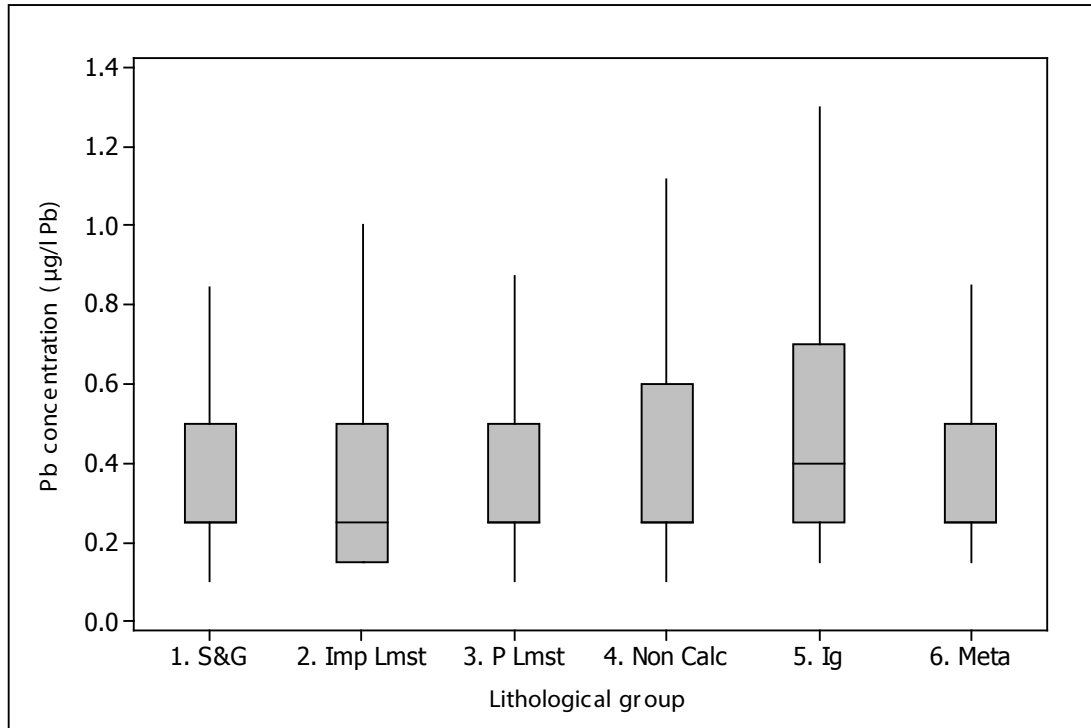


Figure A101. Box and whisker plot summarising total lead from each monitoring point used to establish natural background levels for lead in Irish groundwater presented by lithological group.

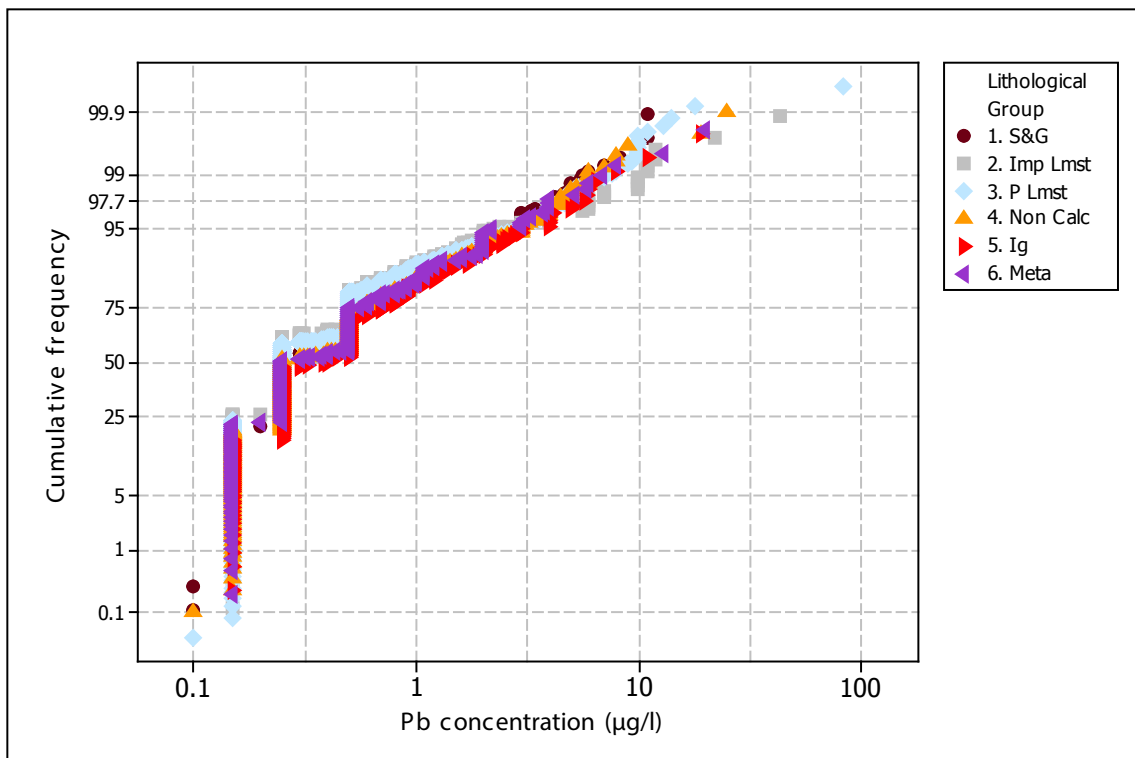


Figure A102. Cumulative frequency diagram showing the distribution of lead data used to establish natural background levels for lead in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Mercury

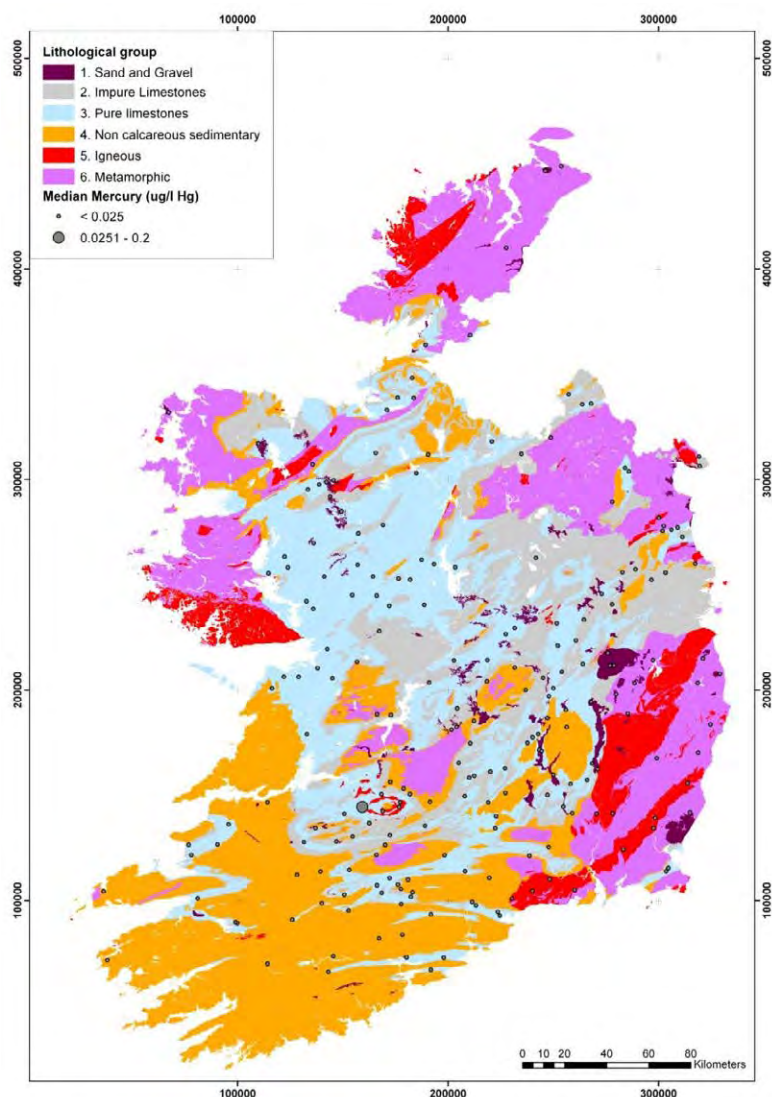


Figure A103. Location and median mercury values of the monitoring points used to establish natural background levels for mercury in Irish groundwater.

Table A35. Descriptive statistics of mercury for monitoring points used to establish natural background levels for mercury in Irish groundwater presented for all monitoring points and by lithological group

Mercury (µg/l Hg)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	215	2	30	29	96	31	13	16
Number of data points	4846	48	656	603	2227	712	297	351
5th percentile	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Median	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
95th percentile	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03

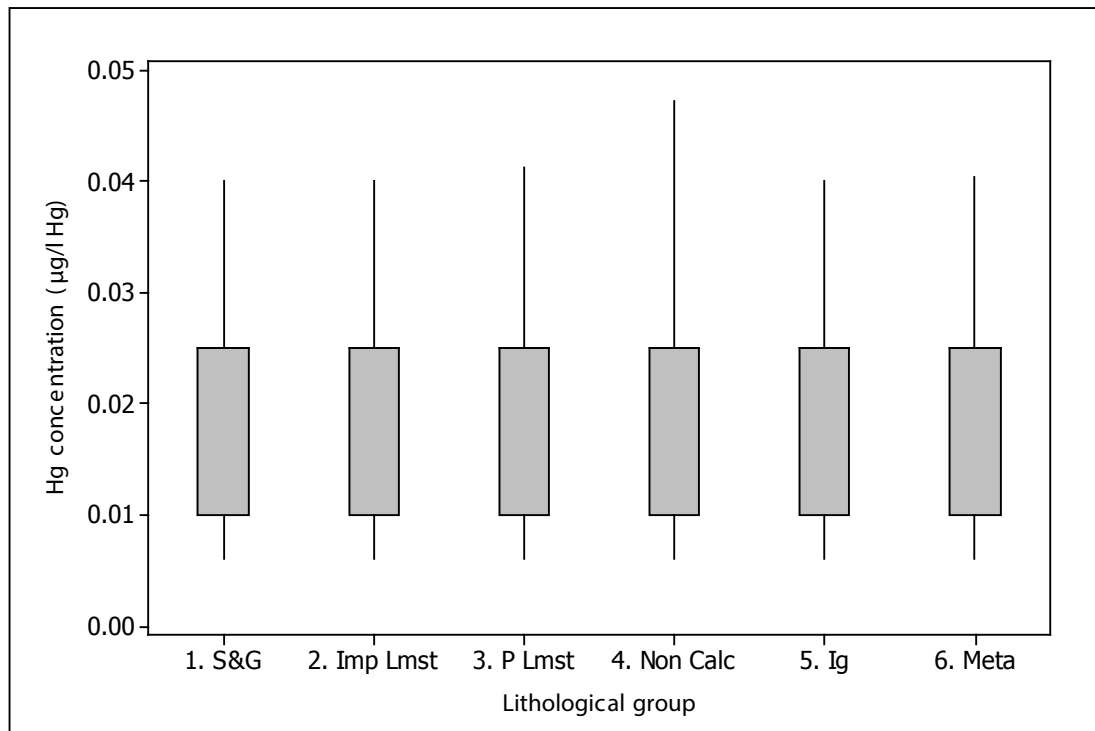


Figure A104. Box and whisker plot summarising total mercury from each monitoring point used to establish natural background levels for mercury in Irish groundwater presented by lithological group.

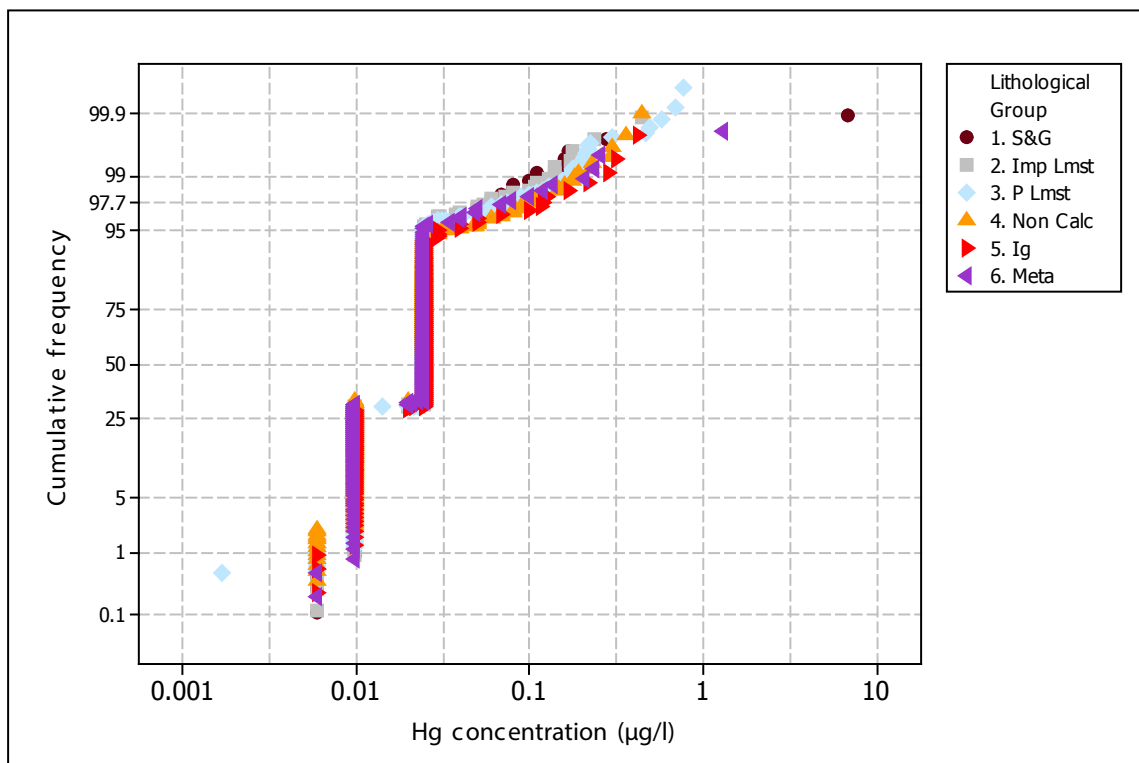


Figure A105. Cumulative frequency diagram showing the distribution of mercury data used to establish natural background levels for mercury in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Molybdenum

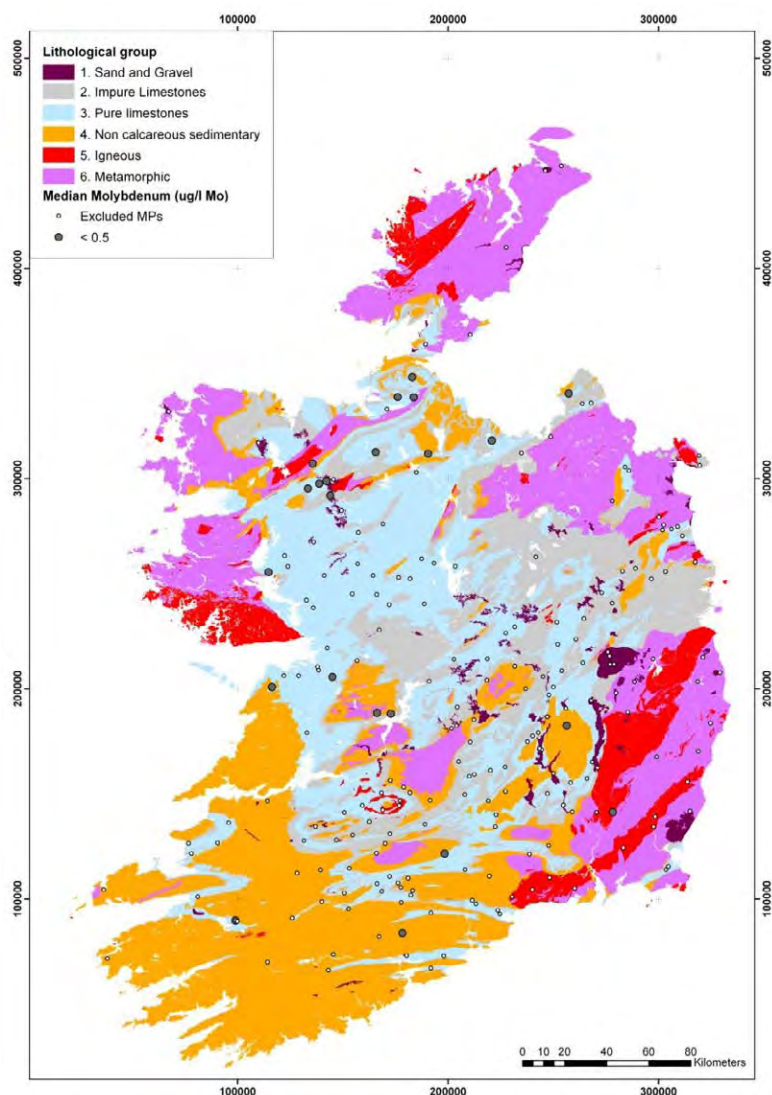


Figure A106. Location and median molybdenum values of the monitoring points used to establish natural background levels for molybdenum in Irish groundwater.

Table A36. Descriptive statistics of molybdenum for monitoring points used to establish natural background levels for molybdenum in Irish groundwater presented for all monitoring points and by lithological group

Molybdenum ($\mu\text{g/l Mo}$)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	416	48	25	44	216	59	24	48
5th percentile	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Median	0.50	0.50	0.50	0.38	0.50	0.50	0.50	0.50
95th percentile	0.63	1.02	0.50	0.50	1.08	0.50	0.50	0.50

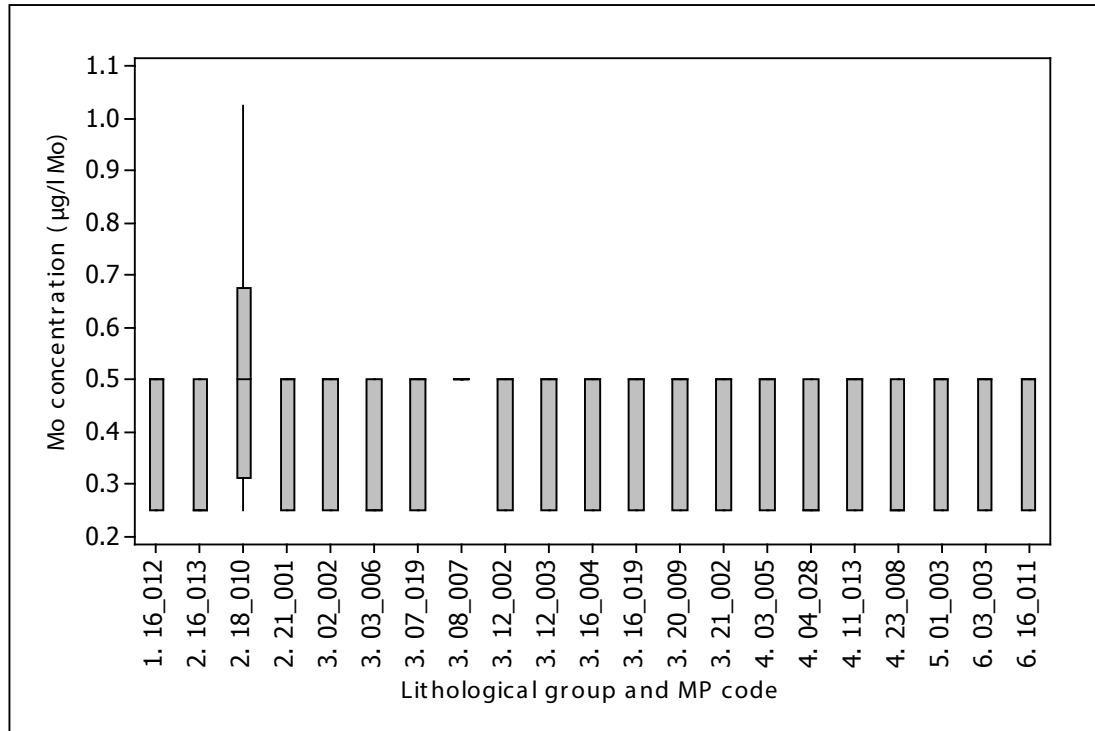


Figure A107. Box and whisker plot summarising total molybdenum from each monitoring point used to establish natural background levels for molybdenum in Irish groundwater presented by lithological group. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

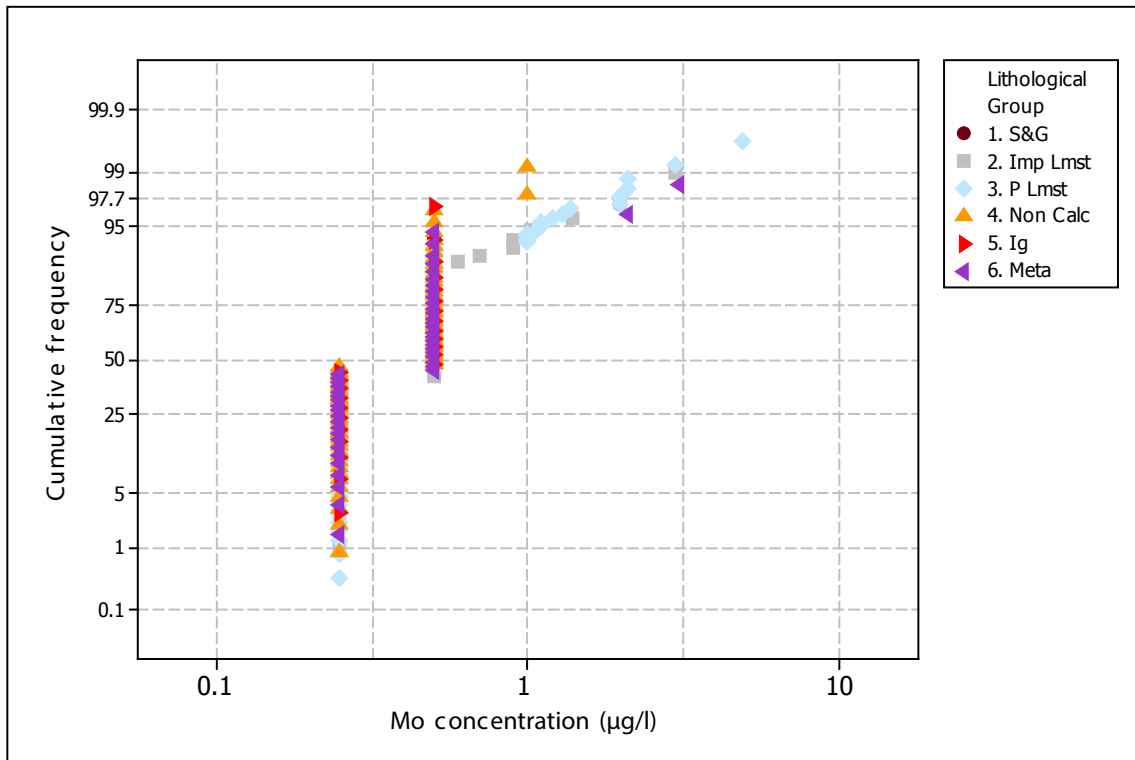


Figure A108. Cumulative frequency diagram showing the distribution of molybdenum data used to establish natural background levels for molybdenum in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Nickel

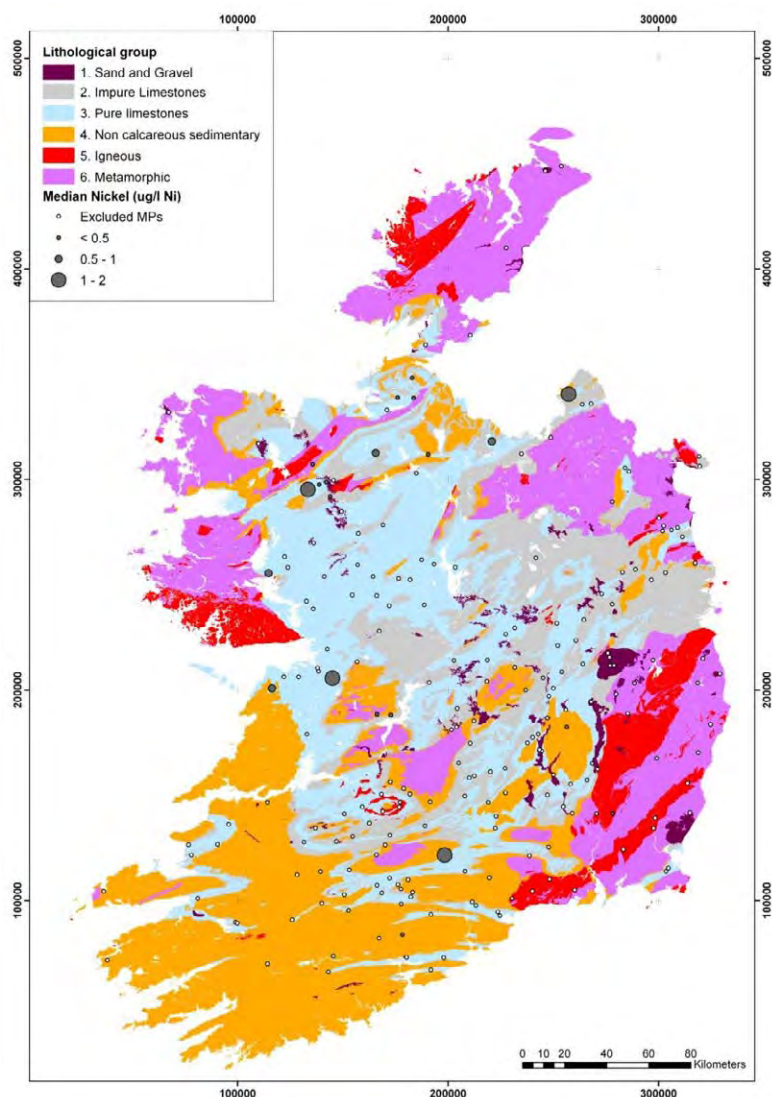


Figure A109. Location and median nickel values of the monitoring points used to establish natural background levels for nickel in Irish groundwater.

Table A37. Descriptive statistics of nickel for monitoring points used to establish natural background levels for nickel in Irish groundwater presented for all monitoring points and by lithological group

Nickel ($\mu\text{g/l Ni}$)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	416	48	25	44	216	59	24	48
5th percentile	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Median	0.50	0.85	0.25	0.38	0.60	0.70	0.25	0.38
95th percentile	2.15	4.65	2.00	2.00	2.53	2.31	0.67	2.08

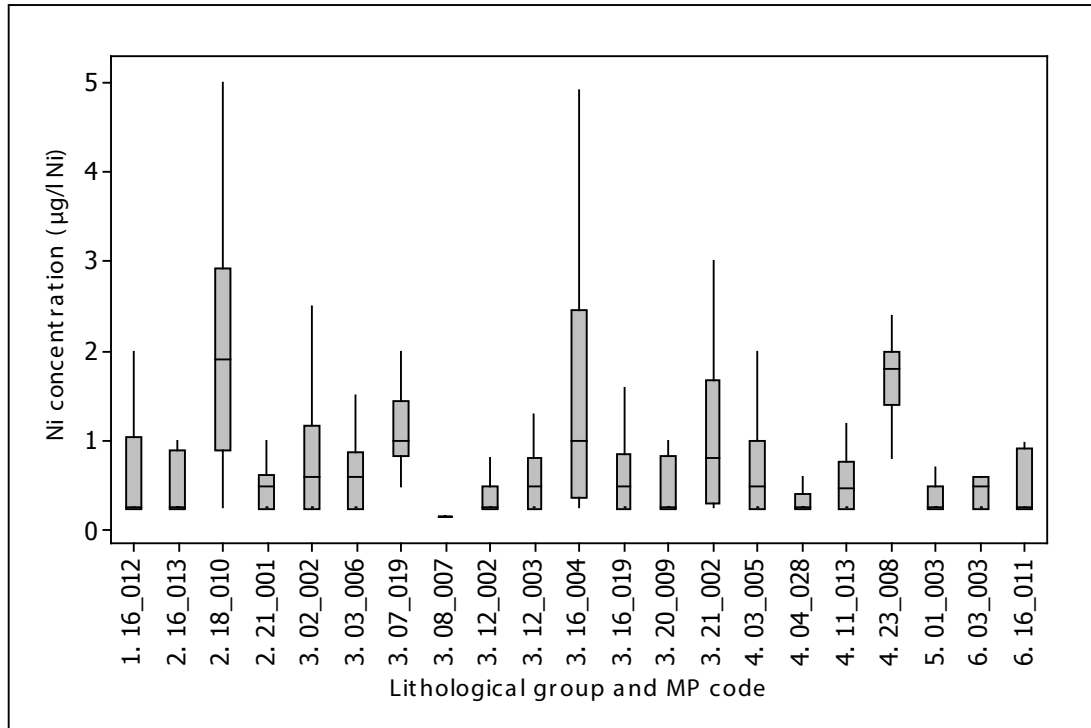


Figure A110. Box and whisker plot summarising total nickel from each monitoring point used to establish natural background levels for nickel in Irish groundwater presented by lithological group. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

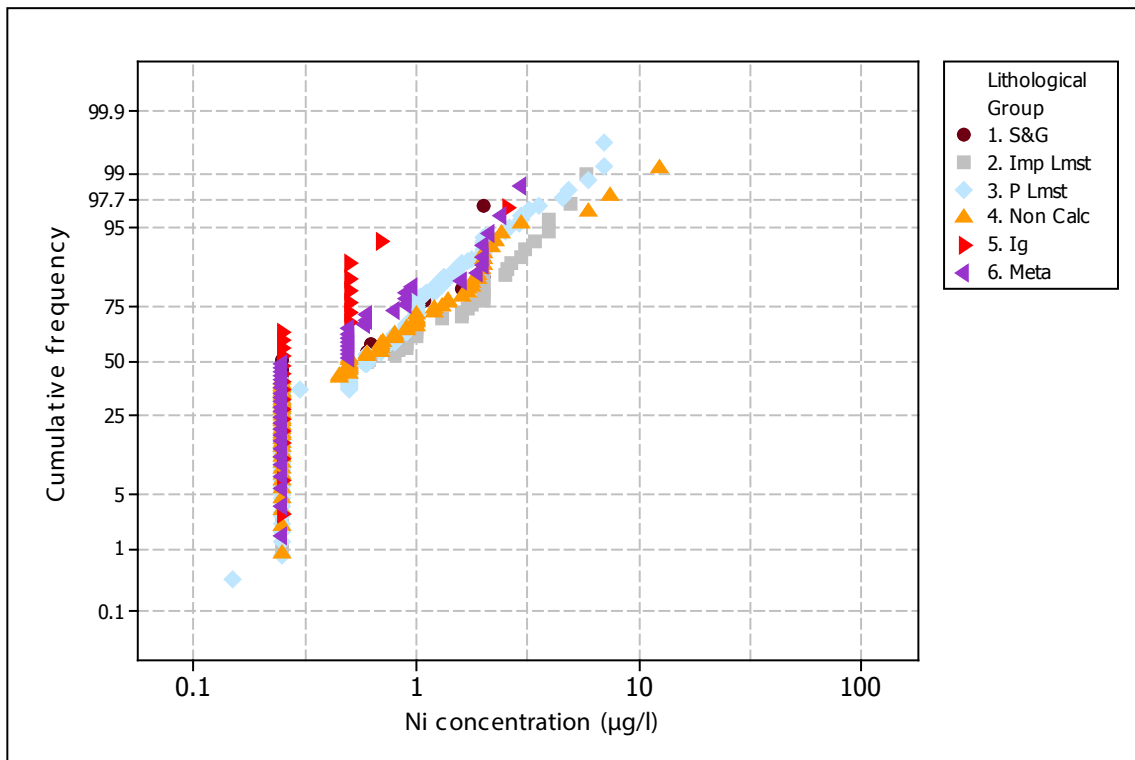


Figure A111. Cumulative frequency diagram showing the distribution of nickel data used to establish natural background levels for nickel in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Radon

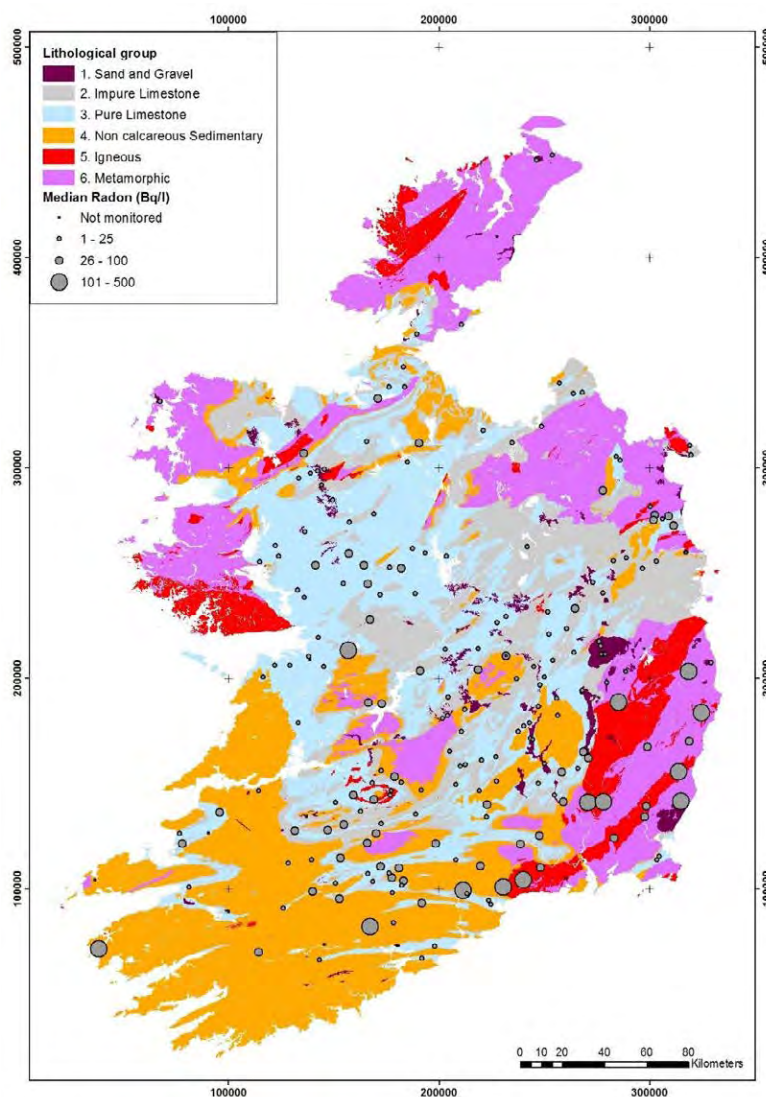


Figure A112. Location and median radon values of the monitoring points used to establish natural background levels for radon in Irish groundwater.

Table A38. Descriptive statistics of radon for monitoring points used to establish natural background levels for radon in Irish groundwater presented for all monitoring points and by lithological group

Radon (Bq/l)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	214	2	31	25	94	38	12	14
Number of data points	579	6	87	69	253	95	36	39
5th percentile	1.31	0.80	0.80	1.32	0.90	3.65	21.35	8.13
Median	17.95	2.10	10.80	11.50	15.40	45.00	85.90	43.40
95th percentile	121.57	10.08	33.49	28.18	35.12	140.93	267.63	163.73

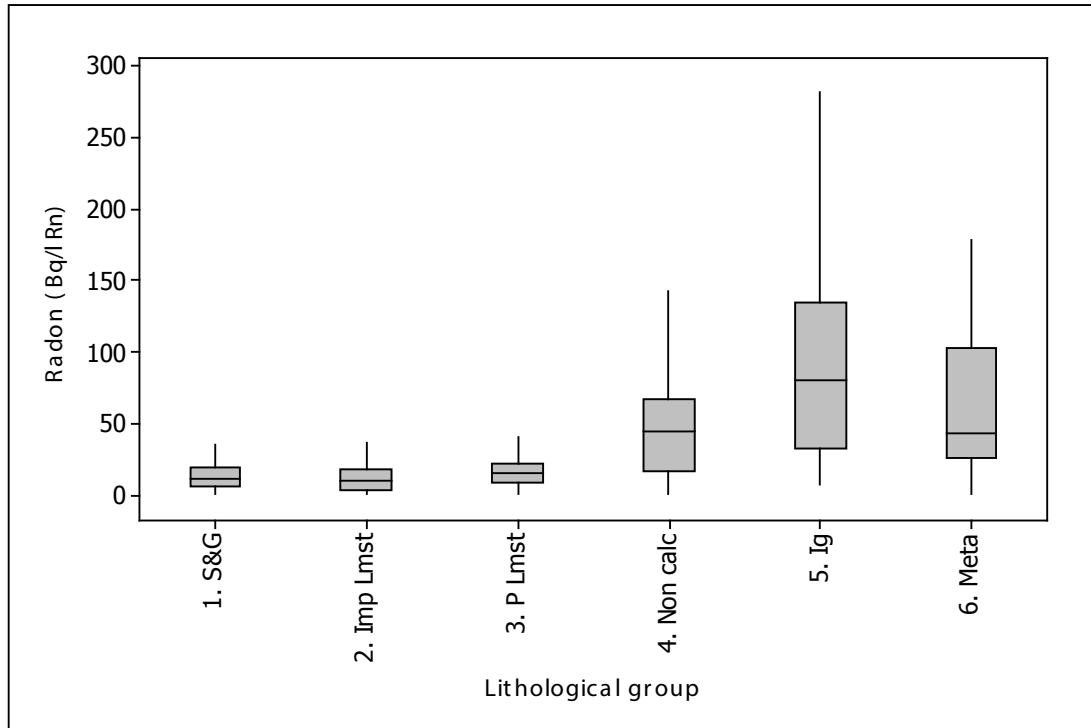


Figure A113. Box and whisker plot summarising total radon from each monitoring point used to establish natural background levels for radon in Irish groundwater presented by lithological group.

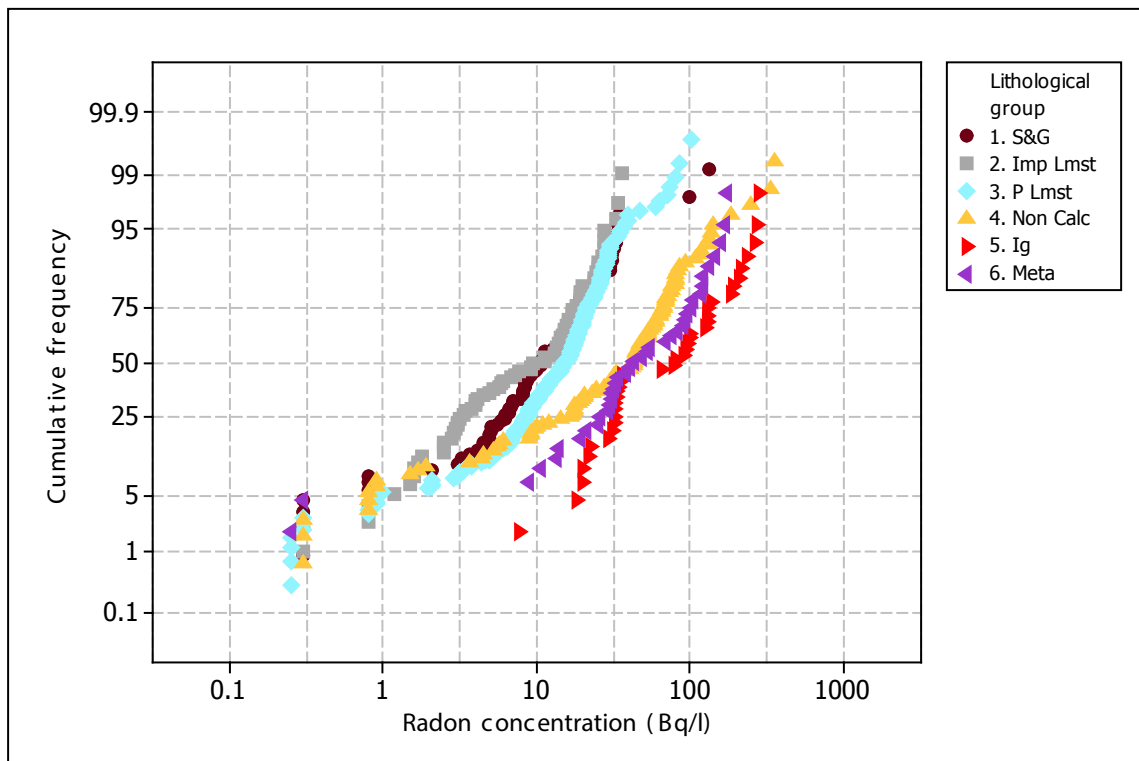


Figure A114. Cumulative frequency diagram showing the distribution of radon data used to establish natural background levels for radon in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Uranium

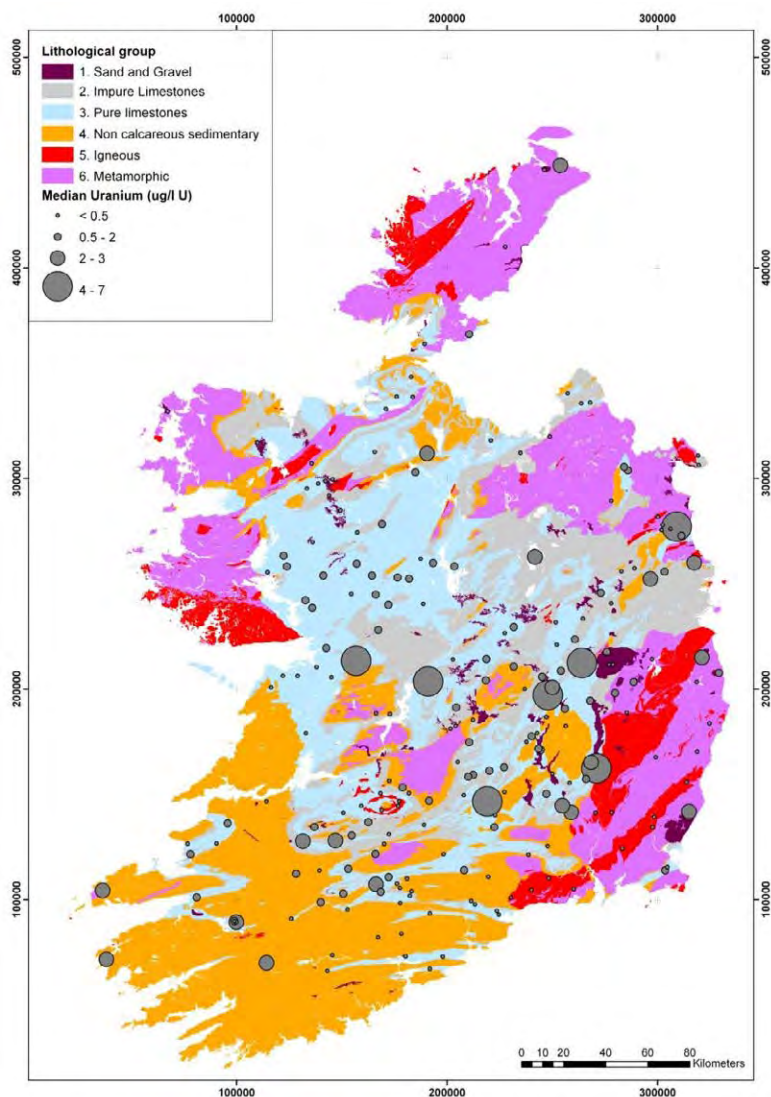


Figure A115. Location and median uranium values of the monitoring points used to establish natural background levels for uranium in Irish groundwater.

Table A39. Descriptive statistics of uranium for monitoring points used to establish natural background levels for uranium in Irish groundwater presented for all monitoring points and by lithological group

Uranium ($\mu\text{g/l U}$)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	215	2	30	29	96	31	13	16
Number of data points	4861	48	659	604	2230	711	297	360
5th percentile	0.10	0.05	0.20	0.30	0.40	0.05	0.05	0.05
Median	0.50	0.50	0.50	0.50	0.60	0.50	0.50	0.50
95th percentile	3.00	1.97	5.00	3.10	2.80	3.75	1.00	2.60

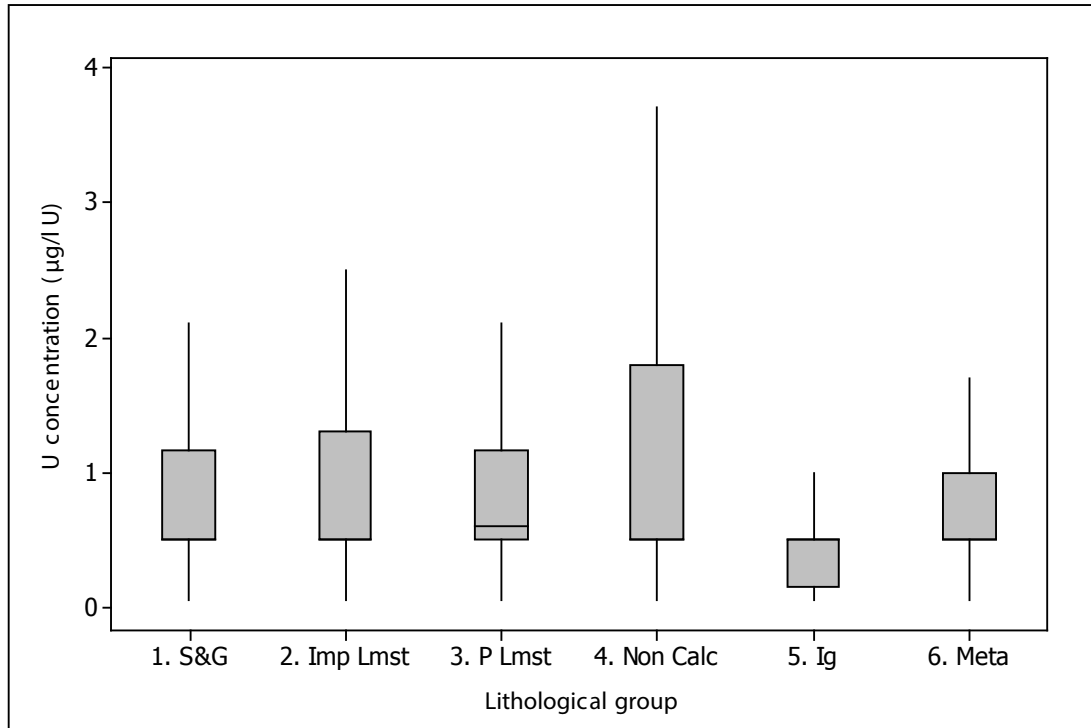


Figure A116. Box and whisker plot summarising total uranium from each monitoring point used to establish natural background levels for uranium in Irish groundwater presented by lithological group.

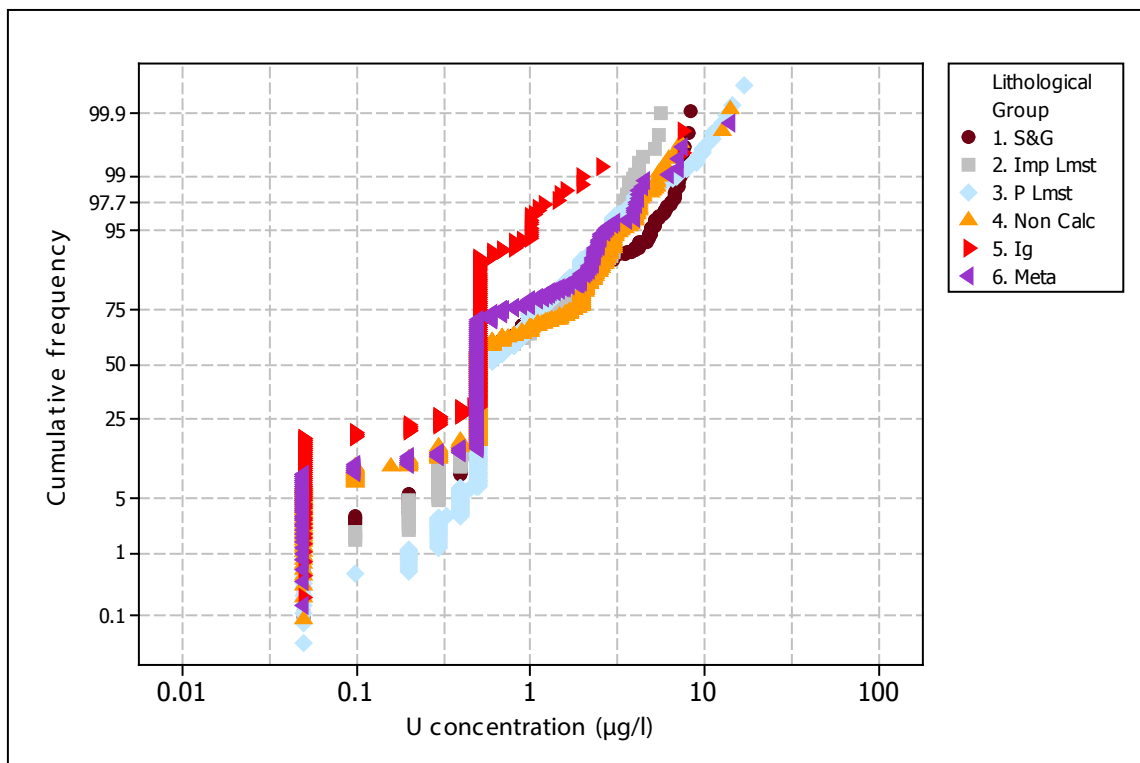


Figure A117. Cumulative frequency diagram showing the distribution of uranium data used to establish natural background levels for uranium in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

Zinc

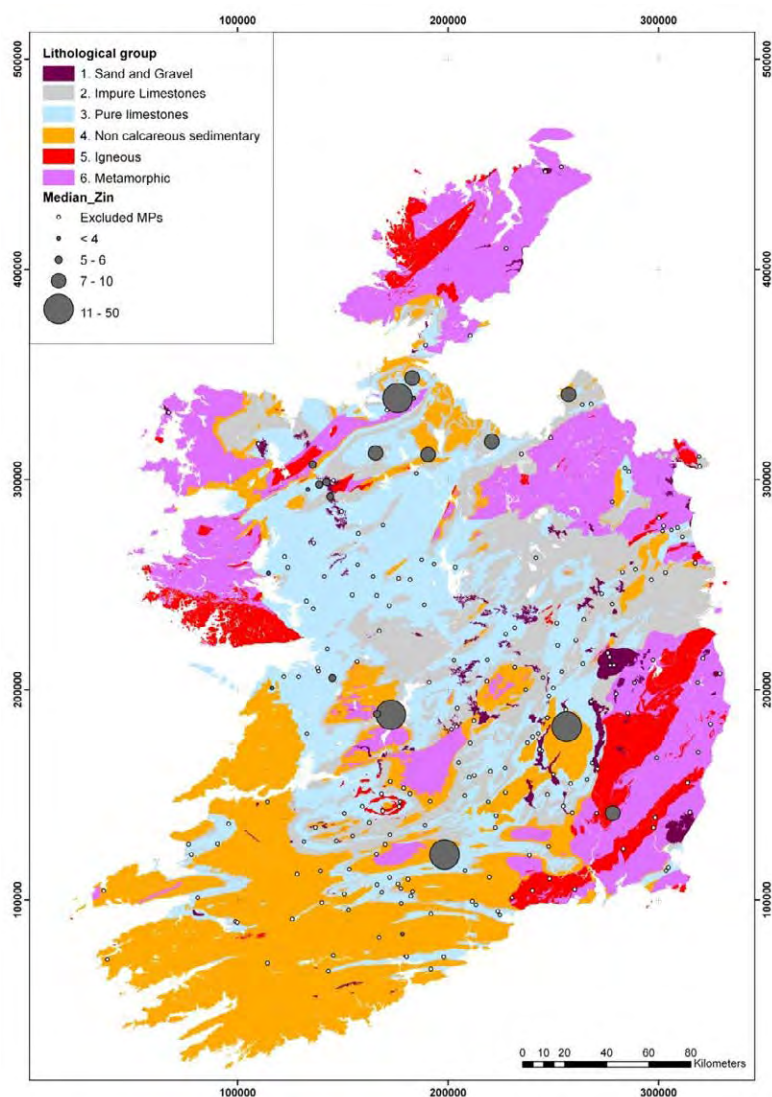


Figure A118. Location and median zinc values of the monitoring points used to establish natural background levels for zinc in Irish groundwater.

Table A40. Descriptive statistics of zinc for monitoring points used to establish natural background levels for zinc in Irish groundwater presented for all monitoring points and by lithological group

Zinc ($\mu\text{g/l Zn}$)								
	Unconfined MPs	Confined MPs	1. Sand and gravel	2. Impure limestones	3. Pure limestones	4. Non- calcareous sedimentary	5. Igneous	6. Metamorphic
Number of MPs	19	2	1	2	10	3	1	2
Number of data points	192	22	11	22	99	28	11	21
5th percentile	1.60	4.08	1.30	1.64	1.69	2.71	2.00	1.90
Median	6.90	12.85	7.00	6.70	6.90	11.35	5.40	5.00
95th percentile	40.00	53.86	16.05	30.00	30.66	66.87	16.80	37.20

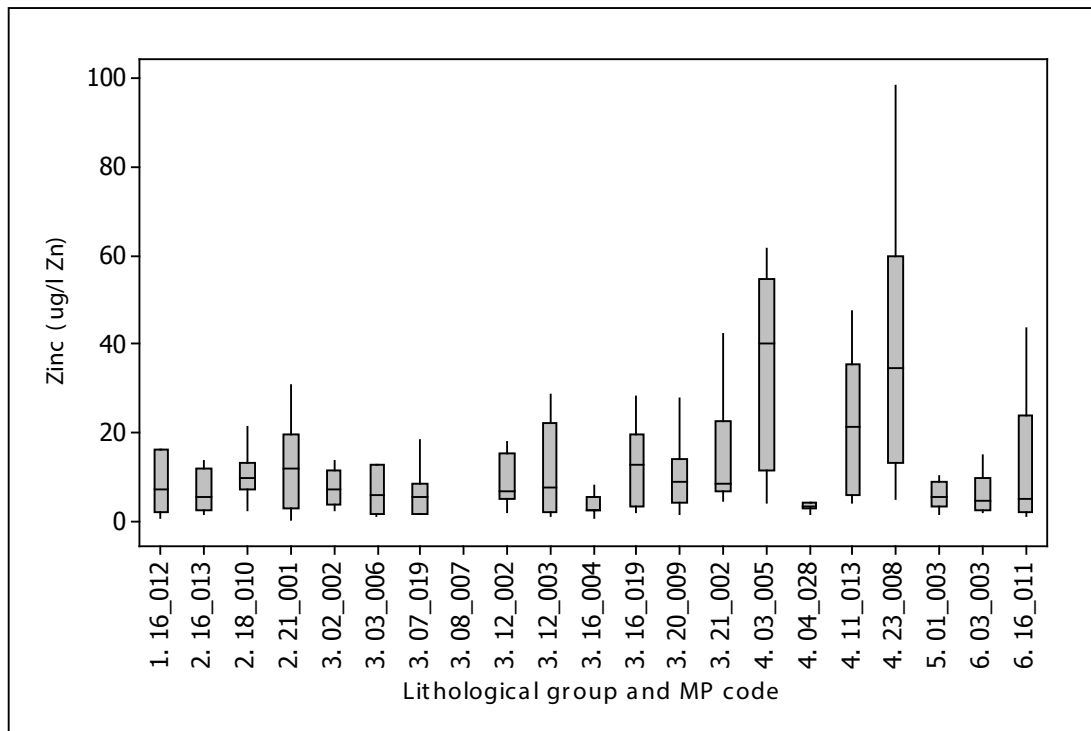


Figure A119. Box and whisker plot summarising total zinc from each monitoring point used to establish natural background levels for zinc in Irish groundwater presented by lithological group. 1, sand and gravel; 2, impure limestones; 3, pure limestones; 4, non-calcareous sedimentary; 5, igneous; 6, metamorphic.

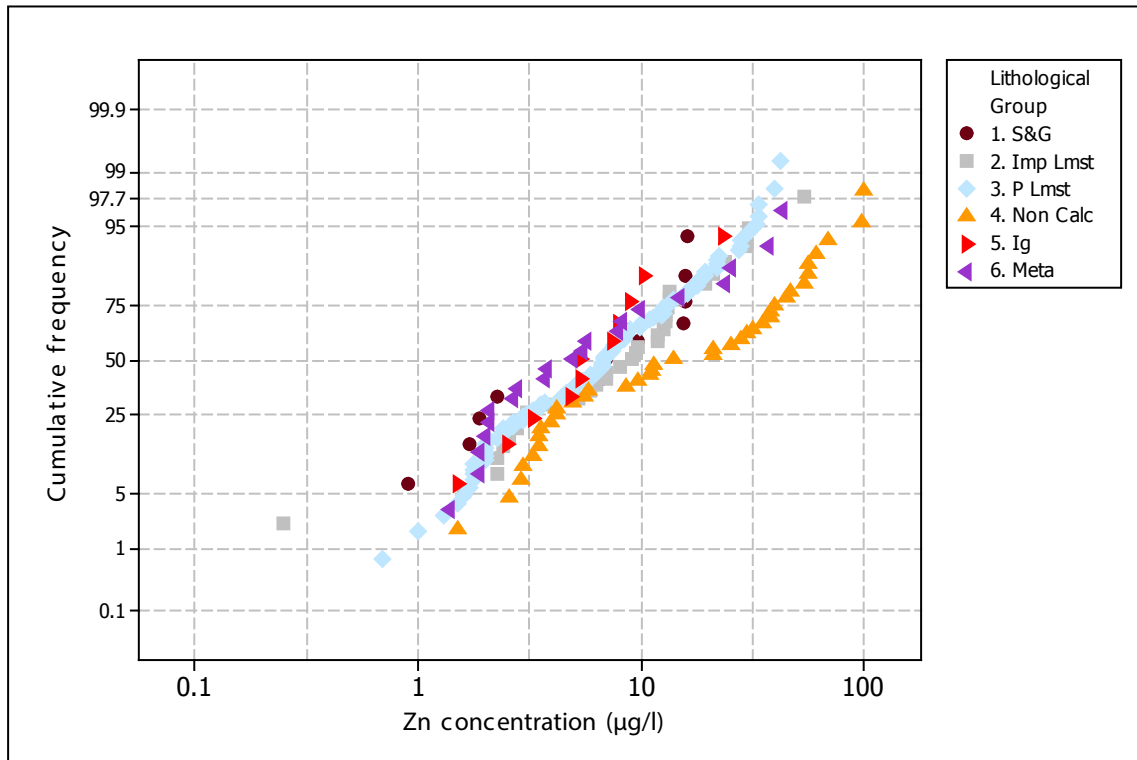


Figure A120. Cumulative frequency diagram showing the distribution of uranium data used to establish natural background levels for uranium in Irish groundwater presented by lithological group. S&G, sand and gravel; Imp Lmst, impure limestones; P Lmst, pure limestones; Non Calc, non-calcareous sedimentary; Ig, igneous; Meta, metamorphic.

AN GHNÍOMHAIREACHT UM CHAOMHNÚ COMHSHAOIL

Tá an Ghníomhaireacht um Chaomhnú Comhshaoil (GCC) freagrach as an gcomhshaoil a chaomhnú agus a fheabhsú mar shócmhainn luachmhar do mhuintir na hÉireann. Táimid tiomanta do dhaoine agus don chomhshaoil a chosaint ó éifeachtaí díobhálacha na radaíochta agus an truaillithe.

Is féidir obair na Gníomhaireachta a roinnt ina trí phríomhréimse:

Rialú: Déanaimid córais éifeachtacha rialaithe agus comhlíonta comhshaoil a chur i bhfeidhm chun torthaí maithhe comhshaoil a sholáthar agus chun díriú orthu siúd nach gcloíonn leis na córais sin.

Eolas: Soláthraimid sonraí, faisnéis agus measúnú comhshaoil atá ar ardchaighdeán, spriocdhírthe agus tráthúil chun bonn eolais a chur faoin gcinnteoireacht ar gach leibhéal.

Tacaíocht: Bímid ag saothrú i gcomhar le grúpaí eile chun tacú le comhshaoil atá glan, táirgiúil agus cosanta go maith, agus le hiompar a chuirfidh le comhshaoil inbhuanaithe.

Ár bhFreagrachtaí

Ceadúnú

Déanaimid na gníomhaíochtaí seo a leanas a rialú ionas nach ndéanann siad dochar do shláinte an phobail ná don chomhshaoil:

- saoráidí dramhaíola (*m.sh. láithreáin líonta talún, loisceoirí, stáisiúin aistrithe dramhaíola*);
- gníomhaíochtaí tionsclaíocha ar scála mór (*m.sh. déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta*);
- an diantalmhaíocht (*m.sh. muca, éanlaith*);
- úsáid shrianta agus scaoileadh rialaithe Orgánach Géinmhodhnaithe (*OGM*);
- foinsí radaíochta ianúcháin (*m.sh. trealamh x-gha agus radaiteiripe, foinsí tionsclaíocha*);
- áiseanna móra stórála peitril;
- scardadh dramhuisce;
- gníomhaíochtaí dumpála ar farraige.

Forfheidhmiú Náisiúnta i leith Cúrsaí Comhshaoil

- Clár náisiúnta iniúchtaí agus cigireachtaí a dhéanamh gach bliain ar shaoráidí a bhfuil ceadúnas ón nGníomhaireacht acu.
- Maoirseacht a dhéanamh ar fhreagrachtaí cosanta comhshaoil na n-údarás áitiúil.
- Caighdeán an uisce óil, arna sholáthar ag soláthraithe uisce phoiblí, a mhaoirsiú.
- Obair le húdaráis áitiúla agus le gníomhaireachtaí eile chun dul i ngleic le coireanna comhshaoil trí chomhordú a dhéanamh ar líonra forfheidhmiúcháin náisiúnta, trí dhíriú ar chiontóirí, agus trí mhaoirsiú a dhéanamh ar leasúchán.
- Cur i bhfeidhm rialachán ar nós na Rialachán um Dhramhthrealamh Leictreach agus Leictreonach (DTLL), um Shrian ar Shubstaintí Guaiseacha agus na Rialachán um rialú ar shubstaintí a ídíonn an ciseal ózóin.
- An dlí a chur orthu siúd a bhriseann dlí an chomhshaoil agus a dhéanann dochar don chomhshaoil.

Bainistíocht Uisce

- Monatóireacht agus tuairisciú a dhéanamh ar cháilíocht aibhneacha, lochanna, uiscí idirchriosacha agus cósta na hÉireann, agus screamhuiscí; leibhéil uisce agus sruthanna aibhneacha a thomhas.
- Comhordú náisiúnta agus maoirsiú a dhéanamh ar an gCreat-Treoir Uisce.
- Monatóireacht agus tuairisciú a dhéanamh ar Cháilíocht an Uisce Snámha.

Monatóireacht, Anailís agus Tuairisciú ar an gComhshaoil

- Monatóireacht a dhéanamh ar cháilíocht an aeir agus Treoir an AE maidir le hAer Glan don Eoraip (CAFÉ) a chur chun feidhme.
- Tuairisciú neamhspleách le cabhrú le cinnteoireacht an rialtais náisiúnta agus na n-údarás áitiúil (*m.sh. tuairisciú tréimhsiúil ar staid Chomhshaoil na hÉireann agus Tuarascálacha ar Tháscairí*).

Rialú Astaíochtaí na nGás Ceaptha Teasa in Éirinn

- Fardail agus réamh-mheastacháin na hÉireann maidir le gáis cheaptha teasa a ullmhú.
- An Treoir maidir le Trádáil Astaíochtaí a chur chun feidhme i gcomhair breis agus 100 de na táirgeoirí dé-ocsaíde carbóin is mó in Éirinn.

Taighde agus Forbairt Comhshaoil

- Taighde comhshaoil a chistiú chun brúnna a shainaitheint, bonn eolais a chur faoi bheartais, agus réitigh a sholáthar i réimsí na haeráide, an uisce agus na hinbhuanaitheachta.

Measúnacht Straitéiseach Timpeallachta

- Measúnacht a dhéanamh ar thionchar pleananna agus clár beartaithe ar an gcomhshaoil in Éirinn (*m.sh. mórphleananna forbartha*).

Cosaint Raideolaíoch

- Monatóireacht a dhéanamh ar leibhéil radaíochta, measúnacht a dhéanamh ar nochtadh mhuintir na hÉireann don radaíocht ianúcháin.
- Cabhrú le pleananna náisiúnta a fhorbairt le haghaidh éigeandálaí ag eascairt as taismí núicléacha.
- Monatóireacht a dhéanamh ar fhorbairtí thar lear a bhaineann le saoráidí núicléacha agus leis an tsábháilteacht raideolaíochta.
- Sainseirbhísí cosanta ar an radaíocht a sholáthar, nó maoirsiú a dhéanamh ar sholáthar na seirbhísí sin.

Treoir, Faisnéis Inrochtana agus Oideachas

- Comhairle agus treoir a chur ar fáil d'earnáil na tionsclaíochta agus don phobal maidir le hábhair a bhaineann le caomhnú an chomhshaoil agus leis an gcosaint raideolaíoch.
- Faisnéis thráthúil ar an gcomhshaoil ar a bhfuil fáil éasca a chur ar fáil chun rannpháirtíocht an phobail a spreagadh sa chinnteoireacht i ndáil leis an gcomhshaoil (*m.sh. Timpeall an Tí, léarscáileanna radóin*).
- Comhairle a chur ar fáil don Rialtas maidir le hábhair a bhaineann leis an tsábháilteacht raideolaíoch agus le cúrsaí práinnfhreagartha.
- Plean Náisiúnta Bainistíochta Dramhaíola Guaisí a fhorbairt chun dramhaíl ghuaiseach a chosaint agus a bhainistiú.

Múscailt Feasachta agus Athrú Iompraíochta

- Feasacht chomhshaoil níos fearr a ghiniúint agus dul i bhfeidhm ar athrú iompraíochta dearfach trí thacú le gnóthais, le pobail agus le teaghlaigh a bheith níos éifeachtúla ar acmhainní.
- Tástáil le haghaidh radóin a chur chun cinn i dtithe agus in ionaid oibre, agus gníomhartha leasúcháin a spreagadh nuair is gá.

Bainistíocht agus struchtúr na Gníomhaireachta um Chaomhnú Comhshaoil

Tá an ghníomhaíocht á bainistiú ag Bord lánaimseartha, ar a bhfuil Ard-Stiúrthóir agus cúigear Stiúrthóirí. Déantar an obair ar fud cúig cinn d'Oifigí:

- An Oifig um Inmharthanacht Comhshaoil
- An Oifig Forfheidhmithe i leith cúrsaí Comhshaoil
- An Oifig um Fianaise is Measúnú
- Oifig um Chosaint Radaíochta agus Monatóireachta Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáideacha

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag comhaltaí air agus tagann siad le chéile go rialta le plé a dhéanamh ar ábhair imní agus le comhairle a chur ar an mBord.

Assessing and Developing Natural Background Levels for Chemical Parameters in Irish Groundwater



Authors: Katie Tedd, Catherine Coxon, Bruce Misstear, Donal Daly, Matthew Craig, Anthony Mannix and Taly Hunter Williams.

Identifying Pressures

The natural background levels established in this report are the range in concentration of chemical parameters in Irish groundwater arising from natural processes. They provide a reference against which to assess whether anthropogenic pollution of groundwater is taking place and potential impacts on an aquifer. They are therefore essential for understanding pollution and for setting regulatory limits. The research fellowship used a pre-selected dataset to exclude groundwater with significant anthropogenic pressures, and identified the pressures using GIS data layers relating to anthropogenic activities.

Informing Policy

In Ireland, the status of groundwater is assessed via the EU Water Framework Directive (WFD 2000/60/EC) which stipulates that groundwater status must be assessed and that good chemical and quantitative status must be achieved in order to protect human health and associated dependent ecosystems. The Groundwater Daughter Directive (GWDD 2006/118/EC) explicitly asks Member States to consider natural background levels when establishing Threshold Values for groundwater pollutants which are used to assess the chemical status of groundwater bodies. The 2014 amendments of the GWDD Annexes placed much greater emphasis on natural background levels. This research fellowship establishes or updates natural background levels for forty parameters, which may be used to set or update Threshold Values.

Developing Solutions

A methodology to establish natural background levels in Irish groundwater was developed following international best practice. Natural background levels were established for forty parameters, comprising field parameters, major ion, minor ions, nutrients and trace elements. This study used a pre-selected datasets of the EPA groundwater quality monitoring data. The most likely hydrogeological and hydrochemical controls for each parameter were considered and the natural background levels were defined accordingly. The natural background levels have made best use of the available data and the results are comparable to natural background levels established in other countries or regions.