## Environmental RTDI Programme 2000–2006

# WATER FRAMEWORK DIRECTIVE – Development of a Methodology for the Characterisation of Unpolluted Groundwater
# (2002-W-DS-7)

## Main Report

Prepared for the Environmental Protection Agency

by

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# EXECUTIVE SUMMARY

The EU Water Framework Directive requires Member States to adopt measures to prevent and control groundwater pollution. Its implementation will be partly via a new Groundwater Directive, currently in draft form. It is the intention that all groundwater bodies be of good status by 2015. Chemical status of a groundwater body is assessed by comparison to the unpolluted condition, and by the requirement that there be no deterioration in the status of receiving surface waters and dependent ecosystems. The natural background water quality of a groundwater can be used as a standard against which to measure anthropogenic impact. It is defined as follows.

> *The range of concentrations of chemical species in solution that are, or would be, derived from the reactions of natural infiltration in a natural soil zone and aquifer system at a given point in the aquifer system.*

For groundwater bodies these calculated values can be compared with the actual background water quality to assist in the determination of which groundwater bodies are of good status and which are not of good status, and which may be at risk of impacting upon the status of receiving surface waters and dependent ecosystems. This will enable prioritisation of actions needed to preserve those of good status, improve those not of good status and encourage trend reversal. However, the defined natural background quality will not necessarily form part of any definition of ‘good status’

The principal aim of this project was to develop a methodology for the derivation of the natural background quality for Irish groundwater bodies (note that it was not the intention to determine the composition of pristine groundwater bodies). International groundwater characterisation methodologies were reviewed as part of the development of a methodology appropriate for Ireland. The methodology was developed and tested on a selected number of groundwater bodies and groups of groundwater bodies in the South Eastern River Basin District. Results from the trials were fed back to the methodology to ensure its applicability in the Irish context.

In detail, the methodology is used to derive limiting concentrations or values that describe the upper and lower bounds of the ranges in concentration of indictor species in groundwater of natural background quality. These indicator species are naturally present in groundwater but concentrations can be affected by pollution. Derivation of these concentration ranges is dependent on access to reliable analytical data. In particular, older data which would not have been influenced by the changes in agricultural practice since the mid-1970s, is preferred. However, more recent data may be used with due allowance for anthropogenic impacts. Regardless of when or where the data were collected, it must be professionally assessed for its reliability before being used for characterisation of natural background quality of groundwater

# A Methodology for the Determination of Natural Background Quality of Groundwaters

## Main Report

## 1. Introduction

### 1.1. Background

The Water Framework Directive 2000/60/EC (WFD) establishes a comprehensive basis for the management of water resources in the European Union and will replace several of the existing directives which deal with individual aspects of the aquatic environment. Of particular note is the objective of attaining or maintaining good status in all unmodified waters by 2015.

For groundwaters, good status encompasses quantitative and qualitative aspects. Good status is assigned to situations where conditions show only minor change compared to the natural state of the water body. The fundamental unit for which these assessments of status will be made is the ‘groundwater body’. It will therefore be necessary for all Member States to first define groundwater bodies and then to assess their status using quantity and chemical measures. Chemical status of a groundwater body is assessed by comparison to the unpolluted condition, and by the requirement that there be no deterioration in the status of receiving surface waters and dependent ecosystems.

The principal aim of defining natural background water quality in groundwater is to use it as a standard against which to measure anthropogenic impact. A mechanism is therefore provided to assess whether groundwater bodies are at risk from pollution, and to identify the nature of potential pollutant sources. These results can be used to classify these bodies and prioritise them for treatment to mitigate the risks.

In 2002 the Environmental Protection Agency (EPA, note that in the following text other national EPAs are explicitly identified) issued a call for research proposals under the EPA-managed ERTDI programme. In October 2002 the EPA awarded a research contract to TMS Environment Ltd and Environmental Simulations International Ltd (ESI) to carry out research project 2002-W-DS/7 – ‘Development of a Methodology for the Characterisation of Unpolluted Groundwater’. Due to changes in the phraseology of the Groundwater Directive, this title was changed to reflect the intention of deriving natural background water quality.

### 1.2. Objectives

The detailed objectives of this project were as follows:

1. Review international groundwater characterisation methodologies with a focus on methodologies proposed by other EU member states.
2. Develop a methodology for an approach to characterising groundwater bodies in Ireland. The methodology should consider a number of aspects including the following: groundwater bodies related to aquifer lithology, hydrogeochemistry, rainfall chemistry, hydrogeological parameters (e.g. hydrological throughput), and geographical location (e.g. coastal).

3. Test the developed methodology using available monitoring data. Any data gaps in the existing monitoring system should be identified.

## 1.3. This Document

This document defines the methodology and its technical basis. It is written to provide an appropriately qualified individual with all of the technical information and references required to characterise the natural background quality of groundwater bodies. Section 1.4 provides the reader with relevant background information on the WFD. Section 2 sets out the key hydrochemical principles whilst Section 3 shows how this issue has been approached in the other countries surveyed. Section 4 provides a step by step description of the methodology whilst Section 5 discusses the results of the trialling of this methodology in representative catchments. The conclusions of the project are summarised concisely in Section 6.

## 1.4. Relevant Aspects of the Water Framework Directive

### 1.4.1. Background

The Water Framework Directive (WFD) establishes a comprehensive basis for the management of water resources in the European Union and will replace several of the existing directives that deal with individual aspects of the aquatic environment. It requires that water resources be managed and protected using a catchment-based approach (River Basin Management Plans). A key outcome will be the identification and reversal of significant and sustained upward trends in the concentration of pollutants.

Groundwater bodies are defined within the context of River Basin Districts (RBDs) and are the fundamental unit of management for groundwater within the context of the WFD. Article 5 of the WFD requires that Member States undertake an analysis of the characteristics of each RBD and review the impact of human activity on surface waters and groundwaters. Annex II presents the staged procedure for assessing groundwater bodies:

1. Initial characterisation to determine whether a body is at risk of failing to achieve the quantitative and qualitative objectives set for it. A preliminary step of the initial characterisation of groundwater is the definition and description of groundwater bodies, currently being undertaken by the Geological Survey of Ireland (GSI).

   External pressures on the groundwater body should be identified, including diffuse pollution, point source pollution, abstractions, artificial recharge, mining and major engineering works. Dependant surface water ecosystems and terrestrial ecosystems should also be identified. In Ireland these activities will be undertaken by consultants in consultation with the River Basin Districts, the EPA and GSI.

2. Further characterisation for groundwater bodies deemed to be at risk of failing the criteria for good status. This stage includes development of full hydrogeological conceptual models of the groundwater bodies and any overlying superficial deposits.

   It explicitly includes ‘characterisation of the chemical composition of the groundwater, including specifying contributions from human activity’. This implies that, during further characterisation, the natural background water quality should be determined. This forms a standard against which anthropogenic impacts can be assessed.

3. Surveillance monitoring of those bodies identified as being at risk to verify whether they are genuinely at risk, and of bodies of water that cross international boundaries.
4. Operational monitoring (at least annually) for bodies confirmed as being at risk, sufficient to establish the chemical status of the water body, and to establish the presence of any significant and sustained upward trend in concentration of any pollutant.

### 1.4.2. Characterisation of Groundwater Body Boundaries

Daly (2003) presents the full methodology for hydrogeological characterisation of groundwater bodies but some explanation is required here to set the scene for their hydrochemical characterisation. Groundwater bodies are initially characterised by GSI in two stages: the definition of aquifers, and their subsequent subdivision into groundwater bodies. Aquifers are mainly defined according to stratigraphical divisions based on the similarity of their hydrogeology. Currently GSI are basing aquifer definitions on approximately 30 bedrock groups plus the superficial sand/gravel deposits.

Boundaries of groundwater bodies are defined according to Daly (2003) as follows.

- No flow, or low flow geological boundaries (including the base of a sand/gravel aquifer and boundaries between good and poor aquifers);
- Boundaries based on groundwater highs (usually coincident with surface water boundaries);
- Boundaries based on different flow systems (e.g. karst vs intergranular) in order to be able to apply different management strategies to each;
- Boundaries based on flow lines (if necessary to separate groundwater bodies which have different status).

Groundwater bodies for the whole of Ireland have yet to be defined, but in the South East River Basin District (SERBD) there are 56 bedrock groundwater bodies and there will be approximately 25 sand/gravel groundwater bodies (Daly, 2003). Six RBDs have provisionally been defined for the country and there are likely to be of the order of 290 bedrock groundwater bodies and 70 sand/gravel groundwater bodies in total (G. Wright pers. comm.).

### 1.4.3. Characterisation of Groundwater Chemical Status

Groundwater status under the WFD is the general expression of the status of a body of groundwater determined by the poorer of its quantitative status and its chemical status. Quantitative status is a measure of the sustainability of abstractions and their impact on dependant ecosystems while chemical status is defined by reference to electrical conductivity and the concentration of pollutants. Good groundwater chemical status is defined such that the concentrations of pollutants:

1. do not exhibit the effects of saline or other intrusions;
2. do not exceed the quality standards applicable under other relevant Community legislation in accordance with Article 17;
3. are not such as would result in failure to achieve the environmental objectives specified under Article 4 for associated surface waters nor any significant diminution of the ecological or chemical quality of such bodies nor in any significant damage to terrestrial ecosystems which depend directly on the groundwater body.

The following issues are noted on the points above:

> Point 2: The measures to be adopted under Article 17 form the proposed Groundwater Directive [2003/0210 (COD)]. These measures include the derivation of concentration thresholds for certain contaminants above which the groundwaters can be considered to have poor quality status.
>
> Point 2: Other relevant Community legislation includes, for example, the Nitrates Directive (91/676/EEC), Drinking Water Directive (80/778/EEC as amended by Directive 98/83/EC) or the Dangerous Substance Discharges Directive (86/280/EEC) etc.
>
> Point 3: This requires an explicit link between groundwater and surface water status assessments. 'Significant' in this context is not defined in the WFD, but based on the definition of significant trends, it implies, 'statistically significant'.

The determination of chemical status does not involve consideration of pressures but only of the concentration of pollutants (or electrical conductivity) in the groundwater body and the qualitative impacts on receiving surface waters and dependent terrestrial ecosystems. Interim standards for the definition of good chemical status are presented in EPA (2003). In assessing status, the results of individual monitoring points within a groundwater body should be aggregated for the body as a whole.

### 1.4.4. The Groundwater Directive

Article 17 of the Water Framework Directive specifies that Member States adopt specific measures to prevent and control groundwater pollution by defining common criteria on good chemical status and on quality trends. These measures are implemented in the new Groundwater Directive, which, at the time of writing this report, is still in proposal form [2003/0210 (COM)].

The proposal sets out criteria for assessing the chemical status of groundwater but does not go so far as to present quality standards for groundwater. Unlike in early drafts, it is recognised that the natural variability of groundwater chemical composition and the present general lack of systematic monitoring data makes this inappropriate. Only EU-wide quality standards that are directly implemented in other Directives, namely the Nitrates Directive (91/676/EEC) and those controlling plant protection and biocidal products (91/414/EEC and 98/8/EC respectively), are adopted.

The Directive requires the definition of threshold concentrations of contaminants above which a groundwater body, or group of groundwater bodies, can be considered to have poor quality. A list of substances is presented for which thresholds should be set:

- ammonium, arsenic, cadmium, chloride, lead, mercury, sulphate, trichloroethene and tetrachloroethene.

These are in addition t o the statutory quality standards for nitrate and pesticides in the Directives given above. Member States may also set threshold values for substances for which the groundwater body is at risk of not achieving Article 4 objectives for maintenance of the status of surface water bodies and dependent ecosystems.

## 1.5 Definition of Natural Background Groundwater Quality

Groundwater contains a mixture of species and properties that reflect natural and human effects. The principal aim of this study is to identify those that are related to the management of land and water (i.e. excluding anthropogenic impacts on rainfall quality). The methodology concentrates on the identification of these human activities on individual chemical species, rather than the overall water quality. Some species are excluded from the analysis, such as CFCs and tritium, because these are not related to the management of land and water.

The aim of defining the natural background concentrations of relevant species in groundwater is to use these as a standard against which to measure anthropogenic impact. It is therefore necessary to define the term 'natural background quality' for a groundwater. The definition used for this project is as follows:

> *The range of concentrations of chemical species in solution that are, or would be, derived from the reactions of natural infiltration in a natural soil zone and aquifer system at a given point in the aquifer system.*

The phrase 'natural infiltration' implies that it does not incorporate atmospheric pollution; therefore, the natural background quality of groundwater should be taken as that arising from rainfall recharge of pre-industrial quality. The locational criterion is included so that the impacts of induced saline intrusion (which occurs by mixing of two natural waters) are included in the definition.

The natural background quality is defined as a range due to the natural variability of concentrations in groundwater. For most chemical species in groundwater, only the higher limit of that range is of particular concern, as an exceedence of that value may indicate that pollution has occurred. Where an upper limiting value for the natural background quality is given, the following definition is proposed:

> *the 95th percentile value of the range of natural background concentrations or values, or, where natural background and anthropogenically-impacted concentration ranges significantly overlap, the maximum concentration at which more samples are at natural background quality than not.*

Lower limiting values are defined where the impact of pollution causes depletion of a substance or property, such as dissolved oxygen in organic pollution or pH with acid pollution. For a lower limiting value the following definition is proposed:

> *the 5th percentile value of the range of natural background concentrations or values, or, where natural background and anthropogenically-impacted concentration ranges significantly overlap, the minimum concentration at which more samples are at natural background quality than not.*

If a groundwater yields natural background concentrations of one or more chemical species, it is not necessarily unpolluted. If concentrations of all relevant chemical species are within all the limits, this may indicate that the groundwater is not polluted. However, a groundwater of natural background quality need not necessarily be a pristine groundwater[1] and may be affected by a degree of human activity (e.g. CFCs or tritium). The definition of 'polluted' groundwater in this context may be obtained from the definition of pollution, the most appropriate of which is in Article 2 of the Water Framework Directive:

> *the direct or indirect introduction, as a result of human activity, of substances or heat into the air, water or land which may be harmful to human health or the quality of aquatic ecosystems or terrestrial ecosystems directly depending on aquatic ecosystems, which result in damage to material property, or which impair or interfere with amenities and other legitimate uses of the environment.*

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[1] A pristine groundwater is one whose chemical composition is completely unaffected by anthropogenic activity. There are likely to be few pristine groundwaters in Ireland, but some have been tentatively identified in Scandinavia.

A groundwater in which some concentrations exceed the natural background concentrations is, therefore, not necessarily polluted: it is merely impacted by human activity. The Water Framework Directive gives the definition of ‘pollutant’ as:

> *any substance liable to cause pollution.*

The presence of a pollutant in groundwater does not, therefore, imply that the groundwater is polluted. A groundwater is only polluted if pollutants are present at sufficient concentrations that may be harmful to humans, ecosystems etc..

The defined natural background quality will not necessarily form part of any definition of ‘good status’. Likewise, threshold values defined in Article 4 of the draft Groundwater Directive may also not be defined in terms of the natural background quality. For example, the threshold value for nitrate in many waters will be 11.3 mg/l as N, which is much higher than any natural background concentration.

The working definition of ‘natural background’ given above is very similar to the definition of the baseline concentration used in the UK (Edmunds *et al.*, 1997) and by the European BaSeLiNe programme:

> *the range of concentrations of a given element, species or chemical substance present in solution, being derived from natural geological, biological or atmospheric sources.*

# 2. Principles Governing the Chemical Composition of Groundwater Bodies

## 2.1. Introduction

The natural chemistry of groundwater is initially determined by the chemistry of rainfall falling on the recharge area of a groundwater body. However in modern times recharge waters will be affected by atmospheric and surface pollution.

On reaching and infiltrating the ground this water rapidly takes on the chemical characteristics of the soluble minerals in the soil zone and unsaturated zone. As groundwater flows through the underlying aquifer, the water chemistry evolves more slowly by a series of geochemical reactions including mineral dissolution and precipitation, redox transformations, cation exchange and mixing. The resulting groundwater chemistry is therefore strongly controlled by the geochemistry and mineralogy of the host aquifer (and those through which it has travelled). In many cases the natural chemical signature of the groundwater can be identified even if it is grossly polluted.

## 2.2. Solute Sources

### 2.2.1. Atmospheric Inputs

**Composition of sea water**

Sea spray can be a significant component of rainfall in coastal areas and all rainfall over Ireland contains ions derived from sea spray (Jordan, 1997). Concentrations derived from seawater are highest on the southwest, west and northwest coasts while the lowest influence is seen in the centre of the island. Were there no anthropogenic influences along these coasts, the rainfall composition would be that of diluted seawater (Appelo and Postma, 1993). Appendix A presents the elemental composition of north-eastern Atlantic seawater in detail.

Table 1 presents the concentrations of oceanic seawater against the 1992-1994 average rainfall concentrations for Valentia observatory (coastal Co. Kerry) and Clones (inland Co. Monaghan). Corrections for marine contributions to rainfall concentrations can be made by assuming that all chloride in a sample is derived from marine sources and that the other sea salt ions are present in the same proportions as in seawater [although Jordan (1997) uses sodium as the conservative tracer, chloride is more traditionally used]. Table 1 shows that, with the exception of nitrogen, the rainfall composition on the west coast at Valentia is quite similar to dilute seawater. Inland at Clones the dilute rainwater is proportionally enriched with several species, although absolute concentrations tend to be lower.

**Table 1. Concentrations of selected species in oceanic seawater and Irish rainwaters [seawater from Li (2000) (1992-94 average rainwater from Jordan (1997)].**

| | | pH | Cl | Na | Mg | S | Ca | K | N |
|---|---|---|---|---|---|---|---|---|---|
| concentration (mg/l) | Ocean water | 7.5-8.5 | 18 790 | 10 805 | 1288 | 898 | 401 | 391 | $7 \times 10^{-5}$ |
| | Valentia rain | 5.13 | 17.78 | 10.24 | 1.17 | 1.08 | 0.54 | 0.43 | 0.18 |
| | Clones rain | 4.60 | 4.47 | 2.74 | 0.30 | 0.86 | 0.48 | 0.26 | 0.73 |
| enrichment relative to Cl | Valentia rain | | 1.00 | 1.00 | 0.96 | 1.27 | 1.42 | 1.16 | $3 \times 10^{6}$ |
| | Clones rain | | 1.00 | 1.07 | 0.98 | 4.03 | 5.03 | 2.80 | $4 \times 10^{6}$ |

Superimposed upon this geographic variation in rainfall composition is a seasonal variation (Figure 1). The seawater influence is more dominant in the winter and, at Malin Head, the mean monthly rainfall concentration of chloride between 1966 and 1975 varied between 69 mg/l in March and 11 mg/l in August (Mathews and McCaffrey, 1977). For chloride this effect propagates inland, but in contrast, there is no consistent seasonal variation in nitrogen deposition. Other species vary between those two extremes depending on their seawater influence. Since most recharge occurs during the winter and spring months, the quality of infiltration will reflect this bias and tend to be slightly enriched over the annual average concentration.

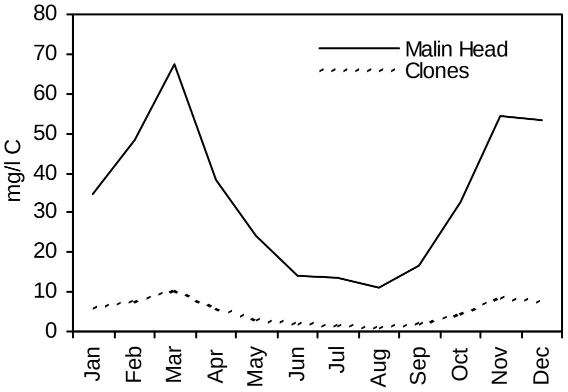

**Figure 1. Average concentrations of chloride in rainfall, 1966 - 1975 (Mathews and McCaffrey, 1977).**

**Continental influences on rainfall composition**

During movement over land, air masses and clouds pick up aerosols and gases from natural and industrial origin. For example, the elevated calcium at Clones is probably due to the erosion and distribution by wind of limestone dust, while the elevated potassium may be due to erosion of silicate soils (or airborne fertiliser dust). Movement of airborne dust and volcanic emissions also redistributes metallic species such as zinc, copper and cadmium.

Deposition of aerosols continues during dry periods, and can be a significant contributor to the deposition of dust, especially at distance from the coast.

**Anthropogenic inputs**

Combustion from power generation and transport emits large quantities of chlorine, sulphur and nitrogen into the atmosphere. These are oxidised and produce the acids HCl, $H_2SO_4$ and $HNO_3$ as aerosols, which, when precipitated, contribute to acid rain. On the other hand, intensive agriculture releases ammonia in the form $NH_4OH$ by evaporation from manure. The enriched sulphur and nitrogen concentrations in Table 1 reflect these impacts (especially inland). Atmospheric pollution operates on a global scale and much of the anthropogenic sulphate and nitrate deposited in rainfall on Ireland will have originated in North America or from the exhaust emissions of ocean-going vessels.

Other atmospheric pollutants of concern are the heavy metals. Deposition rates of heavy metals (as $kg.km^{-2}.yr^{-1}$) for Ireland and the rest of Europe are computed as part of the European EMEP programme (e.g. Ilyin *et al.*, 2003). Maximum and area- and time-averaged rainfall concentrations of heavy metals are presented in Table 2. The greatest contribution to each of these was computed to be anthropogenic emissions from outside the State.

**Table 2. Concentrations of heavy metals in Irish precipitation (Berg *et al.*, 2002).**

| | Rainfall concentration (µg/l) | |
|---|---|---|
| | Average (over 2000) | Maximum (in 2000) |
| Arsenic | | 0.50 (Turlough Hill) |
| Cadmium | 0.04 | 0.11 (Turlough Hill) |
| Lead | 0.80 | 2.80 (Turlough Hill) |
| Mercury | 0.014 | |
| Zinc | | 54.1 (Valentia) |

### 2.2.2. Terrestrial Inputs

Most terrestrial inputs of contaminants are anthropogenic in origin. Natural releases of compounds such as those from manure (from wild animals) and decaying vegetation tend to be insufficiently concentrated to leach through the unsaturated zone (without bypass mechanisms). They are mostly recycled in the soil zone or go to surface water runoff, except where soils are very thin.

**Land use changes**

Were Ireland to have never been colonised by humans, most of the country would be mature forest interspersed with areas of bog. Deforestation and exploitation of the peatlands began thousands of years before present, although their rates increased after the Norman invasion (Edwards and Warren, 1985; O’Connell and Molloy, 2001). These activities affected the chemistry of recharge waters without necessarily directly adding solutes. The process continues today, as deforestation and deep-ploughing cause the leaching of soil nutrients into groundwater. It is because of these processes and the removal of nutrients by export of crops and livestock that artificial fertilisers are used to restore soil productivity. Changing land uses also affect hydrology and it is likely that the evapotranspiration-runoff-recharge balance has been significantly altered by pre-industrial development.

**Agriculture**

Approximately 58% of the land in Ireland is used for grazing livestock and 6% is under tillage (Fingleton and Cushion, 1998). These activities are known to significantly impact the environment and are reflected in atmospheric pollutant concentrations, especially of ammonia (Jordan, 1997), and in the nitrate and phosphate concentrations in rivers (Lehane *et al.*, 2002).

Ploughing causes the development of an aerobic environment in the soil, which can lead to ammonification and subsequent nitrification of otherwise organically-bound nitrogen. In this way, standard agricultural practices lead to the depletion of the soil nutrient store by enhanced leaching from bare soil and by export of goods. These nutrients are often replaced by the application of fertiliser, which, if excess is applied or it rains shortly after application, runs off into surface watercourses or infiltrates into groundwater. Baled and unbunded silage stores produce a leachate that can be readily washed into watercourses.

All types of modern farm tend to be net importers of nitrogen and phosphorus (Frost *et al.*, 2002), the excess of which goes to watercourses and groundwater. Manure from livestock (mostly cattle) is widely applied as fertiliser; in 1998 231 000 tonnes of nitrogen and 39 300 tonnes of phosphorus from organic wastes were spread on land (Brogan et al., 2001). In 2001, Irish agriculture imported 369 000 tonnes of nitrogen and 42 700 tonnes of phosphorus in artificial fertilisers (Lehane *et al.*, 2002). If these solutes were not taken up in the soil zone they can be estimated to contribute approximately 17 mg/l as N of nitrogen and 2.3 mg/l as P of phosphorus to the effective precipitation (assuming a uniform spreading density and a uniform effective precipitation rate of 500 mm/a). Slurry spreading can also contribute significant loads of organic carbon, heavy metals and pathogens to the groundwater.

Heathwaite *et al.* (1996) show how surface waters and groundwaters in many European countries have seen a sustained upward trend in nitrate and phosphate concentrations since the middle of the twentieth century (Figure 2). Although the causes are varied, increased nutrient concentrations are mostly linked to advancement in agricultural techniques such as deep ploughing and use of artificial fertiliser. Ireland's accession to European Community membership in 1973 led to increased subsidy for Irish agriculture via the Common Agricultural Policy and consequently led to the adoption of these techniques.

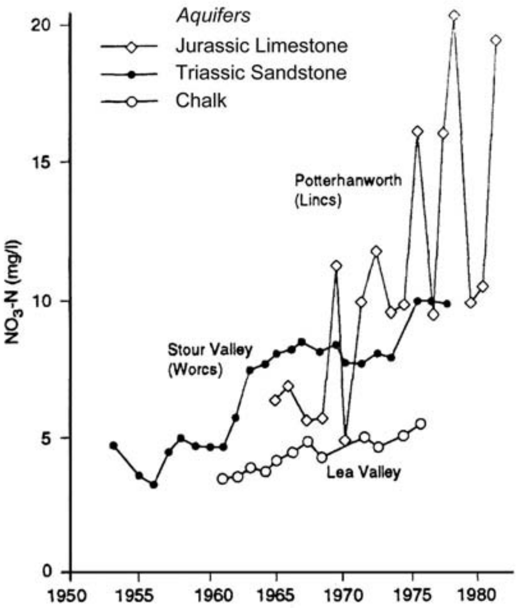

**Figure 2. Long-term trends in nitrate for public water supply boreholes in 3 British aquifers [Heathwaite et al. (1996)].**

Although 9% of Ireland is under forest, only about 10% of this area is under commercial forestry, but this is planned to increase (Allen and Chapman, 2001). Felling operations expose the forest soil and increase nutrient, metal and pesticide leaching (Neal *et al.*, 1998). Actively worked peatlands are also a major source of nutrient release and their drainage can release very high concentrations of iron and manganese into local watercourses and groundwater.

### Settlements and Urbanisation

According to the 2002 Census 31% of dwellings in the Republic are in what is described as rural areas. Most of these rely on on-site facilities for the treatment and disposal of domestic wastewater. The septic tank and associated percolation area is by far the most common treatment/disposal system used. In 1988 it was estimated that there were 350 000 of such treatment/disposal systems in Ireland and the recent census shows the considerable growth in the construction of dwellings in unsewered areas since 1988. There is no evidence to suggest that the rate of growth of such development will diminish significantly in the short-medium term.

There is now considerable evidence, based on groundwater microbiological data for samples collected from private boreholes and wells, to suggest that on-site disposal of wastewater is causing local contamination of a significant number of boreholes and wells. As well as pathogens, these discharges also contribute sodium, chloride, nitrogen and dissolved organic carbon to groundwater. Lack of maintenance and lack of, or poor, percolation area design and construction is probably responsible for some of the contamination problems but locating such systems on land where the soil/sub-soil is not suitable for percolation is also a problem (EPA, 1998).

There has been huge progress in the provision of modern wastewater treatment facilities for the cities and towns over the past ten years. Most of the former pollution 'black spots' have been eliminated, driven by the Urban Wastewater Treatment Directive. It should be noted that the historical impact of untreated or partially treated urban wastewater on groundwater would have been minimal since the major conurbations (Dublin, Cork, Limerick and Galway) and many of the larger towns (e.g., Dundalk, Drogheda, Wexford, Waterford, Sligo) discharged to coastal or estuarine waters. Landfills and contaminated land are concentrated around the main population centres but can introduce significant amounts of contaminants directly into groundwater. These tend to have a fairly local impact but where they are particularly concentrated can cause widespread pollution of aquifers.

With the enactment of the Waste Management Act in 1996 a comprehensive licensing system operated by the EPA for landfill disposal operations was introduced. An immediate consequence has been the closure of many small landfill facilities by the local authorities that either owned or operated the majority of sites. In line with national policy the trend in the future will be for a relatively small number of large regional facilities designed and engineered to best practice. However, the legacy of the old ‘dilute and attenuate’ sites will continue for many years.

The late arrival of industrialisation in Ireland has the fortunate benefit that there is no substantial legacy of industrial brown-field sites and contaminated land. To date disused gas works have been the most common category of site in terms of range and toxicity of contaminants and size of site. Many of the old gas works were located adjacent to coastal or estuarine waters so contamination of groundwater was not usually of great significance in terms of groundwater use for water supply.

## 2.3. Subsurface Processes

Details of the subsurface processes that affect the composition of groundwater are presented in many textbooks, including Lloyd and Heathcote (1985), Appelo and Postma (1993), Stumm and Morgan (1996), Langmuir (1997) and Brady and Weil (2002). These subsurface processes are not described in detail here, but a brief summary of the main points that are discussed in the remainder of the report are given below.

### Evaporation and Evapotranspiration

On reaching the ground surface, the solute concentration in rainfall increases due to evaporation. This may be the only process that affects the concentration of conservative solutes such as chloride (Langmuir, 1997).

### Sequestration and Nutrient Cycling

In the soil zone, vegetation affects the concentration and speciation of nutrient species, such as nitrate, ammonium, phosphate and other trace elements. In a soil system that has not been affected by human influences, nutrient recycling should retain most of the nitrogen and phosphorus within the soil zone (Brady and Weil, 2002). Where there are thin soil zones (e.g. on karstic limestone terrains) the nutrients in rainwater may move through relatively unimpeded.

### Mineral Dissolution

Carbon dioxide in the atmosphere is dissolved by rainfall to form a weak solution of carbonic acid (rainfall pH reaches approximately pH 5.6). Respiration of plants and bacteria in the soil zone increase the partial pressure of carbon dioxide causing the carbonic acid solution to strengthen (to approximately pH 4.6). In soils and subsoils containing carbonate minerals (mainly calcite and dolomite) this percolating acidic water rapidly reaches equilibrium with the carbonates and dissolves the minerals. This releases calcium and magnesium into solution along with any impurities in the minerals (e.g. iron).

Evaporite minerals (e.g. halite, gypsum and anhydrite) dissolve readily into solution irrespective of the pH. Halite dissolution contribute sodium and chloride to the groundwater; gypsum and anhydrite contribute calcium and sulphate. These minerals are, however, rarely found in Irish geological strata.

Silicate minerals (e.g. feldspars, clays etc.) dissolve much more slowly than carbonate minerals and release their constituents as the groundwater moves through the aquifer. Aluminium, potassium, sodium and magnesium are commonly released by silicate dissolution, depending on the minerals present.

### Redox Transformations

Reduction and oxidation processes involve the transfer of electrons between chemical species (Appelo and Postma, 1993) and tend to be mediated by bacteria in the environment. As a species gains an electron (i.e. it is reduced), another always loses an electron (is oxidised). In an aquifer, the microbial population utilises organic carbon from the rock matrix to grow, and obtains metabolic energy by controlling redox reactions. In an unconfined aquifer, dissolved oxygen is preferentially utilised for these metabolic processes. However, in confined aquifers the oxygen cannot be replaced and the microbes start to reduce other compounds. Figure 3 presents a chromatographic sequence of the disappearance and appearance of chemical species in groundwater that illustrates these reactions along a flow line in a confined aquifer.

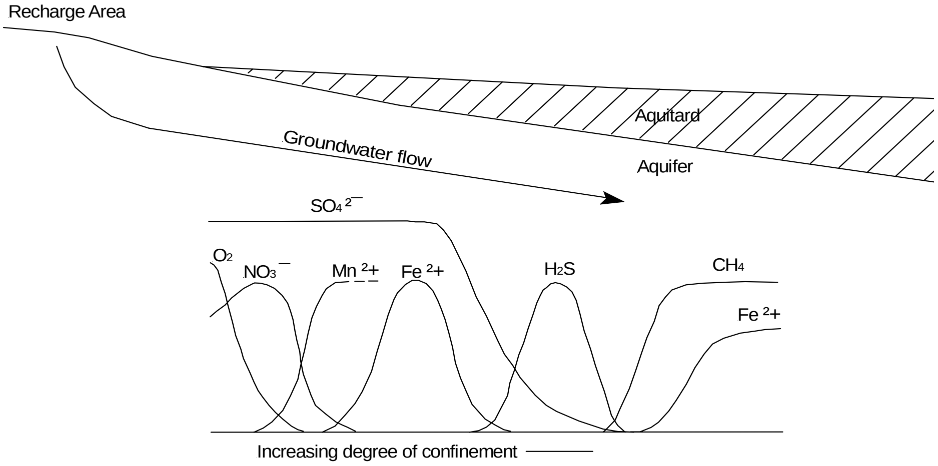

**Figure 3. Redox transformations along a flow line (after Appelo and Postma (1993).**

Key redox reactions in natural groundwaters are (Stumm and Morgan, 1996):

- Reduction of nitrate to nitrogen. Nitrate is the first chemical species to disappear from groundwater once the dissolved oxygen is used up.
- Reduction of iron and manganese oxides. $Fe^{III}$ and $Mn^{IV}$ are relatively insoluble in groundwater, whereas $Fe^{II}$ and $Mn^{II}$ are quite soluble. Therefore, as the groundwater becomes more reduced, iron and manganese appear in solution. This releases other metals from the oxides into solution, typically arsenic which is sometimes present in very minor quantities.
- Oxidation of ammonium to nitrate occurs readily in the soil zone and unconfined aquifers.
- Oxidation of iron pyrites occurs as oxidising recharge waters percolate through pyrite-rich sediments. This releases sulphate into the groundwater, decreases the pH and mobilises heavy metals.

## 3. Review of International Approaches

Concise reviews, outline methodologies and key results for the international approaches reviewed are presented in Appendix B. Detailed methodologies have been published by the UK, Germany and Sweden; a draft methodology (not subsequently adopted) for the Groundwater Directive has also been reviewed. These are summarised below.

**European Union (superseded draft Groundwater Directive)**

The February 2003 draft of the Groundwater Directive defined groundwater typologies according to the lithology of groundwater bodies. It was proposed that ranges of concentrations of indicator species (listed in Appendix B) be defined in each Member State for each typology. It is implied that the 95th percentile concentration be used for the threshold concentration of the indicator species. This methodology was not subsequently adopted because it was considered to be too prescriptive and a more case-by-case approach is adopted in the recent proposal for the Groundwater Directive.

**United Kingdom**

Ireland shares two international River Basin Districts with the United Kingdom. It is important, therefore, that the approaches adopted to the definition of natural background groundwater quality should be compatible. The Environment Agency and British Geological Survey are currently reviewing the baseline groundwater chemistry of major aquifer units; the techniques are presented in Shand *et al.* (1997) and several examples in Shand and Frengstad (2001). The baseline conditions will be used to determine the thresholds that will be used to define ‘good status’.

**Germany**

The German approach to defining natural concentrations is statistical, and relies on the availability of large amounts of data (Wendland, 2003). The natural groundwater quality of a chemical species is assumed to be defined by a log-normal distribution of concentrations, while the anthropogenic impact is assumed to be defined by a normal concentration distribution. For every chemical data set these two are separated and the 10th and 90th percentiles of the natural (log-normal) distribution are reported as the range of natural concentrations.

**Sweden**

Sweden defines a number of geographical regions, partly based on solid geology, and groundwater environments partly based on drift cover (Swedish EPA, 2000). Reference values for natural background concentrations of indicator species have been defined by a variety of methods, for each combination of geographical region and groundwater environment.

# 4. Characterisation Methodology

## 4.1. Introduction and Strategy

This section presents a methodology for the identification and quantification of upper and lower natural background limits for chemical species that may be found as pollutants in groundwater, but that also exist naturally at detectable concentrations. For non-natural species (e.g. chlorinated solvents or pesticides) the upper natural background limit will be zero. Only a selected list of species are presented because they are the most common pollutants, and/or because they are characteristic of a particular type of diffuse pollution impact such as artificial fertilisers or acid mine drainage. These are termed ‘indicator species’ and are listed in Section 4.2. The techniques presented here are transferable to contaminants with similar chemistry.

The following list presents the overall methodology for determining natural background concentrations in a given groundwater body. An outline strategy for dealing with all groundwater bodies in Ireland is presented in Section 6.1.

1. Assess data availability (location and date ranges) within the boundaries of the given groundwater body
2. Consider grouping groundwater bodies if limited data appear to be a problem with individual bodies (Section 4.3)
3. Characterise hydrochemistry of the groundwater body or group of groundwater bodies
   a. Review hydrogeological conceptual model and natural hydrochemical distribution from GSI
   b. Review list of pressures; which indicator species should be adopted?
   c. Collate and assess the quality of the data, apply unit conversions where necessary (Section 4.5.1)
   d. Note any trends, seasonal variation, distribution or depth variation in concentrations of indicator species
   e. Reject any obviously polluted concentrations
   f. Identify best combination of techniques to use for derivation of natural background concentrations (Section 4.6)
4. Derive natural background concentrations where possible using identified techniques
   a. Obtain background concentrations
   b. Remove anthropogenic atmospheric impacts to give natural background concentrations (Section 4.6.4)
5. If natural background concentrations cannot be derived, can they be obtained by comparison with nearby or similar aquifers?
6. Check that natural background concentrations are reasonable in comparison with nearby or equivalent aquifers, or by applying professional judgement

The techniques that can be used to derive background or natural background concentrations are presented in Section 4.6. In order of preference these are:

1. Examination of historical (pre-1973) quality data;
2. Analysis of filtered recent groundwater quality data;
3. Examination of surface water quality data and/or rainfall quality.

## 4.2. Choice of Indicator Species

An environmental indicator is a parameter that describes the state of the environment. The key reason for its use is that the large amount of data currently being collected cannot be comprehensively presented and still be grasped quickly by the intended audience. Use of environmental indicators is well established in the European Environment Agency as the primary tool in its ‘State of the Environment’ reporting (EEA, 2003). A number of member states (including the UK and Germany) have also adopted this approach for reporting environmental trends in groundwater (Buss and Streetly, 2004; *www.stadtentwicklung.berlin.de*). The environmental indicators used in this report are chosen to aid identification of the effects of a wide range of common pollution (mainly diffuse pollution) scenarios. Table 3 lists the indicator species that should be considered in the Irish context. Not all species need be examined for a groundwater body if the initial characterisation shows that there are no pressures that may give rise to any specific contaminant (e.g. indicators of urban sewer leakage in rural areas). However, since Annex V of the WFD specifically identifies a set of core parameters (ammonium, oxygen content, pH, electrical conductivity and nitrate) for surveillance monitoring, natural background limits should be derived for each of those five.

Annex III of the Groundwater Directive lists nine groundwater pollutants for which threshold values for good quality status should be defined. These are also included in Table 3 as knowledge of their natural background concentrations is essential for setting threshold values. However, the natural background concentrations may not ultimately be used in the definition of good status.

A number of other indicator species are listed in Table 3 for which it might be appropriate to determine natural background concentrations in Ireland. If the initial characterisation identifies pressures from pollutant sources that are not represented by the indicator species below, other indicator species should be adopted on a groundwater body specific basis. Annex VIII of the WFD presents an indicative list of main pollutants that should be considered and for inorganic species is similar to Table 3, but with many additional organic species.

Upper limits for natural background concentrations should be defined for each species. Many lower concentration limits will be undetectable and these need not be explicitly set.

For the purposes of characterisation of groundwater bodies it is essential that, in addition to the indicator species listed in Table 3, sufficient analyses be made to enable an ionic balance to be obtained (Section 4.5.1) and to understand the groundwater chemistry. These will include:

- temperature, pH, electrical conductivity
- calcium, magnesium, sodium, potassium,
- bicarbonate (alkalinity), chloride, sulphate and nitrate.

In special cases, concentrations of aluminium or iron may also be required to obtain an ionic balance.

Uranium, radon, barium and fluoride are species of particular interest in Ireland, and it is important to establish a survey of natural background concentrations and variability. The anthropogenic influence on regional concentrations of these species will be, in most cases, very limited but natural background concentrations should be determined for groundwater bodies.

Organic compounds such as chlorinated solvents and pesticides are not natural substances and are not considered to be indicator species for which natural background concentrations need to be set. The Groundwater Directive does require that threshold values for good status be set for trichloroethene and tetrachloroethene, and the threshold for pesticides will be 0.1 µg/l [from the Plant Protection Products Directive (91/414/EEC]. However, these need not influence the selection of natural background concentrations. If they are present in groundwater, the groundwater is not at its natural background quality.

Some halogenated hydrocarbons such as chloroform are naturally formed in soil, peat and marine environments (Euro Chlor, 2002) but they are not normally present at significant concentrations in groundwater. Polycyclic aromatic hydrocarbons (PAHs) occur naturally in high concentrations in peat, but they have a very high affinity to soil organic matter and are not expected to occur in significant concentrations in groundwater other than where there has been some anthropogenic impact (e.g. introduction of co-solvents).

Pathogenic micro-organisms in groundwater also tend only to be due to anthropogenic activities, either directly from human waste (e.g. sewers or septic tanks) or from high stock densities. In both cases, high concentrations of chloride and/or ammonium in the groundwater would be expected – both of which are more mobile than pathogens in the sub-surface environment and are core indicator species.

**Table 3. Indicator species for diffuse pollution.**

| | |
|---|---|
| *Water Framework Directive 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 also 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 high pHs |
| 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 |
| Trichloroethene & tetrachloroethene | Only reach groundwater due to urban anthropogenic inputs. Presence can definitively demonstrate that pollution has occurred; limiting concentrations need not be set. |
| *Other species* | |
| 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 & manganese | High concentrations are indicative of reducing conditions (and are more sensitive indicators than DO measurements). Also released on drainage of peat bogs and in acid mine drainage |
| Microbial pathogens:<br>faecal coliforms,<br>faecal streptococci | Only reach high concentrations in groundwater due to anthropogenic inputs. Presence can demonstrate that pollution has occurred; limiting concentrations need not be set. |
| Pesticides | Only reach groundwater due to anthropogenic inputs. Presence can definitively demonstrate that pollution has occurred; limiting concentrations need not be set. Controlled by the Plant Protection Products Directive (91/414/EEC) and Biocides Directive (98/9/EEC). |
| Phosphate | From artificial fertilisers. 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 |

## 4.3. Grouping or Subdivision of Groundwater Bodies

### 4.3.1 Grouping

The definition of a groundwater body is made on the basis of hydrogeological continuity and flow patterns (Section 1.4.2) rather than on the basis of lithological continuity. It is therefore possible that groundwater bodies with the same lithology will have the same (or very similar) natural background concentrations, although soil and drift type and proximity to the coast will cause variation. Grouping of groundwater bodies in this way is a useful tool in determining natural background concentrations for groundwater bodies with limited data availability.

Several international approaches group groundwater bodies by ‘typology’ (CEC, 2003), ‘groundwater environment’ (Swedish EPA, 2000) and hydrogeological conceptual model [Shand and Frengstad (2002) on Welsh mudstones]. The first two grouping approaches have a formal basis in that the common factors are described in guidance: the CEC (2003) approach by lithology and drift type only, but the Swedish EPA (2000) approach also includes a geographical factor describing vicinity to the coast and general topography. The Shand and Frengstad (2002) approach is more flexible and is made on a case-by-case basis where there are insufficient data to fully characterise one discrete groundwater body.

It is not the intention of this guidance to present a definitive list of the groundwater environments that might be applied to Irish groundwater bodies, as that should be judged on a case-by-case basis. Furthermore, since rainwater (and therefore groundwater) chemistry is partly controlled by proximity to the coast, identical lithologies at different locations may have different chemical compositions. Nevertheless, due to their different solute sources, this will be the case for chloride and sodium, but concentrations of other solutes may be comparable. The following points describe the factors that should be taken into account when considering the grouping of groundwater bodies:

- Bedrock lithology
  Basic grouping of groundwater bodies by bedrock lithology could be accomplished by comparison within GSI’s 30 bedrock groups. However, since these bedrock groups are assigned based on hydrogeological considerations, there may have to be further subdivision within a category. For example, the ‘Igneous Intrusive’ or ‘Igneous Extrusive’ groups might be divided according to the detailed geochemistry of the rocks. Conversely, categories might be able to be grouped further.
- Soil and subsoil type
  The lithology and thickness of overlying deposits will control concentrations of some solutes in groundwater. Nutrients are controlled by the permeability of the soil, while some Glacial Tills may introduce significant sulphate and naturally cause the development of anaerobic environments. Most glacial deposits in Ireland are rich in carbonates which introduce a carbonate signature to groundwater in siliceous rocks (Warren, 1991).

- Proximity to the coast

  Chloride concentrations in Irish rainfall decrease eastwards (Figure 4: Jordan, 1997). Assuming a relatively even evapotranspiration rate across the island, this will also be the distribution of (scaled) recharge concentrations. Grouping of groundwater bodies for comparison of seawater-derived ions should therefore take account of this distribution, although for those solutes that have no atmospheric input, this need not be considered.

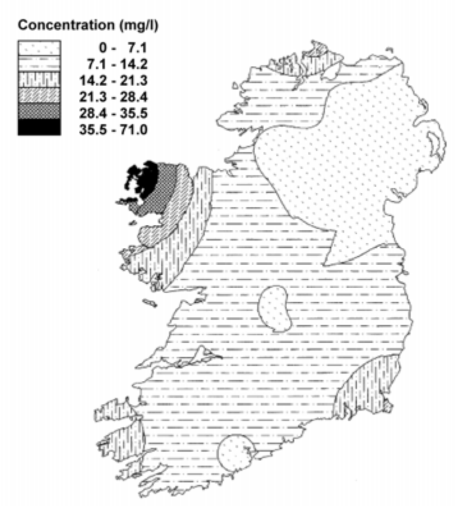

**Figure 4. Annual mean concentration of chloride in rainfall for the period 1992-94 (Jordan, 1997).**

### 4.3.2 Subdivision of Groundwater Bodies

Some groundwater bodies may incorporate a number of different lithologies. Others might be partially confined, leading to a distribution of unconfined and confined conditions, therefore causing oxidising and reducing groundwaters respectively. Although these will be consistent hydrogeological units, the natural groundwater chemistry of each lithology, or confined/unconfined zone might be significantly different, leading to different natural background limits being required for each.

Nitrate, for example, is a key pollutant in unconfined areas, but is removed from groundwater in reducing, confined conditions. In a mixed confined/unconfined groundwater body, if the natural background limit were set based on concentrations in the confined area, natural concentrations in the unconfined area will exceed the upper limit. Likewise, if the higher measured concentrations from the unconfined area were used to set a limit, it would not be a conservative limit for the confined aquifer.

A less severe form of subdivision might be appropriate if, for example, a groundwater body which has uniform lithology and hydrogeology has coastal and inland outcrops. It would be expected that the concentrations of redox indicators might be constant across the groundwater body, but natural chloride concentrations would be elevated in the coastal area. Subdivision might therefore only be appropriate for the subset of indicator species that are derived from sea spray.

Gradational changes in natural groundwater chemistry across a groundwater body (e.g. along a flow line) need to be catered for in the assessment of natural background limits. However, fine-scale subdivision of the aquifer will not be appropriate as sufficient data is not likely to be available to support it. Subdivision will only be possible where there are adequate data for both sets of conditions.

## 4.4. Physical Constraints

The quality of any analysis of historical and recent groundwater monitoring data will be limited by the locations, pumping rates, construction and sampling techniques of the points sampled.

### 4.4.1. Location of Sample Points

As groundwater chemistry evolves along flow lines in an aquifer, sample analyses will vary depending on whether they are taken in a discharge or recharge zone (Appelo and Postma, 1996; Palmer and Cherry, 1984/85). An example is the concentration of total dissolved solids (TDS) in the Westphalian aquifer of the Castlecomer Plateau (Figure 5). In this aquifer TDS increases along a flow line from 100 mg/l at the recharge area to 300 mg/l at the discharge 14 km distant, mainly due to dissolution of calcium-magnesium carbonates (Daly *et al.*, 1980). It is therefore necessary to ensure that the distribution of the sampling points is sufficient that the full range of chemical concentrations in the groundwater body (or group of groundwater bodies) is sampled.

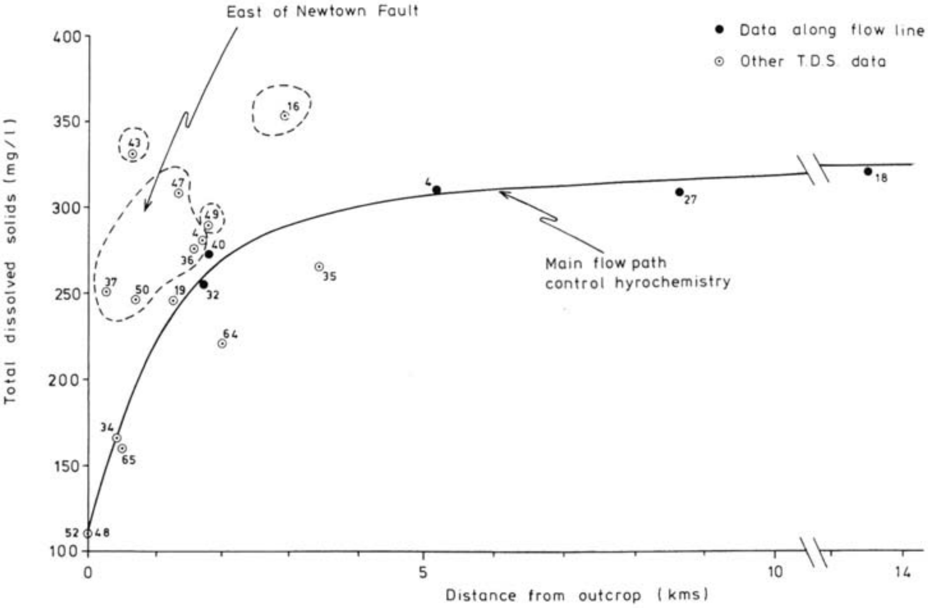

**Figure 5. Evolution of groundwater chemistry along a flow path (Daly *et al.*, 1980).**

Grath *et al.* (2001) present relationships to calculate representativity indices for groundwater bodies in order to check for monitoring homogeneity (Box 1). Representativity indices should only be used to assess monitoring networks in homogeneous aquifers, so are not particularly useful in the Irish context. In heterogeneous aquifers it is recommended that specific features of the flow system, such as karst conduits, should be targeted in order to obtain samples that are representative of the aquifer.

For a monitoring network with scale dependence, BGS (1994) provides a list of recommendations with more specific spatial densities of monitoring points depending on the flow regime of the aquifer:

- one per 25 km$^2$ for the unconfined areas of major aquifers;
- one per 35 km$^2$ for the confined areas of major aquifers;
- one per 50 km$^2$ for minor aquifers;

Note: major and minor aquifers are defined in NRA (1992).

**Box 1: Aquifer Representativity Indices.**

Grath *et al.* (2001) calculate representativity indices for the groundwater bodies examined in order to check for monitoring homogeneity. A perfect triangular network is given a representativity index of 100%. For networks with a representativity index of less than 80%, spatial statistics can be highly biased and therefore may be skewed towards local impacts. Figure A presents example monitoring networks within groundwater bodies from Grath *et al.* (2001) that span the range of representativity indices – only the first aquifer would give a relatively unbiased spatial average. Note that there are no scales against the aquifers, as the representativity index is scale-independent. The sole recommendation for sampling density is that there should be three sampling points per groundwater body.

Where monitoring networks are not sufficiently representative ($R_U < 80\%$) of the groundwater body, Grath *et al.* (2001) recommend dividing the groundwater bodies into sub-bodies. Weights are applied to the statistics derived for each sub-body based on the areal proportion of the total groundwater body.

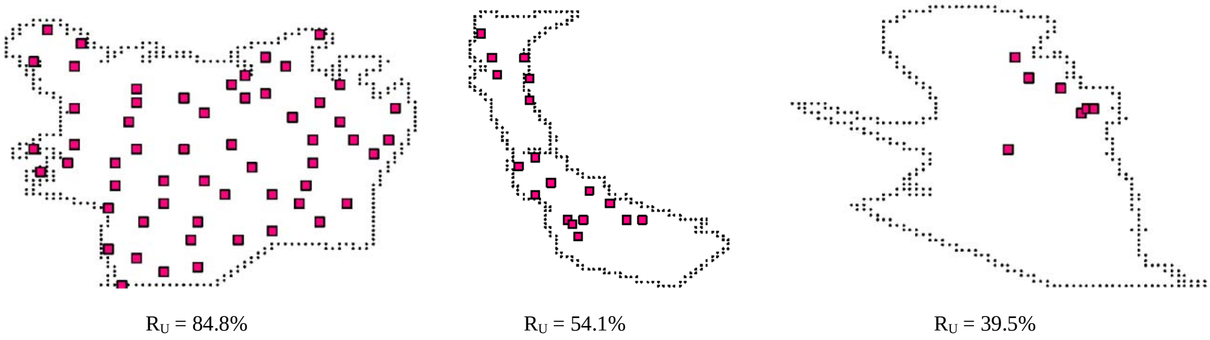

**Figure A. Representativity indices for three European aquifers (Grath *et al.*, 2001)**

A homogeneous network is not recommended in BGS (1994), instead points should be located to take account of the need to monitor in recharge areas to provide early warning of diffuse impacts, geological outcrop patterns, land uses, distribution of groundwater abstractions and local/regional issues such as saline intrusion etc. This scheme was not developed with a view to computing spatial means, and acceptable networks under the BGS (1994) scheme may yield values of representativity index less than 80%.

The EPA has undertaken twice-yearly groundwater sampling at up to 380 strategically located monitoring points since 1995 (McGarrigle *et al.*, 2002), of which 91 are within the South East River Basin District. The average sample density in the SERBD is therefore approximately one point per 140 km$^2$, although it will be higher for groundwater bodies in regionally important aquifers than those in poorly productive aquifers. It appears, therefore, that there should be sufficient spatial coverage for at least some of the groundwater bodies in the country, but this will have to be assessed on an individual basis. Similarly, the representativity of the sample points should be assessed on a case-by-case basis.

Given the size and heterogeneity of the majority of aquifers in Ireland, it is not proposed that numerical indices of spatial density or representativity index are used, instead the following guidelines should be followed:

- There should be at least three points with chemical monitoring data in a groundwater body or group of groundwater bodies under assessment;

- At least one monitoring point should be sited in an area of groundwater recharge, one in an area of discharge (e.g. spring sources), and preferably one along the flow line between the recharge and discharge points.
- Monitoring points should be concentrated in groundwater bodies that are particularly at risk. Greater than three monitoring points should be aimed at in this instance.

This approach should be locally refined with time, as more data are collected and hydrochemical distributions in groundwater bodies are better characterised.

### 4.4.2. Aquifer Sampling Volumes

Large groundwater abstractions such as public water supplies sample a much larger proportion of an aquifer than small farm wells and will therefore be more representative of the background chemistry of the aquifer. In addition, a large abstraction may be sampling older, deeper water than a shallow spring, which might be more affected by recent diffuse pollution. For the purpose of obtaining an average concentration for an aquifer, it might therefore be useful to apply a weighting scheme to concentration results, based on the proportion of groundwater obtained from the groundwater body.

However, there are disadvantages to the method for determining statistics to describe extreme concentrations. If, for example, one large abstraction is located in a recharge area, it will draw on mainly fresh recharge waters. A weighting system will therefore skew the average chemistry of the aquifer towards the recharge quality. For solutes that are naturally obtained during flow through the aquifer (such as metals), this would tend to set the upper natural background limit too low.

### 4.4.3. Timing of Sampling

Notwithstanding any long-term trends in groundwater quality, it should be noted that groundwater chemistry changes seasonally. This is particularly the case in karstic aquifers where, during wet periods, immature recharge water that has had little contact with the host rock, flows through the karst conduits and discharges at springs. During periods without recharge, smaller fractures discharge more mature water that has had time to equilibrate with the rock (Mayer, 1999). It has also already been shown that the chemistry of recharge waters changes according to season (Section 2.2.1) and this can be important in aquifers with high, rapid turnover.

To ensure that the samples obtained are representative of the average annual groundwater chemistry in an aquifer the following guidelines should be followed:

- When assessing the groundwater chemistry of a groundwater body, samples should be taken at a variety of times over the year and under differing flow conditions in the aquifer;
- In a dual permeability aquifer such as karst, sampling points should be located in both the fractured zones and the cave systems. The sampling frequency of the mature waters in the fractured zones can be reduced relative to that in the fast flowing karst zones.

### 4.4.4. Sampling Frequencies

Groundwater data for a groundwater body (or group of groundwater bodies) may have been obtained from a formal monitoring scheme such as that of the EPA, from surveys (academic studies or site investigations) or from opportunistic one-off samples from borehole commissioning. Care must therefore be taken to ensure that there is no bias towards the chemistry of any particular sampling point with significantly more data than the others (except to the extent that more confidence can be placed in the data from that point if the long time series yields consistent results).

A typical technique to counter this bias would be to obtain the time-averaged concentrations at each sampling point. Another technique would be to select the same number of samples from each point, taken almost simultaneously. However, these techniques may obscure or omit early chemical data or extreme values.

Since the methodology for characterising natural background groundwater quality focuses on identifying extreme values of natural background concentrations (i.e. 95th percentiles – Section 1.5) it is recommended that concentration data should not be processed further to eliminate bias due to different sampling frequencies. All sampling results should therefore be used as individual data points.

Selection of almost simultaneous data may prove to be a useful technique in some circumstances, for example, if a long-term record shows that a groundwater body is not anthropogenically impacted prior to a cut-off date. This date could then be used to filter data from the other sampling points, provided that this interpretation (i.e. that one set of data reflects the trend for the whole groundwater body) is consistent with the hydrogeological conceptual model.

### 4.4.5. Physical Sampling

In order to obtain groundwater from an aquifer to assess its quality, samples must be taken. Sampling and subsequent transport to the laboratory, however, can affect solute concentrations, especially if taken from a borehole (Lloyd and Heathcote, 1985). Common factors that can cause distortion of results are:

- Penetration of the sampling point through the aquifer.

  Wells that penetrate the whole of an aquifer mix groundwaters from different depths and therefore different ages. Although a deep well in a moderately permeable aquifer may sample relatively old water at its base, it will be sampling relatively recent water from the top. This leads to mixing and possible reaction of the groundwaters.

- Effects of pumping.

  If a borehole is not constantly flowing, it should always be purged before sampling. Normally three borehole volumes are flushed out before taking samples, but this is not always sufficient to stabilise the redox potential of the pumped groundwater (Lloyd and Heathcote, 1985). Water pumped from a borehole oxidises once in contact with the atmosphere and therefore its redox potential changes. This can lead to reaction within the borehole, such as precipitation of iron.

  A dramatic change in pumping rate associated with sampling of a normally unused or lightly used borehole can cause increased turbidity due to dislodging iron deposits on the borehole screen or to fines being washed out of the aquifer.

- Well-head treatment and storage of the sample.

  Filtering and acidification of groundwater samples improves the accuracy of the final analysis, but older samples may have not been treated. This can, for example, lead to either high (if unfiltered) or low (if unacidified) metal concentrations in an analysis.

### 4.4.6. Chemical Sampling and Analysis

A number of determinands need to be measured at the sample point in the field. pH, alkalinity, temperature and dissolved oxygen (DO) concentration all change with exposure to the atmosphere and should be sampled as soon as possible. DO concentrations can either increase or decrease depending on the initial concentration in groundwater and the ambient temperature. pH and alkalinity are controlled by carbonate system equilibria and sampling can cause degassing of carbon dioxide or precipitation of calcium carbonate. These processes tend to cause increasing pH and decreasing alkalinity.

However, it is sometimes possible that older samples, or those not taken as part of a formal survey, will have had these parameters measured in the laboratory. If the sample bottle was filled to the brim and sealed airtight, this should not cause a large drift in measurements, but if the water stayed in contact with air, pH, alkalinity and DO measurements will be unreliable. This will probably be difficult to ascertain after so much time, so if outliers occur for pH, alkalinity or DO in data that were not collected in a formal survey or monitoring programme, their rejection should be considered.

Analytical techniques for quantifying solute concentrations have changed significantly over the period 1960 to 2003. Older measurements will have been obtained by titration or gravimetric methods while modern analyses have improved to computerised spectrophotometric methods. While the reliability, accuracy and limits of detections will have improved, there has been no systematic increase or decrease in concentration measurements. When examining analyses it should be remembered that they are less precise near the method limit of detection and above the upper calibration point (Appendix C).

## 4.5. Analytical Constraints

### 4.5.1. Interpretation and Analysis

Inaccuracies and errors can arise in the laboratory from a range of issues. These were more prevalent in analyses performed before the 1980s. A number of techniques are useful for gaining confidence in older analyses of groundwater chemistry. The most useful is critical examination for the data for outliers, and when assessing time series data, they should always be plotted and assessed.

When full major ion analyses are available ($Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, $K^{+}$, $SO_4^{2-}$, $Cl^{-}$, $CO_3^{2-} + HCO_3^{-}$), the ionic balance can be checked to see if the analysis results predict a condition of electroneutrality in the water (Lloyd and Heathcote, 1985). Since water is electrically neutral, the sum of cations (in meq/l) should always equal the sum of anions (in meq/l):

$$\text{Ionic balance error} = \frac{\sum \text{cations} - \sum anions}{\sum \text{cations} + \sum anions} x100$$

Ionic balance errors should be less than 5% for modern analyses but this requirement can be relaxed to 10% for pre-1980s analyses. If the ionic balance is greater than these limits, either the analysis was inaccurate or there were other major ions in solution; these are commonly iron, aluminium, nitrate or ammonium. If the balance is perfect (i.e. zero), then it is likely that sodium or sulphate concentrations were calculated by balance – a common situation before the 1980s.

There are drawbacks to this technique, as some errors can cancel themselves out. Furthermore, where a water is dominated by a few ions (e.g. Na and Cl in saline waters), large errors in the other concentrations make little impact on the balance. Also, the technique does not reveal anything about minor components such as the heavy metals. A useful check for heavy metal concentration is to determine if it is above the solubility limit for the sample pH. A poor ionic balance is not necessarily a reason to reject all the results from the failing sample, especially when there are relatively few data. Rather it is an indication that the results should be treated with caution, and perhaps a conservative approach taken to defining natural background limit concentrations.

### 4.5.2. Limits of Detection

Limit-of-detection (LOD) values occur in almost all hydrochemical data sets. This leads to difficulty in computing statistics for a groundwater body as (depending on the statistic being computed) these can introduce bias in the value obtained.

The simplest method for dealing with limits of detection is substitution, in which a value is substituted for each LOD. This can be the detection limit (leading to overestimation of the mean), zero (leading to underestimation of the mean) or half the limit (a compromise). For many determinands, there is little difference between statistics computed by these methods, however if there are a significant number of LOD results or, if most the concentrations are near the LOD, bias can be introduced (Helsel and Hirsch, 1992). This is clearly illustrated with the following data set.

<10, <10, <10, <10, <10, 10, 11, 11, 12, 12, 13

Substituting the LOD result values with zero, half the LOD and the whole LOD gives mean values of 6.3, 8.5 and 10.8 respectively. The median value of the data set is always 10.

Gibbons (1994) states that for data sets where fewer than 15% of results are non-detects, substitution of half the LOD value is acceptable and should introduce little bias to the calculated mean value. Where fewer than 50% of results are below the LOD, a mean can be calculated if some statistical corrections can be made. Where greater than 50% of results were below the LOD, even these corrections are considered invalid and a reliable mean value cannot be calculated.

For calculation of arithmetic mean values for trend analysis, Grath *et al.* (2001) recommend that values lower than the LOD are assigned values of 50% LOD (the arithmetic mean calculated this way is designated AM50). A measurement of whether this substitution might introduce bias is the ratio AM0/AM100. If AM0/AM100 < 0.6, there is significant bias and only limited statements are possible regarding average concentrations or trends. In the case of the example data set above, the AM0/AM100 value is 0.58: too low to be able to reliably calculate a mean value.

When a number of data sets are amalgamated from different sources, there are often different detection limits in the data sets; also the LOD may change with time. This can cause further bias in the averages (Grath *et al.,* 2001).

Limited use is made of the mean concentration in this methodology because of these issues, and because the median concentration always provides a better representation of the background water quality than the mean. In calculating median concentrations, the LOD values are counted (a value of <1 is counted lower than a value of 1, but <2 is counted greater than 1). If more than 50% of the data are below the detection limit, then the median is below the detection limit, otherwise the median is the 50th percentile.

### 4.5.3. Identification of Anthropogenic Impacts

A key challenge in identifying a threshold between unpolluted and polluted groundwaters is distinguishing the natural variation in concentrations of natural background groundwater quality and the continuum of concentrations that exist in anthropogenically-impacted groundwaters. Traditionally, anomalous values have been identified using an upper value such as the 95th percentile (Edmunds *et al.*, 1997). However, this is only of use when the anomalously elevated values are rare such as at point contaminant sources. Many Irish aquifers show the effects of widespread (diffuse) anthropogenic nitrate input and the 95th percentile would identify only the most affected aquifers. The technique of Wendland (2003) attempts to separate the two distributions (natural and anthropogenic) statistically, but requires a considerable amount of data (Section 3 and Appendix B).

The natural variation in natural background concentrations is traditionally assumed to be described by a log-normal distribution but this is only rarely true as natural geochemical distributions are generally polymodal and are usually skewed (Reimann and Filzmoser, 2000). However, the assumption is useful because it enables the analyst to compare statistics between groundwater bodies treated in a similar fashion.

Probability plots are commonly used in the minerals industry to identify anomalous concentrations in geochemical samples. If the concentration scale is logarithmic, a log-normal distribution will plot as a straight line. Where the population is polymodal, the data plot as a curve and points of maximum curvature can be used to delineate threshold values between populations (Sinclair, 1974). Probability plots therefore provide a useful graphical tool for distinguishing natural background from polluted groundwater quality. At the same time they clearly show the range and distribution of concentrations and allow comparison between aquifers, or between different species from the same aquifer. Shand and Frengstad (2001) use the technique very effectively for determining baseline concentrations in a number of UK and Norwegian aquifers. Section 4.6.3 deals with the practical use of cumulative frequency plots in the derivation of natural background limits.

There are a number of statistical tests that are appropriate for the identification of outliers or multiple populations. For example one useful outlier test is applied in the context of contaminant concentrations in soil in the UK CLEA methodology (DEFRA and Environment Agency, 2002).

## 4.6. Assessment of Natural Background Quality – Techniques

### 4.6.1. Hierarchy of Preferred Techniques

Table 4 presents a hierarchy of techniques that can be used to estimate the natural background or background concentration of a contaminant in a groundwater body, or group of groundwater bodies. The usefulness and accuracy of these methods depend on the amount of appropriate data that have been obtained; guidance notes on how much data are required are provided.

**Table 4. Hierarchy of preferred techniques for characterisation of groundwater quality.**

| Rank | Technique | Data requirements |
|---|---|---|
| 1 | Historical data analysis | Measurements from several representative locations for reliable pre-1973 data |
| 2 | Recent data analysis | Ideally > 50 measurements from several representative locations |
| = 3 | Atmospheric inputs | Total rainfall, effective rainfall, rain water chemistry |
| = 3 | Surface waters | Surface water chemistry at medium flows |

These techniques are not to be seen as mutually exclusive as all relevant data should be used to build up a picture of the quality of groundwater in the groundwater body. Furthermore, it is unlikely that, even if sufficient historical data for one contaminant are available, there may be insufficient for another contaminant, so other techniques should be applied.

Detailed descriptions of the individual techniques are presented in the following sections.

### 4.6.2. Analysis of Historical Data

Probably the most reliable method of estimating a natural background concentration for a contaminant species is to examine its concentration at a time before any anthropogenic impact would have affected the groundwater. In rural Ireland this time has been assumed to be prior to 1973 when introduction of the Common Agricultural Policy prompted many farmers to invest in modern, intensive agricultural practices (Section 2.2.2). In urbanised areas this time would have been much earlier as some domestic landfills and gasworks were in operation near urban areas since the 19th Century.

For boreholes with accurate depth sampling, it may be possible to obtain older groundwaters by sampling deeper waters. Given that Irish aquifers have a relatively high turnover, however, it will be necessary to show that the water is of sufficient age by using either isotopic techniques (e.g. absence of tritium, or $^{14}$C concentrations), the absence of CFCs, or by groundwater modelling.

Chemical analyses from before the 1980s were generally undertaken using ‘wet chemistry’ methods (e.g. titrations), which are less accurate than modern spectroscopic or chromatographic methods. It is therefore essential to be confident that the data, which will be sparse, is of good quality. This should be accomplished by obtaining time-series data from multiple sample points. Such data are most likely to be obtained from breweries, distilleries or dairies that used groundwater and that kept records of their process water quality. However, it has been found during this project that the majority of these have been using surface water and have not tended to analyse the water chemistry.

If there are insufficient historical data for any single groundwater body it may be acceptable to group groundwater bodies according to their groundwater environment in order to accumulate a sufficient amount of such data (Section 4.3).

Use of historical surface water chemistry at low flows (i.e. baseflow quality) may also be acceptable if there was no significant upstream urbanisation, forestry or agriculture at the time of sampling. Care should be taken to ensure that the watercourse rises only (or mostly) in the groundwater body being examined. Sampling should have been during different seasons.

The preferred technique for obtaining a natural background limit with historical data is to determine the mean plus or minus two standard deviations (approximately the 95th and 5th percentiles respectively) of the log concentration (see Box 2).

**Box 2. Statistical Treatment of Natural Background Concentrations.**

1. Obtain a data set of groundwater concentrations. Manually examine the data set and omit any samples obviously affected by point source pollution or those that have suspicious analytical results (e.g. ionic balance > 10%). Production of a histogram of the concentration range at this stage may be useful if there are many data.
2. Take the logarithm (base 10) of all concentrations, substituting for LOD values with 50% LOD where necessary. Compute the mean of the log data ($\bar{y}$) and the unbiased standard deviation of the log data ($s_y$).

$$y_i = \log_{10}(C_i) \qquad \bar{y} = \frac{1}{n}\sum_i^n y_i \qquad s_y = \sqrt{\frac{\sum_i^n (y_i - \bar{y})^2}{n-1}}$$

3. The upper limit for natural background concentration ($C_{upper}$) should be set at ten to the power of the mean log plus two log standard deviations. If a lower limit ($C_{lower}$) is to be set for the species being examined the lower limit for natural background concentrations should be set at ten to the power of the mean log of the data set minus two standard deviations.

$$C_{Upper} = 10^{\bar{y}+2\cdot s_y} \qquad C_{Lower} = 10^{\bar{y}-2\cdot s_y}$$

   Check that the limit is greater than the LOD for the species, if not, set the limit to the lowest LOD in the data series.

Note that pH is already a log concentration, so if this technique is being used to determine a background or unpolluted pH value, limits should be determined on the mean pH and the standard deviation of pH.

### 4.6.3. Analysis of Recent Data

Most data obtained for a groundwater body will be much more recent than 1973. For example, the EPA representative groundwater monitoring programme has been operating since 1995. Although recent data are more likely to show the effects of pollution to some degree, unless there is a large quantity of good quality historical data, it should not be ignored. Furthermore, historical data are less likely to provide values for some of the more specialist pollutant species such as heavy metals.

Since at least some of the recent data obtained are likely to show the effects of pollution it is necessary to treat these with more care than the historical data and to try to eliminate the polluted samples (Section 4.5.3). A variety of simple graphical methods are available to accomplish this and each type of plot is useful for illustrating different concepts of the groundwater chemistry. For examples of the techniques, the reader is referred to the trialling of selected groundwater bodies in Appendix D.

**Box plots**

Box plots provide a method of representing on the same plot the statistical distribution of concentrations of all species being examined. The data are plotted on a logarithmic concentration axis and for each species the maximum, minimum, median and quartiles are shown. Edmunds *et al.* (1997) order the species by their abundance in seawater and plot a line on the chart to show relative seawater concentrations for comparison. Since rainwater chemistry has a more direct effect on the groundwater chemistry, it is recommended that the annual average rainwater chemistry for the nearest station be plotted for major ions.

Figure 6 presents an example box and whisker plot from the trialling in Appendix D [generated using the AquaChem software (*www.flowpath.com*)]. The concentration in rainfall of species i, $C_{i,\ rainfall}$ is normalised by multiplying by the ratio of the median chloride concentration in groundwater, $C_{Cl,\ groundwater}$, and the chloride concentration in rainwater, $C_{Cl,\ rainfall}$:

$$C_{i,infiltration} = C_{i,rainfall} \cdot \frac{C_{Cl,groundwater}}{C_{Cl,rainfall}}$$

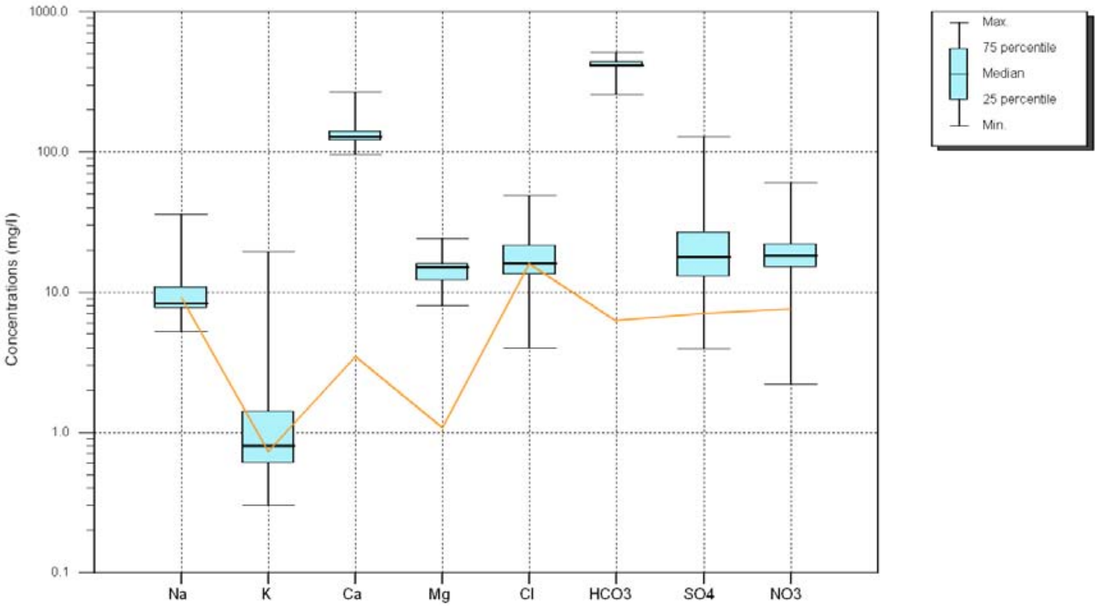

**Figure 6. Box and whisker plot of major ion concentrations. The orange line shows rainfall concentrations normalised to the median chloride concentration in groundwater.**

### Histograms and cumulative histograms

Histograms can be used to illustrate concentration distributions of single contaminant species providing sufficient data are available for their construction. A minimum number of five bins should be used to demonstrate concentration distributions. Histograms might be used to distinguish two very distinct contaminant populations (e.g. natural and grossly polluted) but, if there is overlap between polluted and unpolluted concentrations, this can be very difficult. If limit values are obtained by looking at histograms, the values selected may depend to some extent on the chosen bin ranges.

An alternative method is to plot a cumulative histogram, in which a change in slope may be used to distinguish populations. However, the cumulative frequency plot is more suited for such analysis and is the preferred technique (below).

### Cumulative frequency plots

Cumulative frequency plots display the distribution of data in much the same way as a cumulative histogram but data for more than one species can be presented on the same plot. Furthermore, as the actual data are displayed on the cumulative frequency plot (rather than being assigned to bins) it is easier to extract more accurate concentration values from these diagrams.

Box 3 presents details on the use and interpretation of cumulative frequency plots. Upper and lower limits can be obtained by extrapolating the distribution identified as the natural distribution (i.e. the straight line section) up or down to the 95th or 5th percentiles.

### Time series

Where time series data are available for a groundwater body or group of groundwater bodies, they can be analysed for trends in pollutant concentrations. This may allow tracking of any impact through time and may allow natural background or background concentrations to be hindcasted (backward forecasting) given sufficient independent data.

Hindcasting is not commonly used in groundwater studies but there is some hydrological literature on this technique (e.g. Johnes *et al.*, 1994). However, if correlations can be made, it may be possible to relate historic population changes with ammonium concentrations, or rates of fertiliser use with nitrate concentrations.

### Other graphical methods

Other graphical methods such as trilinear diagrams, cross-plots and maps are not likely to be used in the determination of a natural background limit value. They may, however, be very useful in the development of hydrochemical conceptual models for the groundwater bodies or in the identification of pollutant impact. For further information the reader is referred to Güler *et al.* (2002) and standard hydrochemistry textbooks such as Lloyd and Heathcote (1985), Stumm and Morgan (1996) or Langmuir (1997).

**Box 3: Cumulative Frequency Plots.**

Upper and lower natural background limit values can be obtained from cumulative frequency plots with relative ease, although it is an interpretative technique. Sinclair (1974) presents detailed analysis of the procedure, but Shand and Frengstad (2001) use it in a simpler fashion to assess concentration limits by eye. The shape of the curve on a cumulative frequency plot can be used to assist in understanding the geochemistry of the groundwater body. Some of the qualitative information that can be obtained is shown in Figure B. The most important concepts are (Edmunds *et al.* (1997):

- Log normal distributions are to be expected for many solutes in naturally occurring systems. Hence the concentrations are plotted on a log scale (except pH as it is already a log variable);
- Narrow ranges of concentration may indicate rapid attainment of saturation with minerals (e.g. Ca and $HCO_3$ with calcite equilibrium);
- A negative skew may indicate selective removal of an element by a geochemical process (e.g. denitrification);
- A bimodal distribution indicates a heterogeneous system where several controls or sources are operating. One of these sources may be a pollutant source;
- A positive skew probably indicates a contaminant source for the groundwaters with higher concentrations. This provides a simple way of separating polluted concentrations from background concentrations. Alternatively the highest concentrations may indicate mixing with waters of higher salinity.

Sinclair (1974) recommends that the minimum number of data points required to produce a cumulative frequency plot is 100.

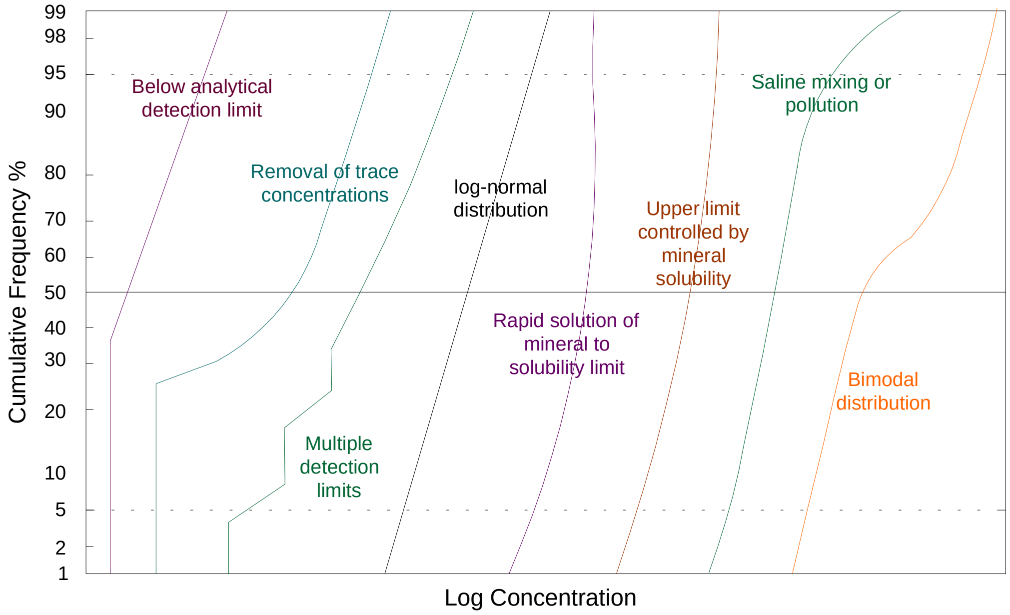

**Figure B. Examples of concentration profiles on cumulative frequency plots.**

Note: Cumulative frequency plots can be drawn with a number of software tools, including Microsoft Excel and Golden Software's Grapher. The scale of the probability axis can be expressed directly as percentages in Grapher but not in Excel. In the latter software the function NORMSINV() should be used to transform the cumulative percentage into a variable that can be plotted on a linear probability scale [for more details see Burmaster and Hull (1997)].

### 4.6.4. Atmospheric Inputs

Met Éireann has been monitoring rainfall quality across Ireland since 1956/57. Monthly samples of precipitation are currently taken at nine synoptic weather stations and analysed for chemical constituents. All stations operate bulk collectors, so wet and dry deposition is summed by the measuring procedure. Concentrations of the following species are measured:

$SO_4$, $NO_3$, $NH_4$, Cl, H, Na, K, Ca, Mg, alkalinity, electrical conductivity

The synoptic stations for which these are recorded are listed in Table 5, together with two stations operated in Northern Ireland by the Department of Agriculture since 1985 (italicised).

**Table 5. Synoptic stations that monitor rainwater chemistry.**

| Coastal stations | Near-coast stations | Inland stations |
|---|---|---|
| Malin Head, Co. Donegal | Shannon Airport, Co. Clare | Clones, Co. Monaghan[1] |
| Belmullet, Co. Mayo | Dublin Airport[1] | Birr & Kinnitty, Co. Offaly[2] |
| Valentia, Co. Kerry | Cork Airport | *Hillsborough, Co. Down* |
| Rosslare, Co. Wexford | | *Lough Navar, Co. Tyrone* |

[1] significant local influences since the early 80s

[2] significant local influences since 1993

Determination of natural background concentrations from atmospheric inputs is simple for conservative species such as chloride by performing a mass balance (Box 4). For species such as sulphate which have both natural and anthropogenic atmospheric sources, the mass balance method also allows the calculation of background concentrations from which natural background concentrations can be obtained. Solutions may de-gas over the period of a month, so alkalinity measurements, for example, might need to be treated with caution.

Effective precipitation (EP) rates should be used for calculation of the quality of infiltration, as a proportion of the solute will be removed by runoff. Effective precipitation is defined as:

$$\text{EP} = (\text{Rainfall} - \text{Actual Evaporation}) = (\text{Recharge} + \text{Runoff})$$

Since there is practically no direct runoff from limestone terrains, the EP value will be approximately equal to the recharge for these groundwater bodies. However, this approximation may not be valid for other lithologies.

Groundwater concentrations of a solute are the result of mixing and dispersion during groundwater flow, possibly over several years or decades. Rainfall, however, reflects relatively recent contributions to the atmosphere [sulphate ions reaching Ireland from North America can take just a few days (Appelo and Postma, 1993)]. It is therefore necessary to take long-term average rainfall concentrations as inputs so that emissions trends can be accounted for in the mass balance.

**Box 4. Mass Balance Technique for Rainfall Concentrations.**
The mass balance for conservative ions† (i.e. none lost or gained in the soil zone) is expressed as follows:

$$C_{recharge} = C_{rainfall} * Q_{rainfall} / Q_{recharge}$$

where $C_{recharge/rainfall}$ = concentration of solute in recharge or rainfall (mg/l)
$Q_{EP/rainfall}$ = flux of effective precipitation (EP) or rainfall (mm/a)

If deposition rates are presented rather than rainfall concentrations such as in Jordan (1997), the concentration in recharge is given by:

$$C_{recharge} = 100\ F_{rainfall} / Q_{recharge}$$

where $F_{rainfall}$ = mass flux of solute in rainfall ($kg.ha^{-1}a^{-1}$)

† The results of aquifer trialling in Appendix D suggest that chloride is conservative through the soil zone, but nitrate, ammonium and sulphate are not.

Scaling Concentrations of Non-Conservative Species

To determine upper concentration limits, it is necessary to scale the average concentrations in infiltration (obtained above) to obtain an estimate of the 95th percentile concentration. Evapotranspiration in the soil zone act enriches all chemical species equally, so if an estimate of the 95th percentile natural concentration of a conservative species (e.g. chloride) is obtained, this can be used to scale the concentrations of other species in the rainfall (e.g. nitrate):

$$C_{NO3,\ Upper} = C_{NO3,\ Average} \text{ x } C_{Cl,\ Upper} / C_{Cl,\ Average}$$

Correction for Anthropogenic Atmospheric Inputs

When background concentrations have been obtained from groundwater chemistry data (such as by using a cumulative frequency plot) it should be corrected for anthropogenic atmospheric inputs by expanding the mass balances above:

$$C_{natural\ background} = C_{background} - (100\ F_{anthro\ rainfall} / Q_{recharge})$$

where $F_{anthro\ rainfall}$ = mass flux of anthropogenic solute in rainfall ($kg.ha^{-1}a^{-1}$)

### 4.6.5. Analysis of Surface Water Data

Systematic surface water monitoring in Ireland has taken place since 1971. McGarrigle *et al*. (2002) use the water quality monitoring results from 3166 locations on streams and rivers, and 304 lakes. Surface water quality is compared with river baseline concentrations that are derived from biotic indices, and assessment of inorganic water quality judged by comparison of drinking water standards. According to these assessments 62% of monitoring locations are judged to be unpolluted.

Major ion suites do not tend to be analysed for in surface waters, so ionic balance checks will not be possible.

Surface water at moderate flow rates reflects the quality of infiltration water in the catchment, as much of the water has passed through the soil zone but not deeper groundwater (i.e. it is mostly interflow). The exact definition of ‘moderate flow’ in this case is dependant upon the type of aquifer system, particularly the soil and drift cover. If concentrations obtained by this method are to be used for anything other than indicative values, analysis of flow hydrographs should be performed to ensure that interflow constitutes the greatest component of flow at the time of sampling.

Baseflow concentrations can be used directly as natural background concentrations if they are of sufficient age (i.e. pre-1973). The same quality assurance and statistical assessments should be applied for baseflow quality as for groundwater quality. As baseflow represents an integration of all the groundwater qualities in an aquifer, the representativity concerns listed in Sections 4.4.1 and 4.4.2 are less of an issue if the size of the surface water catchment is a significant proportion of the groundwater body.

Standing water in most lakes is unlikely to represent the natural quality of groundwaters, but since turloughs are entirely fed by groundwater, they may reflect the groundwater chemistry (though this should be checked on a site-by-site basis if the results are relied upon). Hence the water quality of a turlough can be used as if it were a borehole or spring sample as long as there is groundwater throughput, and the species being examined are not affected by sub-aerial exposure.

It is especially worth looking at concentrations of pesticides in surface water data. If pesticides are present, this indicates that there is a high proportion of runoff and therefore the inorganic chemistry reflects rainfall rather than infiltration. It also suggests that the measured concentrations of fertiliser compounds (nitrate, phosphate, sulphate, potassium, ammonium) may not be natural, if they were dissolved with the pesticides.

It is essential when examining surface water chemistry data that all (or at least a large proportion of) the water comes from within the boundaries of the groundwater body or group of groundwater bodies.

## 4.7. Assessment of Natural Background Quality – Species

### 4.7.1. Alkalinity / Acid Buffering Capacity

Alkalinity is the quantity of strong acid required to bring a water to a specified end point by titration, usually the bicarbonate end point at around pH 4.5. In carbonate rich aquifers, carbonate alkalinity is the dominant acid buffering mechanism that resists acidification. Total alkalinity can also be contributed to by acid-base systems other than the carbonate system; $H_3PO_4$ and $HBO_3$, organic acids and suspended metal hydroxides are others.

Risk of acidification can be assessed by comparison of this buffering capacity with the atmospheric deposition rates of sulphate and nitrate [Jordan (1997) detects rainfall chloride only as NaCl, so it is not an acidification risk]. The highest non-marine sulphate and nitrate deposition rates for the period 1992 to 1994 were observed at Dublin airport (Jordan, 1997). Non-marine concentrations were approximately 1.3 mg S/l and 1.6 mg N/l. Assuming that no other species were available to buffer these inputs (for example ammonium in the rainfall), the amount of alkalinity that would be used up in neutralising the inputs would be 12.3 mg $HCO_3$/l. Acidification due to anthropogenic terrestrial nitrate inputs is not accounted for in the above calculation.

Soil water in contact with air and calcite has an alkalinity of approximately 300 mg/l. This is far in excess of that required to buffer atmospheric inputs, hence acidification is not an issue in carbonate aquifers or siliceous aquifers covered with calcareous drift. The following guidelines apply for the calculation of natural background quality limits for alkalinity:

- Alkalinity measurements can be reported as a variety of determinands. It is recommended that, on receiving new data, all concentrations should be converted to mg/l as $CaCO_3$ using the conversions in Box 5 and all natural background concentrations should be reported as mg/l as $CaCO_3$.
- Alkalinity values obtained in the field are always preferred to those obtained in the laboratory.

- Siliceous aquifers without calcareous drift are considered at risk of acidification and natural background concentrations of alkalinity should be determined. As there are no diffuse pollution sources of alkalinity only the lower natural background limit need be determined.

Where alkalinity measurements are unavailable for a groundwater body, an estimate may be made from total hardness values using the following approximate empirical relationship (EPA, 2000b). The relationship only holds in groundwaters with relatively high hardness where most of the hardness is contributed by calcium and magnesium bicarbonate.

Alkalinity as $CaCO_3 \approx 0.4$ x Total Hardness as $CaCO_3$

### 4.7.2. pH

The pH of a groundwater reflects the concentration of hydrogen ions ($H^+$) in solution and is measured on a log scale:

$pH = -\log_{10}[H^+]$, therefore,$[H^+] = 10^{-pH}$

where [ ] indicates a molar concentration (mol/l).

Hence more acidic waters have lower pH values. Decreased pH values can be indicative of many types of groundwater pollution, including direct discharges of acid solutions, acid rainfall, and oxidation of dissolved organic material and ammonium in sewage or animal wastes. Low pH groundwaters are also more prone to pollution by heavy metals, because they are more soluble under low pH. Where high concentrations of ammonium are combined with high pH values, the toxicity of the ammonium to fish is increased as it is exsolved into dissolved ammonia.

The strongest natural control on groundwater pH in an aquifer is the alkalinity, i.e. the presence of bicarbonate and carbonate ions in solution. This is controlled, in turn, by the presence of carbonate materials in the aquifer and/or the soils through which recharge percolated. High alkalinity values in aquifers where carbonate minerals are present effectively buffer the groundwater against changes in pH. Definition of a natural background limit for pH in a carbonate aquifer is therefore meaningless as the presence of carbonate will tend to maintain the pH at a constant value. In siliceous aquifers without carbonate-rich drift, changes in pH will be observed more readily in response to pollution.

The pH of rainfall is determined by the partial pressure of carbon dioxide in the atmosphere; Appelo and Postma (1993) calculate this as pH 5.6. In the soil zone the partial pressure of carbon dioxide increases due to respiration of soil organisms; Appelo and Postma (1993) calculate the equilibrium value pH 4.6 for soil pore water. No aquifer pH values should be less than pH 4.6 except in very special circumstances.

Rainfall deposition of acid has been noted across most of Ireland by Jordan (1997). The additional acidity is introduced to the rainfall by association with anthropogenic sulphate and nitrate. To obtain a natural background limit pH value ($pH_{NatB}$) from the groundwater background pH value ($pH_B$), the background pH should be corrected by subtraction of the anthropogenic (non-marine – NM) input:

$$10^{-pH_B} - 10^{-pH_{NatB}} = 2 \cdot \left[SO_4^{2-}\right]_{NM} + \left[NO_3^-\right]_{NM}$$

where square brackets indicate molar concentrations. Jordan (1997) gives non-marine contributions of rainfall sulphate and nitrate for each rainfall quality monitoring station.

The most common reason for a high pH in a borehole is reaction of the groundwater with the grout, which is not a pollution problem in itself. With the exception of direct release of alkaline solutions, few pollution mechanisms can cause an increase in groundwater pH. An upper natural background limit is therefore not required.

- A lower natural background limit concentration should be defined for all groundwater bodies with no significant amount of carbonate material in their matrix.
- Where the recharge area of a carbonate-poor aquifer is completely covered with carbonate-rich drift, a natural background limit need not be determined.
- Natural background limit pH values should be obtained by correction of the background value (obtained using groundwater data) for the additional acidity associated with anthropogenic sulphate and nitrate.
- A natural background lower limit concentration should not be less than the pH of soil porewater, pH 4.6.

Since pH is a log concentration already, when deriving background limits the pH values should not be log-transformed like concentrations. Therefore in Box 2, the mean and standard deviation should be obtained for pH values directly, and in cumulative frequency plots the pH values should be plotted on with a linear x-axis.

### 4.7.3. Electrical Conductivity

Increased electrical conductivity (EC) is usually an indication that solutes are being mixed into the groundwater. Introduction of any charged species to groundwater normally leads to an increase in EC, and most of the contaminant sources discussed in this report will cause some change in EC. Changes in concentration of different ionic species contribute to changes in the conductivity by different amounts (Lloyd and Heathcote, 1985).

Anthropogenic pollution is, however, best quantified by measurement of the other indicator species listed here, as they are much more sensitive. Most Irish groundwaters are naturally hard and this imparts a relatively high background EC (Table 6), but these concentrations will be stable over long periods (though they may vary seasonally).

EC is most commonly used to detect the effects of saline intrusion in aquifers and the WFD specifies that EC should be monitored for that purpose. Chloride concentrations may also be used to refine observations based on EC. The electrical conductivity of seawater is approximately 50 000 µS/cm at 20ºC and therefore it is easily detectable when mixed with groundwater even in small amounts.

Since EC is a result of the integration of all charged ions in groundwater, each of which has a different contribution, it would be extremely difficult to reliably obtain a natural background value from a derived background value. It is therefore recommended that only background values are reported.

- An upper limit background value of electrical conductivity should be reported for groundwater bodies.
- If EC measurements are unavailable, hardness values may be converted using the relationship in Box 5 to give estimates. For hardness values less than 100 mg $CaCO_3$/l these should be treated with caution.

**Table 6. Ranges of water hardness with their corresponding approximate ranges of conductivity for carbonate waters (EPA, 2000b).**

| Hardness | Total hardness range mg $CaCO_3$/l | Approx. conductivity range µS/cm at 20ºC |
|---|---|---|
| Soft | 0 – 50 | <160 |
| Moderately soft | 50 – 100 | 160 – 230 |
| Slightly hard | 100 – 150 | 230 – 340 |
| Moderately hard | 150 – 200 | 340 – 410 |
| Hard | 200 – 300 | 410 – 550 |
| Very hard | >300 | >550 |

**Box 5: Alkalinity conversion factors.**

| | |
|---|---|
| Alkalinity: | mg/l as $HCO_3$ to mg/l as $CaCO_3$: multiply by 1.63 |
| Alkalinity: | mg/l as total hardness: multiply by 0.4 – a very approximate relationship that breaks down at low total hardness (EPA, 2000b) |

### 4.7.4. Chloride

With halite rarely present in the geological sequence of Ireland, the dominant natural source of chloride to recharge and groundwater flow is the contribution of sea-spray. Its concentration in rainwater at a given location is directly related to the proximity of the coast and the direction of the prevailing wind. Consequently, in Ireland, the highest concentrations of chloride in rainfall are found along the western coast and the lowest are inland (Jordan, 1997).

Although coal-fired power stations emit chloride into the atmosphere as hydrochloric acid, Jordan (1997) found that essentially all the chloride deposition on Ireland through the period of monitoring had a marine origin. Since there appear to be no anthropogenic atmospheric sources of chloride, limits obtained by the methods in Section 4.6 will be for natural background concentrations, rather than just background concentrations.

Chloride concentrations will not be depleted by pollution so lower natural background limits need not be determined. Upper natural background limits should be determined for chloride using appropriate techniques. If reliable limits are obtained from groundwater concentrations, these should be compared with values obtained by the precipitation mass balance method of Section 4.6.4 so that the reliability of the latter method can be judged. This comparison can be used to determine its reliability when obtaining natural background concentrations from background concentrations for other species.

### 4.7.5. Sulphate

Sulphur concentrations in precipitation derive from both marine and anthropogenic sources and occur as the sulphate anion ($SO_4^{2-}$). In Ireland this balance is approximately even, with 55% derived from marine sources in 1992-94 with the highest proportion (80% marine) in the west and the lowest (20% marine) in Northern Ireland (Jordan, 1997). The distribution of total sulphate shows the deposition rate decreasing eastwards.

Anthropogenic sulphate in groundwater is derived from a variety of sources, primarily disposal of waste iron and concrete, from slag heaps and mine drainage. Sulphate is one of the species in groundwater that correlates with the source aquifer – for example, sediments with much pyrite (e.g. Westphalian sandstones and shales) impart high sulphate concentrations to the groundwater. There is also gypsum in the Permo-Triassic deposits in the Kingscourt Graben, Co. Louth.

Sulphate is not readily broken down in oxidised groundwaters so it is almost conservative, but concentrations can be depleted by reduction.

- Both high and low limits of sulphate concentrations should be derived. High concentrations denote direct pollution, while concentrations near zero indicate that the groundwater is highly reduced (Section 2.3).
- To obtain natural background concentrations from background concentrations of sulphate, appropriate corrections should be made according to the methods in Section 4.6.4.
- Concentrations of sulphate can be reported either as sulphate or as sulphur. It is recommended that on receiving new data, all concentrations should be converted to mg/l as S using the conversion in Box 6 and all natural background concentration limits should be reported as mg/l as S.

**Box 6: Sulphur species conversion factors.**

Sulphate: mg/l as $SO_4$ to mg/l as S: multiply by 0.334

### 4.7.6. Nitrogen Species

Nitrogen occurs in precipitation as both nitrate ($NO_3^-$) and ammonium ($NH_4^+$) and in contrast with chloride, there is no marine contribution to either species (Jordan, 1997). As a worldwide average, pristine surface waters and therefore groundwaters should have 0.015 mg N/l as ammonium and 0.1 mg N/l as nitrate (Heathwaite *et al.*, 1996). These are extremely low in comparison to typical modern groundwater concentrations and only 10% of surface water globally is thought to be pristine.

Atmospheric nitrate is primarily due to combustion of fossil fuels and is mainly derived from outside Ireland, whereas 90% of ammonia deposition is due to sources inside the state, primarily intensive agriculture (de Kluizenaar and Farrell, 2000). The distribution of nitrogen deposition therefore increases eastwards with high concentrations of ammonium correlating well with the highest livestock densities (Jordan, 1997). Rainwater concentrations of both species are also increasing with time.

Nitrate and ammonium concentrations are sensitive to redox conditions in the groundwater. Ammonium is microbially oxidised to nitrate in soil and groundwater when dissolved oxygen is present. Natural attenuation of ammonium pollution therefore increases the concentration of nitrate in groundwater, and depletes the dissolved oxygen (Section 2.3). Since ammonium is relatively well immobilised in clayey soils and aquifers, these indicators (increased nitrate and decreased DO) may be the only signs that ammonium pollution has occurred.

By contrast, in naturally reducing groundwaters, ammonium is the dominant natural nitrogen species and higher ammonium limits may need to be set. Unusually low concentrations of nitrate can be indicative of polluted groundwater, as reduction of nitrate occurs when dissolved oxygen has been depleted. This can be used to assist the understanding of redox conditions in the aquifer.

Because of the high nitrogen input from anthropogenic atmospheric sources, only background concentrations (not natural background) of nitrogen species can be obtained from post-industrial groundwater samples. The recommended procedure for obtaining unpolluted concentrations of nitrate is therefore as follows.

- Upper background concentration limits should be obtained for nitrate and ammonium for all groundwater bodies.
- To obtain natural background concentrations from background concentrations of nitrate and ammonium appropriate corrections should be made according to the methods in Section 4.6.4. Since there is no marine contribution of nitrogen to rainwater, all rainwater nitrogen is assumed to be anthropogenic.
- Concentrations of nitrogen species can be reported in a variety of determinands. It is recommended that on receiving new data, all concentrations should be converted to mg/l as N using the conversions in Box 7 and all unpolluted concentrations should be reported as mg/l as N.

**Box 7: Nitrogen species conversion factors.**

Nitrate: mg/l as $NO_3$ to mg/l as N: multiply by 0.226

Nitrate: mg/l as total oxidised nitrogen: multiply by 1.00 as in unpolluted groundwaters this will be >90% nitrate

Nitrite: mg/l as $NO_2$ to mg/l as N: multiply by 0.304

Ammonium: mg/l as $NH_4$ to mg/l as N: multiply by 0.776

Ammonium: mg/l as $NH_3$ to mg/l as N: multiply by 0.822

In unpolluted groundwaters dissolved ammonia dissociates readily to the ammonium ion

Ammonium: mg/l as total Kjeldhel nitrogen: multiply by 1.00 as in typical groundwaters this will be all ammonium but in peaty groundwaters will also determine organically bound N

### 4.7.7. Phosphate

Phosphorus has been traditionally thought to be readily immobilised in soil by metal complex formation or adsorption to clay particles and so is often not expected to reach groundwater. However, in surface water, concentrations in excess of 20 µg/l as P may trigger eutrophication (Champ, 1998) and diffuse leakage from soils via groundwater is believed to be contributing to surface water quality deterioration in Ireland (Brogan *et al.*, 2001).

Levels of phosphate in rainwater are available for Northern Ireland stations only. Jordan (1997) found that there was significant marine input of phosphorus even in the north east of the island, and that the concentrations were independent of location.

Phosphorus is strongly bound to soils and aquifers and in strongly alkaline groundwaters forms insoluble calcium salts. Concentrations in groundwater are therefore likely to be very low, and many values will be at the limits of detection. Where there are insufficient data to determine an upper limit, it should be set at the detection limit and re-assessed at a later date as non-LOD data are collected. Concentrations in karst groundwater may, however, be detectable

- Upper natural background limits of phosphate should be derived for groundwater bodies wherever possible (i.e. if there are sufficient data above the LOD). Otherwise the upper natural background limit should be set at the detection limit.
- Concentrations of phosphate can be reported using a variety of determinands. It is recommended that, on receiving new data, all concentrations should be converted to mg/l as P using the conversions in Box 8 and all natural background concentrations should be reported as mg/l as P.

**Box 8: Phosphorus species conversion factors.**

| | |
|---|---|
| Phosphate: | mg/l as $PO_4$ to mg/l as P: multiply by 0.326 |
| Total reactive phosphorus: | mg/l as TRP to mg/l as P: multiply by 1.00 |

Note that ‘orthophosphate’ is synonymous with ‘phosphate’

### 4.7.8. Dissolved Oxygen / Redox State

Rainfall will generally be saturated with dissolved oxygen (DO) at the partial pressure of the atmosphere. Depending on the atmospheric pressure and temperature this ranges between 10 and 12 mg/l. A number of natural processes in the soil zone, unsaturated zone and groundwater deplete this, especially through oxidation of organic matter and sulphide minerals. DO concentrations are also naturally depressed beneath peaty soils and lakes. Oxygenated groundwaters also slowly react with aquifer organic materials, and very old groundwaters tend to also be depleted.

Microbial degradation of ammonium or organic compounds depletes the DO store in groundwater, so a relatively low DO can be indicative of either type of pollution. Reduced groundwaters also tend to pose problems with water supply pipework as they often contain high concentrations of iron and manganese which precipitate out as the waters are exposed to the atmosphere.

The simplest measurement of the redox state of a groundwater is the DO concentration, but DO probes have a lower limit of accuracy at approximately 0.3 to 0.4 mg/l, which may not be sufficiently accurate for some naturally reduced waters. Furthermore, the current EPA groundwater monitoring suite does not include dissolved oxygen as a determinand. The measured redox potential ($E_H$) of a water is a poor indicator of its redox state because it is very difficult to measure accurately in practice and can be significantly affected by mixing in the pumped borehole (Lloyd and Heathcote, 1985).

Iron and manganese become more soluble in reduced groundwater and are good indicators of redox state that are more accurate than using DO alone. Manganese becomes soluble under less reducing conditions than iron, so a continuous scale of solubility can be developed using: DO at high saturation; then manganese; and then iron concentrations. Natural concentrations of these metals are difficult to predict as they depend on the mineralogy of the host aquifer. All Irish rocks contain significant proportions of both metals with the possible exception of the pure limestones, however, these are karstic and unconfined so should always have DO concentrations around 10-12 mg/l. Waters that are reduced will also have very low concentrations of nitrate as it is reduced once the dissolved oxygen has been depleted.

Natural background concentrations of dissolved oxygen in most Irish aquifers will be between 10 and 12 mg/l as most aquifers are unconfined and the limestones have relatively low organic content. However, beneath lakes or peaty soils, or where aquifers are rich in organics or sulphides occur, groundwaters will be naturally reduced. Unpolluted limits should therefore be derived for the following species in order to quantify the natural redox state of a groundwater body:

- A lower natural background limit for dissolved oxygen. If this limit is less than approximately 4 mg/l it should not be considered accurate, and iron and manganese limits used alone;
- Upper natural background limits for manganese and iron;
- A lower natural background limit for sulphate (see also Section 4.7.5).

Note: in older analyses, the dissolved oxygen concentration is sometimes reported as a percentage of the saturation limit. Concentrations are temperature dependant so the following formula should be used to determine the dissolved oxygen concentration in mg/l (Appelo and Postma, 1993):

$$C_{DO} = 6686 \times \%\mathrm{sat} \times 10\text{^}{-}\left(2.89 + 523 \times \left(\frac{1}{298} - \frac{1}{T}\right)\right)$$

where %sat is the measured percentage saturation of oxygen,
^ is the power operator, i.e. 10^2 = $10^2$
T the water temperature in Kelvin.

Note: iron concentrations are sometimes reported in analyses as µg/l and sometimes as mg/l. Care should be taken that all measurements being compared are in the same units. Also note that iron and manganese concentrations used in determining the natural background quality must always be filtered concentrations.

### 4.7.9. Heavy Metals

Heavy metals in groundwater derive from a variety of anthropogenic sources, primarily from slag heaps and mine drainage but arsenic is present in some forestry pesticides and lead occurs in high soil concentrations along roadsides. Like sulphate, metal concentrations correlate well with the source aquifer and each imparts a characteristic geochemical signature to the water. Consequently there are naturally high occurrences of these heavy metals in some Irish groundwaters (e.g. cadmium in alum shales, arsenic in the granites, zinc and lead in the Silvermines area) that need to be accounted for in the determination of natural background concentrations.

Rainwater concentrations of heavy metals are significant in comparison to natural groundwater concentrations (Section 2.2.1) so background concentrations will be obtained from groundwater data, rather than natural background concentrations. However, heavy metals are readily sorbed to aquifer solids and the derived background concentrations may actually be natural background concentrations.

Concentrations of most heavy metals can increase with decreasing pH; for every one pH value dropped, the solubility of a divalent heavy metal increases by 100 times. Hence an appreciation of the groundwater pH may assist in characterising the heavy metal chemistry of a groundwater body

- Upper limits for arsenic, cadmium, lead, mercury, zinc, copper and chromium should be derived for groundwater bodies.
- Metal transport and enrichment in the subsurface is not well understood so derivation of natural background limits from background concentrations using atmospheric inputs may be unreliable.

Cadmium is chemically very similar to zinc and readily substitutes for it in chemical reactions, therefore it should naturally occur in similar environments. It is normally present at concentrations less than 1/100 that of zinc. The Zn:Cd ratio of groundwaters should be examined in assessments, and if it is significantly less than 100 this may be an indication of either pollution or of natural chemical enrichment.

Measurements of mercury concentrations are very prone to analytical error and should be approached with caution.

### 4.7.10. Urban Indicators

Boron is a constituent of domestic and industrial detergents and, as such, occurs widely in waters affected by anthropogenic discharges. Of the trace elements that are commonly found in higher concentrations in urban environments, boron has sometimes proved useful to identify the impact of sewer leakage, but Barrett *et al.* (1997) found that there was too much dilution in the Nottingham (UK) aquifer to make it a generally useful indicator.

The principal anthropogenic source of fluoride in groundwater is the leakage from sewers of fluoridated drinking water, but it also arises from application of phosphate fertilisers. Concentrations in groundwater bodies, however, tend to be limited by sorption and solubility controls (Barrett *et al.*, 1997). Natural fluoride concentrations arise from the slow dissolution of apatite and can be very good indicators of groundwater age. However, this means that fluoride concentrations continually change along groundwater flow lines (e.g. Heathcote and Lloyd, 1985) and care must be taken when defining natural background concentrations that this variability is taken into account.

- Upper natural background limits for fluoride should be derived for all groundwater bodies. Upper natural background limits for boron should be derived for groundwater bodies that might be affected by urban pressures.

## 4.8. Reporting

Appendix D presents four examples of the characterisation of natural background limits for some groundwater bodies in Ireland. The conclusions of the trialling exercise are discussed in Section 5. However, they can be used to provide example templates for future reporting.

It is not expected that the geological or hydrogeological sections will be so detailed in the final set of reports, as these will have previously been completed by the GSI. However, there should be sufficient detail in the report to demonstrate that the hydrogeological conceptual model has been considered in the assessment, and the conclusions should be consistent with it.

### 4.8.1. Definition of Limiting Concentrations

The definition of upper limit concentrations will be quite straightforward using the techniques presented in Section 4.6, however, the definition of lower limit concentrations may be complicated due to issues with limits of detection (LOD) in the data series (Section 4.5.2).

Lower natural background limits are required when describing the concentrations of species that can be depleted by reactions with pollutant species (e.g. dissolved oxygen or sulphate can be depleted where organic pollutants are oxidised). If a lower limit needs to be defined, and its calculated value is less than the LOD for the species, the limit should be set at the lowest LOD in the data set. Setting a numerical value for the lower limit allows the value to be reconsidered as laboratory techniques improve in the future, whereupon LODs may decrease below the actual lower limit for natural background concentrations.

### 4.8.2. Figures

The use of figures in a report is to be recommended. A standard list of figures is not proposed, because those required will depend on the complexity of the conceptual model and on the amount of data available. However, the following should always be included:

- Location map with sample points and features of hydrogeological interest (e.g. watercourses, large abstractions, landfills, contaminated land, groundwater contours, etc.).
- A box and whisker plot for the major ions; with normalised rainwater and/or sea water concentrations presented. The examples in this report normalise the rainfall concentrations by the chloride concentrations, but normalising using sodium concentrations is equally valid if it appears that the median chloride concentration of the groundwater is affected by pollution.
- Plots of time series concentrations for indicator species, where they are useful to illustrate a point in the conceptual model, trends, or to identify concentration outliers.
- Cumulative frequency curves, when there are sufficient data, are very valuable figures. They are not only useful for identifying natural background limits, but also for spotting bimodal distributions or subtle changes in slope that may be indicative of pollutant impacts.

# 5. Application of the Methodology to Trial Groundwater Bodies

A number of groundwater bodies and groups of groundwater bodies were chosen to test the methodology presented in Section 4. The purpose of undertaking the trials was twofold:

1. to demonstrate the applicability of the selected methodology in a relevant and representative range of hydrogeological conditions;
2. to modify the methodology in the light of the trialling exercise and, in particular, to ensure that it is relevant to the amount and quality of data available.

The individual trialling reports are presented in Appendix D. This section describes the trialling methodology, the reasons that the groundwater bodies were chosen, and then describes the lessons learned from the exercise. The trials were all conducted by consultant hydrogeologists with experience in data handling and interpretation of regional hydrochemistry, under the supervision of the principal author of this report.

## 5.1. Trialling Methodology

Groundwater bodies were selected with the aim of meeting the following criteria:

- Varied hydrogeological conditions, e.g. lithology, nature of flow, drift cover, recharge;
- Some individual groundwater bodies, some cross-catchment groups of groundwater bodies;
- All groundwater bodies should have some reliable recent groundwater monitoring data, but the amount of data will be varied.

Four groundwater bodies or groups of groundwater bodies were selected in discussion with GSI as follows (Figure 7). All were within the South Eastern River Basin District (SERBD), as this district had the most detailed geological characterisation available when the trialling was undertaken.

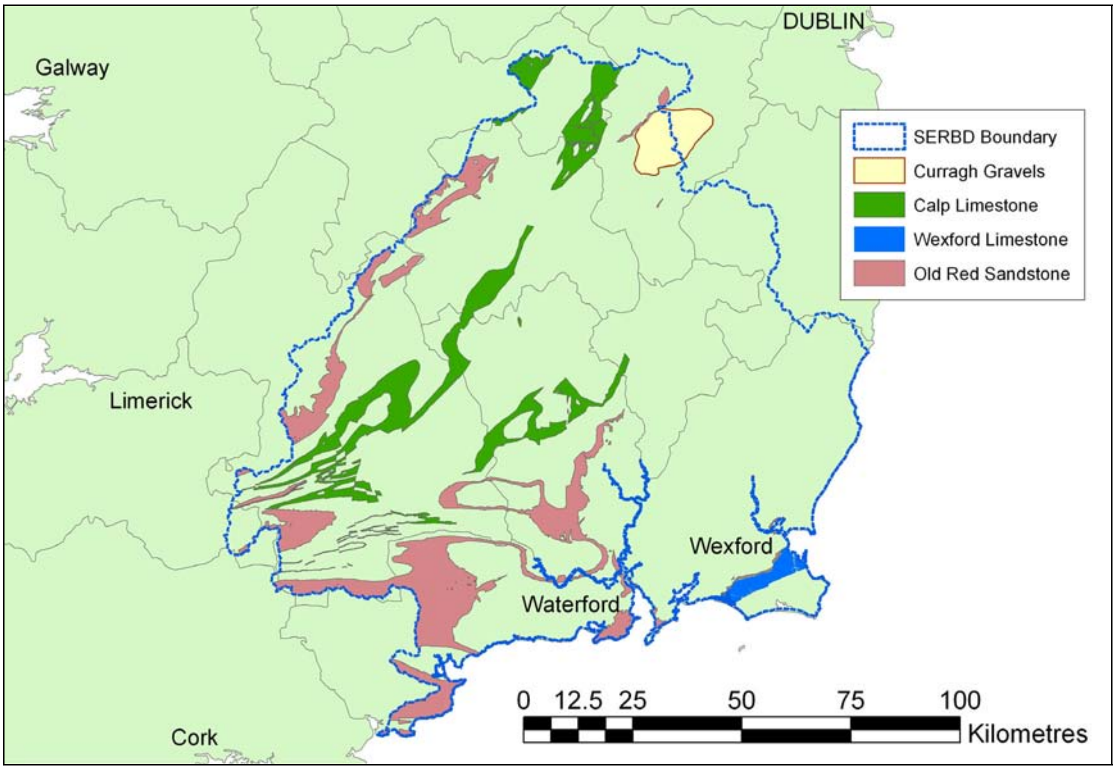

**Figure 7. Location of trial groundwater bodies and groups of groundwater bodies.**

### The Curragh Gravel groundwater body
### (Appendix D1)

An extensive inland gravel aquifer with several groundwater quality monitoring points and historical sampling to develop the hydrogeological conceptual model for the Kildare Bypass scheme. Subject to intensive arable agriculture and some landfilling pressures.

### The Wexford Limestone groundwater body
### (Appendix D2)

A dolomitised coastal limestone aquifer (Lower Carboniferous) with possible saline intrusion. Semi-independent sand and gravel aquifers at the surface. A number of large public water supplies, several monitoring boreholes and a hydrochemical survey in 1978.

### Old Red Sandstone in the SERBD (Appendix D3)

A continuous but multiple-catchment group of groundwater bodies, primarily inland, mostly in Co. Waterford. The ORS sandstones and ORS conglomerates are grouped into one aquifer unit on the basis of lithological similarity. Some agricultural development but mountainous terrain means it is not intensive.

### Calp Limestone outcrop in the SERBD
### (Appendix D4)

A continuous but multiple-catchment group of groundwater bodies mostly inland, primarily in Co. Tipperary and Co. Laois. A partly dolomitic limestone. Some agricultural development has taken place but mountainous terrain means it is not intensive.

## 5.2. Lessons Learned

### 5.2.1. Data Availability

Figure 8 presents the years for which groundwater quality data are available for the four trialling areas. The confidence in the results of the Curragh Gravels and Wexford Limestone trials was greatly improved by having had historical hydrochemical surveys, in 1987-1989 and 1978 respectively. This is partly because of the increased date range, but also because the monitoring points were more widely spaced across the aquifer, leading to more representative data. Without these studies, there would have been insufficient data to make confident estimates from the Curragh Gravels and Wexford Limestone, which have only three EPA monitoring points each at present.

Data from the 2001 Group Water Scheme monitoring programme were made available but, because sample points are not geo-referenced, the aquifers that they sampled could not be identified. This information would have led to improved estimates for sanitary parameters.

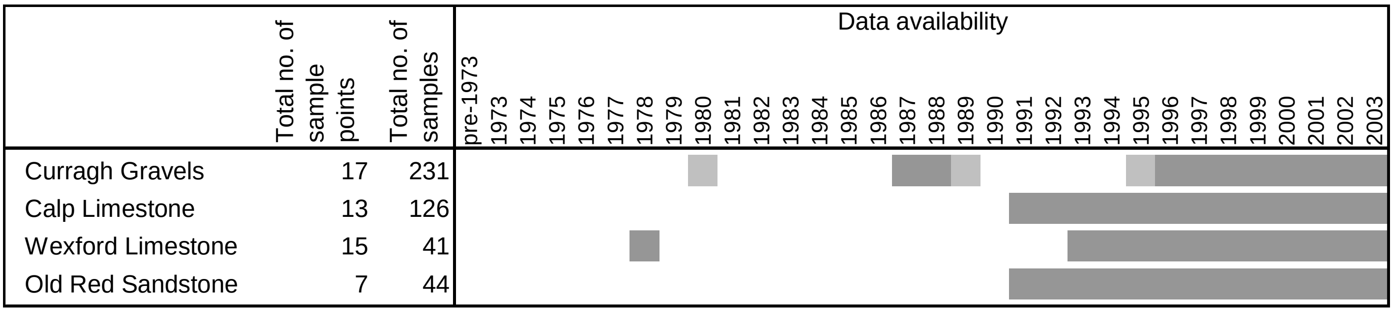

**Figure 8. Data availability for trialling areas (light grey bar indicates only one data point for that year, dark grey bar, greater than one).**

### 5.2.2. Data Quality

A number of data quality issues were identified during the course of the project:

- A number of analyses from the EPA monitoring programme did not have ionic balances of within the ±10% quality threshold. Results from these samples were not omitted from the analyses used to derive natural background limits because data are currently sparse.
- In the EPA database there were a number of concentration results that appeared to be much lower than the analytical detection limit. These tended to be for metals, which are stored in the database as µg/l, but appeared to have been entered as mg/l (i.e. values were 1000 times too low).
- It is sometimes not obvious from historical data what values for nitrogen and sulphur species are recorded as (e.g. mg/l as N or mg/l as $NO_3$ for nitrate). This was also the case for alkalinities (sometimes stored as $HCO_3$, sometimes as $CaCO_3$).

### 5.2.3. Groundwater Quality

The importance of developing and using a robust conceptual model for the hydrochemistry of the aquifer cannot be overstated. It is not sufficient to derive natural background limits for species without considering the conceptual model. This is especially the case for aquifers that have reducing conditions; for example, under reducing conditions, low nitrate concentrations can equally be due to a lack of pollution, or to the reduction of pollutant nitrates in the aquifer.

Variations in major ion chemistry are key to understanding the overall hydrochemical processes along flow lines. This is especially the case in the single groundwater bodies; for the grouped groundwater bodies, it is less obvious whether the boreholes were in recharge or discharge zones because of their narrow outcrops. This could have been achieved by a more detailed review of topography than was possible during this study.

The most noticeable differences in natural groundwater quality were when the redox conditions of a groundwater body changes along the flow path. Natural background concentrations for nitrogen species and the redox indicators are then difficult to set for the whole groundwater body. If, for example, upper natural background limits are set for iron and manganese based on aggregated data from a partly confined aquifer, they will be set quite high. However, if these species are present at detectable concentrations but do not exceed the limits in an unconfined part of the aquifer, that part of the aquifer has probably been impacted by anthropogenic activity, but comparison with the limit will not flag that up. In this instance, assuming that there are sufficient data from a representative monitoring well network, it would be worthwhile subdividing the groundwater body into different redox zones.

### 5.2.4. Effectiveness of Individual Techniques

#### Statistical Considerations

The statistical approach that uses the mean plus or minus two standard deviations of the log concentration is simple to undertake and appears to work well. With few data, this sometimes predicts concentrations much higher than the highest apparent natural background concentration. This was particularly an issue with the metal species, for which there were seldom more than a few data, and the results tended to have wide ranges. This uncertainty will reduce with time as more data become available.

Almost all data sets had several values for the limit of detection for any one species. In unconfined, well-oxygenated groundwater bodies with naturally very low iron and manganese, there were so few positive results for those two species that the AM0/AM100 ratio (Section 4.5.2) was greater than 60%. Calculated natural background concentrations may therefore have been subject to some bias.

#### Cumulative Frequency Curves

It was possible to construct cumulative frequency curves for many (but not all) species in all the groundwater bodies. These were not only useful for identifying natural background limits, but also for spotting bimodal distributions or subtle changes in slope that may be indicative of pollutant impacts.

Although Sinclair (1974) recommends that cumulative frequency curves should be constructed with no less than 100 data points, it has been found in this exercise that general patterns and trends can be seen with only 40 or 50 points. This number of values appears to be sufficient to quantitatively extrapolate straight lines (i.e. log-normal distributions) to the 5th or 95th percentile limits.

#### Scaling Rainfall Concentrations

The fundamental assumption in the use of scaled rainfall concentrations as natural background limits is that the species is conservative through the soil zone. It appears that this can be said for chloride only, as median concentrations in groundwater tend to be similar to calculated scaled rainfall concentrations (Table 7).

Sulphate and nitrate become enriched in the unconfined aquifers, possibly due to diffuse pollution. Atmospheric ammonium appears to be completely utilised in the soil zone or oxidised to nitrate in the sub-surface.

**Table 7. Comparison of estimated infiltration concentrations and median groundwater concentrations.**

| | | Chloride (mg/l) | Sulphate (mg/l as S) | Nitrate (mg/l as N) | Ammonium (mg/l as N) |
|---|---|---|---|---|---|
| Curragh | Calc*. | 14.7 | 2.49 | 1.77 | 0.50 |
| | Median* | 16 | 5.94 | 4.1 | <0.01 |
| Wexford | Calc. | 47.2 | 4.18 | 1.22 | 0.82 |
| | Median | 39 | 20.7 | 0.2 | 0.018 |
| Old Red Sandstone | Calc. | 21.5 | 2.65 | 0.62 | 0.57 |
| | Median | 17 | 8.4 | 3.5 | <0.01 |
| Calp | Calc. | 16.6 | 2.05 | 0.48 | 0.44 |
| | Median | 22 | 16 | 6.2 | <0.01 |

### 5.2.5. Key Issues for Professional Judgement

During the characterisation of groundwater bodies and definition of natural background limit concentrations, two key issues arose several times for all the groundwater bodies. These were:

**Which sample results have been impacted by anthropogenic activity?**

Because sources of pollution are potentially widespread within any particular groundwater body, Question (1) is not easily answered. Temporary point source pollution (e.g. chemical spillage) is relatively easy to identify as its impact is limited in space and time. Longer-term pollution (e.g. landfilling) is a little more difficult to identify unless the concentrations observed are extremely high compared to the background water quality. A careful study of the pressures on the groundwater body should aid in the identification of such impacts.

Diffuse pollution (e.g. fertiliser application, multiple dispersed septic tank systems) is quite difficult to identify, however, as a considerable proportion of the groundwater body might be affected. A cumulative frequency plot can be invaluable in the identification of diffuse pollution, but it can be uncertain whether a bimodal distribution is representative of diffuse pollution or a second natural distribution (e.g. due to natural variation in redox conditions). In these circumstances only analysis of historical data might be able to distinguish the natural background concentration from the diffuse pollution impact.

**Which method to use to determine natural background limits?**

No pre-1973 data were identified for the trial groundwater bodies used in this project; therefore use of historical data was not tested. Only relatively modern groundwater quality data were available. A number of techniques were therefore available to choose from to derive natural background groundwater concentrations:

- Use of a cumulative frequency plot was preferred, where possible, as this provided graphical support to the decision making process. However, no line of data was ever perfectly straight, which left some latitude in the interpretation of where the line intersected the 5th and 95th percentile lines.
- Where data points were sparse, perhaps less than forty, the mean plus or minus two standard deviations of the log concentration was computed. Even when using this technique, it was often found that a cumulative frequency plot aided the decision making process because this makes it easier to spot outliers due to pollution impacts, which are omitted from the statistics.

- Where there were insufficient data to enable the calculation of a statistical natural background limit, or where there appears to be widespread pollution, scaled rainfall concentrations were used. Table 7 shows that this approach is reliable for chloride, but it was most often used on nitrate concentrations. In most of the groundwater bodies this was due to the suspicion that all samples were impacted with anthropogenic nitrate.

  However, in the Wexford Limestone groundwater body, this approach was chosen because groundwater concentrations were typically much lower than the predicted concentration in infiltration, due to the prevalence of reducing conditions. An apparently high (relative to the groundwater) natural background limit was therefore set to account for unconfined patches of the aquifer. Ideally, the groundwater body might be subdivided into confined and unconfined areas (Section 4.3.2), but the available data are insufficient to support this.

Natural background limits were not obtained from surface water chemistry because none of the groundwater bodies completely enclosed the catchment of a monitored watercourse.

# 6. Summary of Recommendations

## 6.1. Recommended Strategy for Characterisation

The paucity of data for many individual groundwater bodies will be the driving force for grouping of groundwater bodies within, and perhaps between, river basin districts. It will therefore be essential that, before embarking on characterising individual groundwater bodies, an overall strategy be developed. This will include the following procedures (Figure 9):

1. **Data collation and handling procedures and protocols**. Collation of the data for all groundwater bodies together will be a significantly more time-efficient process than carrying this out for individual groundwater bodies. The data storage structure will then be consistent and quality assurance issues can be dealt with once, rather than for every groundwater body. However, it is essential that the data remain available for updating as some may be found to be invalid as the characterisation is undertaken.

2. **Identification of groundwater bodies and groups of groundwater bodies**. Once the data are collated, the number of sampling points and samples available will be known. It is at this stage that groundwater bodies should be grouped if necessary; some understanding of the lithological variations across the outcrop will be required at this stage to ensure that the groups have constant lithologies. Some groundwater bodies might be subdivided at this stage (e.g. confined vs unconfined), but it is expected that justification for subdivision can only come on examination of the groundwater chemistry data.

After all the groundwater bodies have been characterised (Section 6.2), it is essential that the following step be undertaken:

1. **Collate and compare natural background limits**. To gain confidence in the natural background limits developed, it will be necessary to compare them for consistency. Formations that cross River Basin District boundaries with no change in lithology, for example, should have similar limits. Likewise, gravel aquifers in the same general area should have similar limits, perhaps with gradual change across that area. Groundwater

bodies with limits dissimilar to the rest should be re-examined to identify the cause, and limits might be re-assessed.

2. **Aggregate natural background limits**. At this stage it might be found that one average limit might be appropriate for many groundwater bodies. A consistent limit for multiple groundwater bodies should be adopted wherever it is conservative, but still reasonable given the natural chemistry of each groundwater body.

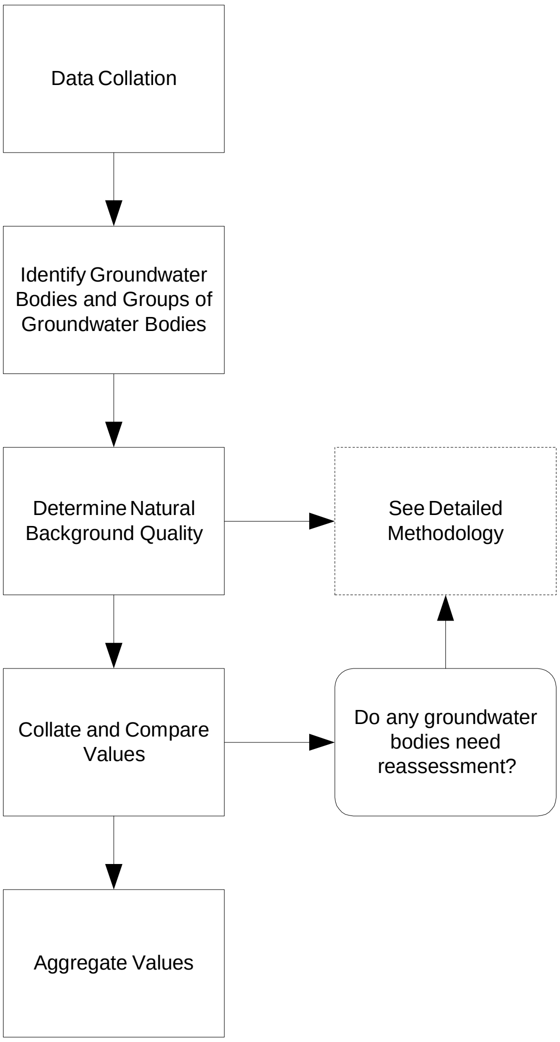

**Figure 9. Recommended overall strategy for characterisation.**

## 6.2. Recommended Methodology for Characterisation

The recommended methodology and techniques are presented in detail in preceding sections. The following is a summary of the methodology in approximate order of execution for each groundwater body or group of groundwater bodies (Figure 10).

1. **Hydrogeological conceptual model**. Obtain and review the hydrogeological conceptual model for the groundwater body.
2. **Identify pressures**. Identify the pressures that might impact upon groundwater quality at the sampling points used. If any might involve direct or indirect discharge of substances to the groundwater body, consider whether additional indicator species might need to be adopted. If the groundwater body is not at risk from a particular pressure, consider whether some of the existing indicators need to be used (e.g. alkalinity in a carbonate aquifer, boron in rural areas).
3. **Determine chemistry of indicator species**. This step is necessary to identify the sources and chemical transformations of a pollutant substance. It is critical to determine the particular technique used to define a natural background limit. This interpretation must be consistent with the hydrogeological conceptual model.
4. **Identify polluted samples**. Identification of polluted samples is essential so that they may be omitted from the statistical analyses.
5. **Data quality assurance**. At this stage, data quality issues may become apparent and the results might have to be omitted from further analysis or adjusted to the correct values. Statistics used in reporting must be consistent with the data considered to be reliable.
6. **Compute natural background limits**. A variety of techniques have been proposed in this report for the determination of natural background limits. The particular technique chosen will be dependant on the chemistry of the indicator species, the amount of data available, and whether anthropogenic impacts have been identified.

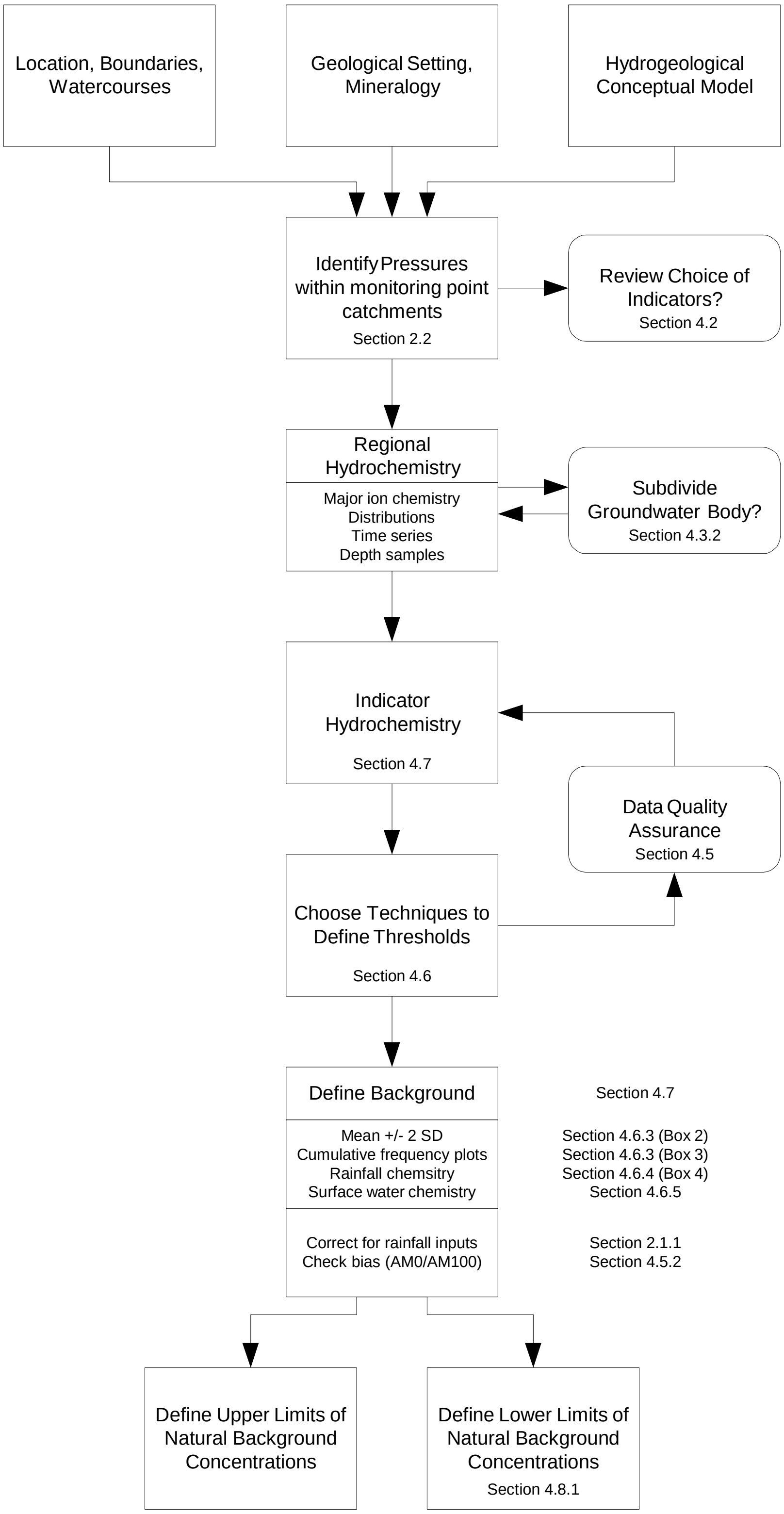

**Figure 10. Recommended detailed methodology for characterisation. Section numbers refer to detailed guidance in the main report**

## 6.3. Recommendations for Groundwater Quality Monitoring

Based on the data reviewed, it is clear that the extent and frequency of sampling, and the range of determinands analysed in Ireland’s groundwater should be enhanced. Although analyses for some monitoring points have improved in scope since 2001, this has not been applied generally across the country.

This is treated in detail in EPA (2003), which provides a consistent suite of core parameters that should be analysed for in all groundwater samples, and a guide list for site specific substances that should be analysed for in certain circumstances. For the purposes of characterisation of the natural background quality of groundwaters, it is recommended that fluoride, lead, barium, radon and uranium be consistently monitored for as a core parameter at the initial stages.

Samples from the monitoring network have been taken sporadically, although this frequency has improved to twice annually in recent years. This frequency is probably adequate for high storage, slow-flowing granular or poorly fractured aquifers. However, the groundwater chemistry of a heavily fractured or karstic limestone aquifer can change very rapidly, and these fluctuations cannot be observed at the current frequency of observations. It is recommended that the frequency of monitoring in the most vulnerable aquifers be increased significantly. Before setting a standard frequency this aspect should be explored in detail to better understand flow processes in the fractured flow systems of Irish aquifers.

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# Appendix A
## The average concentrations of elements in the surface waters of the Atlantic Ocean.

Source: Li, Y-H., (2000). A Compendium of Geochemistry: From Solar Nebula to the Human Brain. Princeton University Press.

| Element | mg/l | Element | mg/l | Element | mg/l |
|---|---|---|---|---|---|
| Cl | 18790 | Al | 9.9831E-4 | Sc | 6.2938E-7 |
| Na | 10805 | Cs | 3.0568E-4 | Er | 6.0214E-7 |
| Mg | 1288.2 | Cr | 1.8199E-4 | Gd | 5.3465E-7 |
| S | 897.68 | Sb | 1.2175E-4 | Yb | 5.1912E-7 |
| Ca | 400.80 | Ni | 1.1740E-4 | Hg | 5.0148E-7 |
| K | 390.98 | Fe | 1.1169E-4 | Pr | 4.2272E-7 |
| Br | 67.119 | Mn | 1.0438E-4 | Sm | 4.0608E-7 |
| C | 24.022 | Cu | 8.2610E-5 | Ho | 2.4440E-7 |
| Sr | 7.7982 | N | 7.0034E-5 | Te | 1.6588E-7 |
| B | 4.5402 | Zn | 5.2304E-5 | Lu | 1.3997E-7 |
| F | 1.2919 | Se | 4.1849E-5 | Tm | 1.3515E-7 |
| Li | 0.18047 | Pb | 3.1080E-5 | Tb | 1.1125E-7 |
| Rb | 0.11965 | Tl | 1.4101E-5 | Eu | 9.1176E-8 |
| I | 0.052035 | Ce | 9.2479E-6 | Be | 9.0121E-8 |
| Si | 0.028086 | Ga | 3.1381E-6 | Ag | 7.5508E-8 |
| Mo | 0.010266 | Ti | 2.8740E-6 | Ge | 7.2590E-8 |
| Ba | 0.0048066 | Sn | 2.3738E-6 | Pt | 5.8527E-8 |
| U | 0.0032134 | Nd | 1.8751E-6 | In | 5.7410E-8 |
| V | 0.0017830 | La | 1.8058E-6 | Bi | 5.2245E-8 |
| P | 0.0015487 | Cd | 1.1241E-6 | Ra | 3.6164E-9 |
| As | 0.0014984 | Dy | 8.1250E-7 | Au | 1.0439E-9 |

Note: $E = 10^x$

# Appendix B
# Survey of Current International Approaches to Chemical Characterisation of Groundwater Bodies

## Ireland

As part of the on-going project to delineate groundwater bodies, the GSI is using hydrochemical indicators as part of the conceptual model development. Where groundwater samples are available, hardness and electrical conductivity are noted and the groundwater is categorised as siliceous or calcareous (to enable classification of surface waters under the WFD).

Unlike surface waters, which are classified according to degree of pollution (none, slight, moderate, very), groundwaters in Ireland are not currently systematically classified, except to determine whether they meet drinking water standards (Page *et al.*, 2002).

Interim standards for the definition of good chemical status are presented in EPA (2003). These are based mainly on drinking water or environmental quality standards, hence the standards are likely to be higher than natural concentrations in groundwater bodies.

## European Union

### Early Draft Groundwater Directive Approach

The February 2003 draft of the new Groundwater Directive (CEC, 2003) presented a methodology for the determination of concentration ranges of indicator species against which to compare individual sample chemistries. This methodology does not appear in the current proposal for the Groundwater Directive, but it may appear in associated guidance in due course. However, it is useful to examine as these techniques may be adapted to the approach presented in this report. The methodology is presented in Annex 1 of the draft Directive (CEC, 2003) and summarised here:

- Each groundwater body, or group of bodies, shall be attributed to one groundwater typology. These eleven typologies are grouped into three classes: sand and gravel units (glacial sediments, fluvial sediments, basin deposits and recent coastal deposits), jointed sedimentary rocks (sandstones, fractured carbonates, karsts and shales) and hard rocks (plutonites, metamorphites, vulcanites).

- Concentration ranges for the indicator species shall be established for each of the defined groundwater bodies and related typologies.

- The indicator species are listed as aluminium, ammonium, arsenic, cadmium, chloride, chromium, copper, mercury, nickel, nitrate, oxygen, potassium, sodium, sulphate, zinc and total organic carbon. In addition physico-chemical parameters should be considered: conductivity, $E_H$ and pH. Other member state-specific indicator species can be adopted if required.

- Ranges should be determined by different specifications according to which particular species is being analysed. For major elements, corrections should be made for atmospheric and anthropogenic input, while for minor elements, the chemical status should be compared with lithology, and anthropogenic influences only need to be corrected.

- The establishment of natural groundwater concentrations should consider interactions with lithology, residence time, ‘processes’, atmospheric sources and interactions with soils.
- The methodology continues by describing techniques for comparison of monitoring results from groundwater bodies with the ranges developed above, with the aim of detecting possible differences that might require further investigation, excluding monitoring data from risk management zones.
- 95th percentiles of the selected parameter distributions are to be used as threshold values for the groundwater body. It is implied that the threshold value represents the upper limit of natural background concentrations.

### BaSeLiNe Study

The EU BaSeLiNe project has the following terms of reference:

- Establish criteria for the baseline concentrations of a wide range of substances that occur naturally in groundwater, as well as their controls, based on sound geochemical principles, as a basis for defining water quality status and standards in Europe.
- Establish a series of reference aquifers across Europe that can be used to illustrate the ranges in natural groundwater quality as a basis for understanding natural groundwater quality evolution and the interfaces with modern, probably contaminated water. [None of the reference aquifers are in Ireland]
- Establish long term trends in water quality at representative localities in the selected reference aquifer and to interpret these in relation to past changes in hydrochemistry in order to predict future changes caused by natural geochemical and anthropogenic effects.
- Provide a scientific foundation to underpin EU water quality guideline policy, with the emphasis on the protection of high quality groundwater and to contribute to sustainable development.

The programme is being coordinated by the British Geological Survey and the methodology is described in detail in the following section that deals with the United Kingdom (below). Other participants in the programme are Denmark, Spain, Portugal, Belgium, France, Estonia, Poland and Switzerland, all of which are trialling the methodology on some of their own aquifers.

## United Kingdom

### Overall Strategy

Outline procedures for the delineation and characterisation of groundwater bodies have been developed in the UK (Allen *et al.*, 2002). There appears to be no definitive guidance on how to define natural background water quality in the UK but it seems that the baseline approach (Shand *et al.*, 1997; Shand and Frengstad, 2001) is currently preferred.

The British Geological Survey and Environment Agency are currently (1999-2004) engaged in an extensive groundwater sampling programme to trial the baseline methodology. Groundwater samples from 25 aquifer areas (mostly major aquifers) in the UK are being obtained and analysed for a comprehensive range of inorganic species. Results are to be analysed and used to define baseline groundwater concentrations for these aquifers.

### Baseline Approach

The baseline methodology approaches aquifers (or groundwater bodies) as individual entities. It therefore relies on there being sufficient high quality data for a groundwater body to be fully characterised without reference to other similar groundwater bodies (as in the typology approach above, or the Swedish methodology below).

To this end the following determinands are explicitly selected for baseline investigation (Shand *et al*., 1997). Residence times will be determined where possible to distinguish water of different ages (i.e. palaeowaters, pre-industrial waters, pre-1940 waters, modern waters).

*Physical/chemical parameters:*
pH, Eh, dissolved oxygen, temperature

*Major determinands:*
Ca, Mg, Na, K, $SO_4$, Cl, $NO_3$, $HCO_3$

*Minor determinands:*
Organic carbon (TOC), Fe, Mn, F, As, P, Al, $NH_4$, B, Cu, Zn, Cd, Ni, Cr, Co, Pb, Ba, Sr, Sb, Be, Hg, Mo, U

*Residence time indicators:*
$^3H$, $^{14}C$, $\delta^{18}O$, $\delta^2H$, $^{13}C$

Concentrations for each determinand are presented on box plots showing key statistics (median, 25th and 75th percentile, 5th and 95th percentiles, minimum and maximum) and on cumulative frequency plots. The 95th percentile of the concentrations distribution is regarded as the upper threshold of baseline concentrations.

The baseline approach has been trialled on the following UK areas:

### Permo-Triassic Sandstone aquifer of Cumbria (Shand et al., 1997)

A large data set of BGS and EA groundwater sampling results was available for this aquifer (designated a Major Aquifer) of 100 $km^2$. Up to 93 individual samples were available for the major determinands, and almost that number for some metallic species. It was possible, therefore, to construct well-constrained cumulative frequency diagrams for all these chemical species.

For most major determinands, these clearly showed a significant positive skew above the 95th percentile concentration that was thought to reflect anthropogenic influence. However, nitrate concentrations appeared to have a more normal distribution at high concentrations and a negative skew at low concentrations, probably reflecting denitrification. This aquifer is known to suffer from patchy but widespread nitrate contamination so the 95th percentile cut-off may not be appropriate for use where extensive diffuse pollution is suspected. In general, metallic species showed normal distributions, reflecting the dominantly rural land use on the aquifer (i.e. very little metallic contamination).

### The Chalk of Berkshire, Southern England (Shand and Frengstad, 2002)

This study area included both unconfined and confined Chalk (designated a Major Aquifer). Groundwater concentrations were significantly different for each zone so samples were treated differently; up to 28 samples were available for the unconfined aquifer and 48 were available for the confined zone.

The cumulative frequency plot for nitrate in the unconfined aquifer samples shows a distinct change in slope at a concentration of 4 mg/l. It was suggested that that is the upper limit of natural concentrations in the aquifer. Nitrate concentrations in more than 70% of the samples exceeded 4 mg/l.

### Lower Palaeozoic mudstones of Wales (Shand and Frengstad, 2002)

The Lower Palaeozoic mudstones of central and southern Wales form a large belt of fractured, weakly metamorphosed argillaceous sediments (a non-aquifer, but it can sustain some local supplies). Two areas were identified that had good quality data (the Plynlimon experimental catchment and the River Teifi catchment), representing of the order of 50% of the total mudstone outcrop. Despite its non-aquifer status, up to 65 groundwater analyses were available.

In contrast to the Permo-Triassic Sandstone and Chalk baseline studies, because this study bulked data from two separate areas, distributions with more than one population were observed for some major determinands in the cumulative frequency plots. This proved to be because groundwater flow was much shallower in the Plynlimon area.

The cumulative frequency plot for nitrate shows that concentrations in more than 20% of the samples were below the detection limit. A break in slope of the curve between 2 and 3 mg/l is interpreted as showing the baseline concentration; more than 50% of the samples showed higher concentrations.

### Devonian sandstone, Fife, Scotland (Shand and Frengstad, 2002)

These sandstones occupy the base of the Eden Valley in central Scotland. Groundwater flow is by a combination of fracture flow and porous flow, with vertical anisotropy caused by mudstone and siltstone layers. Up to 113 sample analyses were examined for this baseline study, although for a limited range of determinands – major ions and some metallic species.

Nitrate concentrations are very variable, but the cumulative frequency plot changes slope at a threshold value around 5 mg/l, which is assumed to be the upper limit of natural concentrations. 50% of concentrations exceed this value.

### Permian granite of Cornwall (Shand and Frengstad, 2002)

The granite in this study area is of plutonic origin and outcrops form the highest land across Cornwall and Devon. As a consequence, groundwater flows radially outwards from the granite towards the coast. Up to 23 sample analyses were examined for the baseline study.

Groundwaters here show the greatest marine influence of the British aquifers examined above, with a Na:Cl ratio very close to that of seawater. Nitrate shows a possible upper natural concentration at 8 mg/l (the 75th percentile). This is higher than the other UK aquifers, but is thought to be due to the freely draining coarse soil that is unlikely to promote denitrification.

Similar baseline studies were also performed on three Norwegian hard rock aquifers (Shand and Frengstad, 2002). Since this review was performed, the Environment Agency and BGS have published many more detailed assessments of the baseline groundwater composition, mainly for the major aquifers.

## Germany

Germany approaches the problem of defining natural concentrations in groundwater by the definition of a number of groundwater typologies in order to aggregate groundwater data into a large, statistically useful dataset. Wendland (2003) identifies the following four typologies as examples:

- Sediments of the Saale glaciation (up to 4846 samples),
- Jurassic Limestones (up to 923 samples),
- Triassic Limestones (up to 650 samples), and
- Triassic Sandstones (up to 1469 samples).

With so many samples of each determinand, the distribution of observed groundwater concentrations [$f_{obs}(C)$] is modelled as the sum of two statistical distributions, representing natural [$f_{nat}(C)$] and anthropogenic components [$f_{anth}(C)$]:

$$f_{obs}(C) = f_{nat}(C) + f_{anth}(C)$$

The distributions are not known *a priori* but the natural distribution is assumed to be log-normal, whereas the anthropogenic distribution is assumed to be normal (Figure B.1). This assumption appears to be valid given the excellent fit of the real data to this model. Once a satisfactory fit is made to the observed concentrations, the natural groundwater concentrations are characterised by the 10th and 90th percentile concentrations of the distribution function of the natural component.

Concentrations of the major ions (Ca, Mg, Na, K, $HCO_3$, Cl, $SO_4$), nitrogen species ($NO_3$, $NH_4$), environmental parameters (EC, DO, pH, DOC), Fe and Mn are assessed in this way. Upper and lower estimates of the natural groundwater concentrations are then obtained.

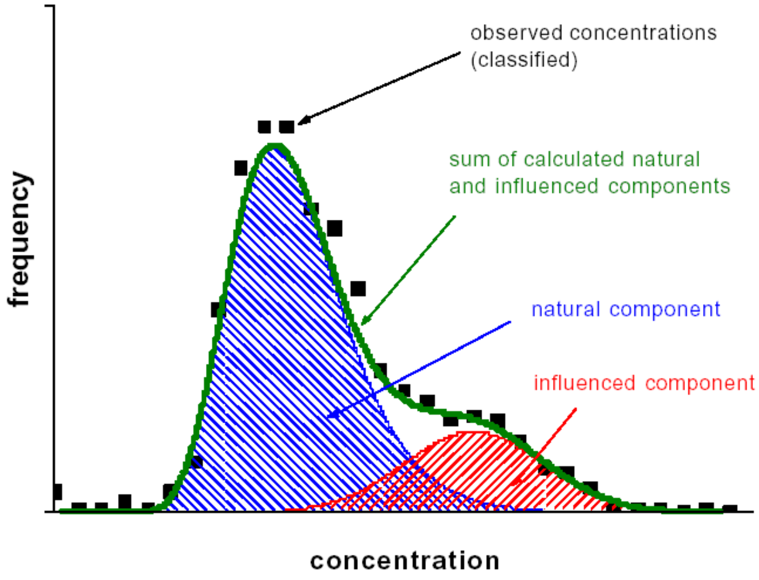

**Figure B.1. An approach to separating natural and anthropogenic influenced components from an observed groundwater concentration distribution (after Wendland, 2003).**

## Sweden

The Swedish Environmental Protection Agency classifies groundwater quality by comparison of concentrations of indicator species to reference values (Swedish EPA, 2000). These values have been derived by a number of methods depending on the indicator species and the available data. In most cases the reference value represents an estimate of the range of natural concentrations, although it is acknowledged that observations tend to be made in areas that have hade some anthropogenic impact. Reference values have not been derived for some parameters (e.g. alkalinity and redox conditions) because of difficulty in estimating a natural range.

The reference values for each indicator species are mostly common for all well depths, aquifer types and all geographic locations, but do vary across the country in some cases (e.g. the reference condition for chloride is higher in the south, which has a more marine climate). In some cases, natural concentrations of a species can naturally exceed the reference value (e.g. cadmium from alum shales) and are identified separately although there tend to be insufficient data to develop specific local reference values.

**Table B.1. Swedish EPA methods for derivation of reference conditions for indicator species.**

| **Indicator Species** | **Reference Condition** | **Comments** |
|---|---|---|
| Alkalinity – risk of acidification | Not estimated.<br>A ratio of ≥10:1 alkalinity in well to sulphate in recharge (meq/l) is used to predict insignificant impact of acidification. | Local variation in sulphate and nitrate deposition, mineralogy and groundwater flow patterns leads to difficulty in estimating original and exhausted alkalinity in any given groundwater body.<br>As an alternative, measured alkalinity is compared with estimated regional sulphate concentration in recharge. |
| Nitrogen as nitrate | 0.5 mg/l as N | Obtained by comparison with measured and computed nitrogen leaching rates under a variety of land uses. |
| Salt as chloride | Central and northern Sweden: 5 mg/l<br>Southern Sweden: 20 mg/l | Obtained by estimation of the range of concentrations in recharge. Chloride concentrations in rainfall increase southwards as the climate is more marine. |
| Redox | Not estimated. | Description of redox conditions is more complex than merely stating a concentration or redox potential.<br>Groundwaters are classified according to adverse effects on the water supply network (e.g. iron precipitation) and concentrations of iron, manganese and sulphate are considered. |
| Metals:<br>Cadmium,<br>Zinc,<br>Lead,<br>Arsenic,<br>Copper,<br>Mercury,<br>Aluminium | <br>µg/l Cd<br>100 µg/l Zn<br>µg/l Pb<br>µg/l As<br>not estimated<br>not estimated<br>not estimated | Cd, Zn, Pb and As reference values based on data from Swedish Geological Survey groundwater monitoring programmes (mostly of uncontaminated sources). 90th percentile values for each species were chosen as the upper limit of the natural range. Insufficient data were available to identify reference conditions for locally elevated natural concentrations of Cd and As.<br>Cu and Hg concentrations in Swedish groundwater are very low and are not perceived to be an issue:<br>Cu: 90th percentile = 5 µg/l<br>drinking water limit = 2000 µg/l<br>Hg: 90th percentile < 0.01 µg/l<br>drinking water limit = 1 µg/l<br>Al concentrations in Swedish groundwater are also very low and are not perceived to be an issue except in very low pH groundwaters (pH<5.5). |
| Pesticides | Not estimated | Pesticide vulnerability classifications are used to prioritise groundwater sampling. These classifications are based on local soil conditions and agricultural activity patterns. |

# Appendix C
# Analytical Aspects

## C.1 Introduction

The determination of the natural background quality of groundwater bodies is fundamentally dependent on chemical data generated by analytical laboratories. This appendix is intended to give general guidance about possible sources of analytical error to those who will use the methodology.

The fact that errors are made can be seen from a recent (2004) EPA laboratory proficiency test sample distribution. The reported results for sulphate ranged from 10 to 254 mg/l $SO_4$ where the mean value was 94 mg/l $SO_4$.For chloride the reported range was 20 to 154 mg/l Cl with a mean value of 44 mg/l Cl. For electrical conductivity, perhaps the easiest test to perform, the reported range was 484 to 827 µS/cm (20$^{o}$C) with a mean value of 615 µS/cm (20$^{o}$C). At least 40 laboratories participated in the tests. It should be remembered that most of the laboratories that participate in the EPA proficiency scheme have been, are, or will be, analysing samples for groundwater body natural background quality purposes. The majority of the laboratories reported data that were within the EPA acceptance criteria but clearly there are a few that have quality control difficulties.

It will be apparent from the text of this report and from the trialling results presented in the Appendix D that analytical data must be carefully assessed before it is used for characterisation of groundwater bodies. Failure to do this, and then to exclude dubious data could lead to erroneous conclusions and a designation of a groundwater body's background quality that is not appropriate.

Availability of historical analytical data is of great utility in determining natural background groundwater quality particularly if the data was generated prior to the early 1970s. In Ireland much of the pre-1973 data for groundwater used for public supply would have been generated by the various Public Health Analytical Laboratories using recognised analytical procedures and under the direction of qualified analytical chemists. Such data should be regarded as reliable.

## C.2 Uncertainty of Measurement

All measurements, be they chemical, microbiological, or engineering, are subject to error. The result of the measurement is an approach to the 'true' value. Results from analytical laboratories are no different; errors (human and equipment) occur, but the key difference between a good and a poor laboratory is that the former are aware that errors occur and they have procedures in place to identify and control them. The procedure is often termed analytical quality control (AQC). Moreover, a good laboratory will have quantified the potential error and will express the result along with the uncertainty of that measurement, e.g. 6.54 ± 0.05 mg/l $NO_3$. In many cases the uncertainty will have been estimated so that it is 95% certain that the result lies between 6.49 and 6.59 mg/l $NO_3$ in the case of this example.

## C.3 Analytical Limit of Detection

Every analytical method for the parameters listed in Table 3 has a limit of detection and there are well established statistical procedures for determining the limit. With the exception of electrical conductivity, there is usually more than one method of analysis for these parameters, and frequently the limit of detection will differ depending on the method used in the laboratory. It should be noted that some laboratories state a ‘reporting limit of detection’ which is always numerically greater than the ‘method limit of detection’.

For any parameter the method used should be appropriate for the purpose for which the analysis is undertaken. For example, there are several methods in Standard Methods for The Examination of Water and Wastewater (Clesceri, et al., 1998) for determining phosphorus but use of the particular method where the limit of detection is 100 µg/l P would be inappropriate for groundwater characterisation as concentrations as low as 5 µg/l P would generally be regarded as significant from a contamination standpoint. This method would be appropriate if the performance of a phosphorus removal treatment plant was been monitored.

Conversely there is little to be gained by using an analytical method that has the capability of determining chloride at sub-mg/l levels since the concentration of chloride in Irish groundwaters nearly always exceeds 5 mg/l Cl and in most groundwaters lies between 10 and 30 mg/l Cl. A limit of detection of about 5 mg/l Cl would be more appropriate in this case. Note that the sub-mg/l method would be appropriate for rain water analysis.

It is likely that most problems with the limit of detection will arise for the trace or so called ‘heavy’ metals. One reason for this is the increasing availability of analytical instruments that do not required qualified analysts for operation. This point is explained in more detail in Section C.5 below. A second reason relates to the purpose as to why data was collected in the first place. In most cases it was collected to assess compliance with drinking water standards and for many trace metals a limit of detection of about 10 µg/l was deemed suitable for practicable reasons. However, in terms of groundwater natural background quality, a concentration of this magnitude for, say, cadmium, chromium, lead, arsenic and mercury would be significant.

### C.4 Significant Figures

Even today it is not unusual to find data reported to more decimal places than is statistically valid. Thus it is highly unlikely that for a reported pH of, say, 7.698 that the terminal ‘8’ has any significance. Indeed, depending on how the electrode and meter were calibrated the significance of the ‘9’ could be in doubt. There are well established procedures for ‘rounding’ results but this should always be done in the laboratory.

### C.5 Some Sources of Error

Since about 1980, affordable, relatively sophisticated instruments such as atomic absorption spectrophotometers and ultraviolet-visible spectrophotometers have become available for routine water analysis. In many cases the calibration procedures used at that time would not comply with modern laboratory accreditation standards, and few laboratories would have carried out a rigorous, statistically based procedure for establishing the limit of detection. This comment applies particularly to metals analyses. It was a common practice to record whatever number appeared on the instrument display without any critical evaluation of the result. At very low concentrations it is possible that the number was no more than detector ‘electronic noise’. Data from atomic absorption spectrophotometers dating from the early 1980s should be regarded with suspicion if the results are around 1µg/l (0.001 mg/l). Analytical quality control as a routine practice was in its infancy at the time.

Handheld instruments for measuring parameters such as pH, electrical conductivity, redox potential and dissolved oxygen are well established. For these unstable parameters on-site measurements are to be preferred over those subsequently determined in a laboratory some hours later. However, the validity of on-site data is totally dependent on proper calibration of the measuring instrument and verification of this at the time of sample measurement. In particular, pH, redox and dissolved oxygen electrodes are easily damaged on-site. Dissolved oxygen results such as '0.05 mg/l $O_2$' should be regarded with suspicion as most portable electrodes do not give reliable results if the concentration is less than about 0.1 mg/l $O_2$.

Small, inexpensive, menu driven spectrophotometers are now widely available and can be used with minimal training but in inexperienced hands can generate data that is not correct particularly at the lower concentration ranges. Most of these instruments are of the single beam type with simple optics and detectors and feature built-in calibration curves. Most optical systems suffer from deterioration over time and it is essential therefore that the instrument's performance be verified on a routine basis. Often a manufacturer's instruction manual might state that the analytical range is from 0 (zero) to 10 mg/l for parameter X when they really mean from, say, 0.1 to 10 mg/l for X. For many parameters the limit of detection in practice can be higher because of sample matrix effects and so, using this example, the limit of detection could be 0.5 mg/l X. These instruments can be used for analysis of a wide range of parameters from nutrients (N and P) to metals. A number will always appear in the instrument display and it is essential that the data be critically evaluated before being reported by the operator.

A bimodal frequency distribution, apart from indicating a change in quality, may also indicate a change in analytical methodology for a given parameter. Sulphate provides a good example. The wet chemistry turbidimetric method, which is still in use in many laboratories and is generally reliable, is not as good as the ion chromatography method particularly if the concentration is less than about 10 mg/l $SO_4$. Reliable determination by the wet method is dependent on the operator and reagent preparation to a considerable degree.

Selective ion electrodes (SIE) are widely used for determination of fluoride, nitrate and ammonia, and most manufacturers provide detailed guidance on their use. These electrodes have a non-linear response near to the limit of detection and unless the analyst is aware of this, erroneous results will be reported. For trace level analyses the normal routine analytical procedure must be adapted sometimes by using different electrode filling solutions and sometimes by using additional calibration solutions. If fluoride is reported as < 0.1 mg/l F or ammonia as < 0.005 mg/l N it is possible that such results are in error unless the special precautions noted above were taken by the laboratory.

### C.6 Data – Results of Expression

Data should not be hastily rejected just because it looks suspicious and does not 'fit'. For example, if there are two abstractions from a groundwater body and if one has an average nitrate concentration of 7.31 mg/l and the other has an average of 1.65 mg/l then it is likely that the former result is expressed in units of nitrate as nitrate ($NO_3$) while the other is expressed in units of nitrate as nitrogen (N). The ratio between the above two results is 4.4 which is almost exactly the factor used to convert a result expressed as nitrate nitrogen-N to nitrate as $NO_3$ (see Box 7 Main Report). Therefore it is more than likely that both sets of data are reliable and should be included in the data set and in subsequent calculations. Similar tests can be applied to ammonium (N or $NH_3$ or $NH_4^+$), nitrite (N or $NO_2$), phosphorus (P or $PO_4$) and alkalinity ($HCO_3^-$ or $CaCO_3$) using the appropriate conversion factors (see Boxes 5, 6 and 8 Main Report).

Similar, though different, considerations apply to electrical conductivity. All modern good quality conductivity meters have the facility to display the measurement result referenced to either 20 or 25°C provided that a temperature sensor is used. A calibration or reporting mistake could give rise to significant error. An electrical conductivity result of 500 µS/cm at 25°C would have a value of 451.5 µS/cm at 20°C. Two sets of data from the same groundwater body differing by about 10% may well be due to a different reference temperature. It is possible, using a temperature correction factor, to calculate the electrical conductivity at either standard reference temperature.

Some old data may be expressed in units of micromhos/cm. This is numerically equivalent to the µS/cm. Old data may also be expressed in electrical resistance units of ohm-cm (Ωcm). Since electrical conductivity is the reciprocal of resistance such data can be converted to units of µS/cm.

## C.7 New Data Collection

If new data is needed then there is the opportunity for avoiding some of the pitfalls discussed above, by careful planning of the project and preparation of specifications for the analytical tasks. This should allow those responsible for interpreting the data to do in the confidence that the data are correct and fit for the purpose.

The procedures adopted for the Three Rivers Project (M C O'Sullivan, 2002) are a good example of how to ensure analytical reliability from the start. The laboratory selected for the analytical work should ideally be accredited to ISO 17025 by INAB and all relevant analytical parameter methodologies should be fully documented. Those parameters which are in the scope of accreditation will be fully documented and the limits of detection established. The documentation for non-accredited parameters must include the limit of detection for each parameter to be measured.

The EPA has published a draft of the new manual for implementation of the drinking water regulations (EPA, 2004). This is available on the Agency's web site in PDF format. Chapter 5 describes the specifications for the analysis of parameters and it includes a section with specified minimum performance criteria for the analytical methods for 35 chemical species or groups of species. Much useful guidance is given but it is essential to note that this document is concerned only with drinking water and for many parameters, e.g. chloride; the parametric value (250 mg/l Cl) in the regulations is well above the concentration that would indicate pollution of a groundwater body. The same is true for nitrate where the parametric value is 50 mg/l $NO_3$. Nevertheless, the performance criteria in respect of 'trueness' and 'precision' are generally worth adopting for work concerning groundwater body characterisation. For those indicator parameters in Table 3 of the main report that are common to those listed in the draft Groundwater Directive, the Water Framework Directive and the Drinking Water Regulations, the criteria are given in Table C.1.

**Table C.1. Analytical Performance Minimum Criteria for Selected Relevant Parameters**

| Parameter | Source Document (Note 1) | Parametric Value DW Regulations (Note 2) | Trueness % of parametric value (Note 3) | Precision % of parametric value (Note 4) | LOD % of parametric value |
|---|---|---|---|---|---|
| Ammonium | DWD WFD GWD | 0.30 mg/l $NH_4$ | 10 | 10 | 10 |
| Dissolved oxygen | WFD | Note 5 | --- | --- | --- |
| Electrical conductivity | WFD | 2500 µS/cm $20^oC$ | 10 | 10 | 10 |
| pH | DWD WFD | ≥6.5 & ≤9.5 | 0.2 pH unit | 0.2 pH unit | |
| Nitrate | DWD WFD | 50 mg/l $NO_3$ | 10 | 10 | 10 |
| Arsenic | DWD GWD | 10 µg/l | 10 | 10 | 10 |
| Cadmium | DWD GWD | 5.0 µg/l | 10 | 10 | 10 |
| Chromium | DWD | 50 µg/l | 10 | 10 | 10 |
| Lead (Note 6) | DWD GWD | 10 µg/l | 10 | 10 | 10 |
| Mercury | DWD GWD | 1.0 µg/l | | | |
| Sulphate | DWD GWD | 250 mg/l $SO_4$ | 10 | 10 | 10 |
| Chloride | DWD GWD | 250 mg/l Cl | 10 | 10 | 10 |
| Trichloroethene & Tetrachloroethene | DWD GWD | 10 µg/l Sum of both | 25 | 25 | 10 |
| | | | | | |
| Note 1: DWD = Drinking Water Directive; WFD = Water Framework Directive; GWD = Groundwater Directive | | | | | |
| Note 2: European Communities (Drinking Water) Regulations, 2000: Statutory Instrument No. 439 of 2000. | | | | | |
| Note 3: Trueness is the systematic error and is the difference between the mean value of the large number of repeated measurements and the true value. (Further defined in ISO 5725) | | | | | |
| Note 4: Precision is the random error and is usually expressed as the standard deviation (within and between batch) of the spread of results about the mean. Acceptable precision is twice the relative standard deviation. (Further defined in ISO 5725) | | | | | |
| Note 5: Dissolved oxygen is not a drinking water parameter | | | | | |
| Note 6: This value must be met by December 25, 2013. | | | | | |

## References

Clesceri, L. S., Greenberg, A.E. and Eaton, A.D. (eds), (1998). *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association, Washington, DC, USA.

M C O’Sullivan (2002). *The Three Rivers Project – Final Report*, M C O’Sullivan, Consulting Engineers, Carnegie House, Library Road, Dun Laoghaire, County Dublin.

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# Appendix D
# Results of Trialling the Methodology on Example Groundwater Bodies

# *The Curragh Gravel Aquifer*

## Study Area

Location & boundaries

The Curragh Gravel (Mid-Kildare Gravel) forms a major aquifer in central County Kildare The deposit is one of the most extensive sand & gravel bodies in Ireland. It is classed as a **regionally important sand & gravel aquifer (Rg)**. It consists of glacial outwash plain deposits in places up to 70 m thick (though more commonly less than 15 m). It is roughly ovoid in shape (Figure D1.1), with a maximum length of 21 km and a maximum width of 13 km, and extends from near Naas in the northeast to Nurney in the south, and from Kildare town in the west to Kilcullen in the east (Wright 1988). The formation lies in a shallow trough, oriented northeast-southwest. To the southeast, this trough is bounded by the Lower Palaeozoic rocks (slates, etc.) of the Leinster Massif, and to the northwest by the low ridge of the Chair Hills - again mainly composed of pre-Carboniferous rocks. Between these hills, the Carboniferous Limestone that underlies the Curragh aquifer is composed of bedded limestones and dolomites.

The aquifer and its attendant soils were described in Kelly and Fitzsimons (2002), who defined the extent of the aquifer as that portion of the deposit that is at least 5 m thick. On this basis it covers an area of approximately 180 km$^2$. The land is largely classified as good arable land but there is a significant amount of forestry across the aquifer.

The Curragh aquifer is a feeder for the Grand Canal and is an important source of baseflow for the streams and rivers, including the River Liffey. This is supported by the estimated flow from the aquifer to the Milltown Feeder at Pollardstown Fen of approximately 25,000 m$^3$/day (Daly, D. 1981). It also feeds the springs that maintain Pollardstown Fen, an environmentally important wetland on its northern edge. The Defence Forces use the aquifer to supply over 1400 people in the Curragh Camp and the surrounding houses and village.

The main pressures on the aquifer are the impact of agricultural activities (chiefly spreading of artificial fertilisers and animal slurry) and waste disposal. Immediately to the north of the Hare Park Waterworks there is a disused landfill filling an old gravel pit, where tipping ceased in the mid 1990s. The fill mostly comprised builders rubble and tipping was carried out for at least twenty years (Kelly & Fitzsimons, 2002).

Hydrogeology

Grain size data show the aquifer to be well sorted, with less than 8% of fines (Kelly and Fitzsimons, 2002). It is also noted that there are occasional Till horizons within the sands and gravels, and that these also cap large parts of the surface. The gravel aquifer is however unconfined in most places. Basin peat deposits are infrequent, but important in the area of Pollardstown Fen.

Aquifer porosities are estimated to be of the order of 30-40% (Hayes *et al.*, 2001). Productivity data are sparse but available data from tests around the Curragh Military Camp and on the Kildare by-pass indicate good aquifer properties. Permeabilities are estimated from test pumping and modelling to be between 15 and 100 m/day (Hayes *et al.*, 2001) and transmissivities up to 1500 m$^2$/day (Edwards and Warren, 1985). Well hydrographs show seasonal variations in water level of 1.25 to 2.5 m with an unsaturated zone thickness in the vicinity of the camp of around 16m thickness (Kelly and Fitzsimons, 2002)

Regional groundwater flow directions show that groundwater in the area of the Curragh Camp flows northwest and north towards Pollardstown Fen, where it is observed to discharge in springs. The hydraulic gradient towards Pollardstown Fen is estimated to be of the order of

0.002 (White Young Green, 2002). The extent of interaction with other surface watercourses including the River Liffey is not clear, but are thought to be important.

Aquifer mineralogy

In the absence of any specific references on the mineralogy of the Curragh gravels, one can assume that the composition will depend on the source rocks. These belong to the underlying Carboniferous Limestone, which is composed of interbedded dolomite and calcite. Since the Curragh gravels are fluvio-glacial in origin, they are clean of silty and clayey material. Grading shows them to be 70% gravel (Edwards & Warren, 1985). Till horizons reported within the gravels contain much finer material. They are likely to hold clay minerals and others such as pyrite and gypsum, which may be sources of ions including magnesium, sodium, iron and sulphate. GSI drilling at the aquifer identified a thin layer of granite gravels at the base of he deposit.

Rainfall and recharge

The Curragh aquifer is approximately halfway between the rainfall chemistry monitoring stations in Kinnitty and at Dublin Airport; average rainfall statistics for 1992-1994 are presented in Table D1.1. Kelly and Fitzsimons (2002) estimated the recharge rate at the Curragh Camp area as 415 mm/a. This is used in Table D1.1 to estimate solute concentrations in infiltration, assuming that the recharge is approximately equal to effective precipitation, and that the species are conservative through the soil zone.

**Table D1.1. Rainfall statistics and quality**

| Station | Rain (mm/a) | $SO_4$ (mg/l S) | Cl (mg/l) | $NO_3$ (mg/l N) | $NH_4$ (mg/l N) |
|---|---|---|---|---|---|
| Dublin Airport | 763 | 1.69 | 7.98 | 1.63 | 0.43 |
| Kinnitty | 904 | 0.78 | 6.68 | 0.12 | 0.07 |
| Mean rainfall/conc. | 834 | 1.24 | 7.33 | 0.88 | 0.25 |
| Recharge depth/conc. | 415 | 2.49 | 14.7 | 1.77 | 0.50 |

## Hydrochemistry

Sample Locations

231 analyses are available for the Curragh gravels aquifer, but these have generally been analysed for different determinands (Table D1.2). Data collection has been sporadic: one sample is available for 1980 (Edwards and Warren, 1985), then there was an extensive survey between 1987 and 1988 for the Kildare Bypass project (Coxon and Thorn, 1989) until the EPA started systematic monitoring of three boreholes in 1995. No historic data prior to the intensification of agriculture around 1973 are therefore available. Note that all the sample points listed in Table D1.2 are assumed to lie within the superficial aquifer rather than the Carboniferous aquifer beneath.

Ionic balances are in general, good, however, several of the recent samples from the EPA database have ionic balance errors greater than ±10%.

**Table D1.2. Sample point locations and dates**

| Sample Point | Source | Samples | Period |
|---|---|---|---|
| ‘bro’ | Coxon and Thorn | 1 | Jun 1989 |
| ‘cf’ | Coxon and Thorn | 2 | Dec 1988 – Jun 1989 |
| Curragh View | Coxon and Thorn (‘cv’) | 28 | Oct 1987 – Sept 1988 |
| Day Pump (Curragh Camp) | Coxon and Thorn (‘cdp’) | 27 | Oct 1987 – Sept 1988 |
| Engineers Cottage (Curragh Camp) | Coxon and Thorn (‘cec’) | 27 | Oct 1987 – Sept 1988 |
| ‘eyr’ | Coxon and Thorn | 2 | Dec 1988 – Jun 1989 |
| Hare Park (Curragh Camp) | EPA + Coxon and Thorn (‘hpk’) | 15 | Oct 1987 – Mar 2003 |
| ‘hp5’ | Coxon and Thorn | 2 | Dec 1988 – Jun 1989 |
| ‘hp9’ | Coxon and Thorn | 2 | Dec 1988 – Jun 1989 |
| McDonagh (Curragh Camp) | EPA + Coxon and Thorn (‘mdo’) | 16 | Oct 1987 – Mar 2003 |
| National Stud Tully (St John’s Well) | Coxon and Thorn (‘nst’) | 28 | Oct 1987 – Sept 1988 |
| ‘pat’ | Coxon and Thorn | 2 | Oct 1987 – Mar 2003 |
| Pollardstown Church | Coxon and Thorn, (‘pch’) | 6 | Nov 1987 – Aug 1988 |
| Pollardstown Fen | EPA | 15 | Oct 1987 – Apr 2003 |
| Railway Bridge | Coxon and Thorn (‘rb’) | 27 | Oct 1987 – Sept 1988 |
| ‘rc’ | Coxon and Thorn | 2 | Oct 1987 – Mar 2003 |
| Seven Springs | Edwards and Warren + Coxon and Thorn (‘ss’) | 29 | Mar 1980 – Oct 1987 |

### Major ion chemistry

The groundwater chemistry is dominated by calcium bicarbonate, reflecting the limestone nature of the sand and gravel clasts of the aquifer (Figure D1.2). Sulphate and chloride occur as minor anionic components. Magnesium is a minor cation component. Sodium and potassium are present at very low concentrations except at Hare Park, where sodium becomes more dominant.

### Regional variation

There are no systematic variations in major ion chemistry across the aquifer, suggesting that there is no significant evolution between the recharge area along the Curragh ridge and the discharge area at Pollardstown Fen (Figure D1.3).

Two sample points appear to yield inconsistent results: those at Curragh View and Hare Park. Samples from Curragh View show a relatively high TDS, although the ratios of the major ions are generally consistent with the rest of the aquifer, except potassium, which is present at concentrations almost 20 times higher than the average for the rest of the aquifer (Table D1.3).

**Table D1.3. Concentration distributions for TDS and potassium at Curragh View and elsewhere**

| | TDS (mg/l) | Potassium (mg/l) |
|---|---|---|
| Curragh View | 684 ± 25 | 17.2 ± 0.4 |
| Rest of the aquifer | 528 ± 32 | 0.9 ± 1.0 |

At Hare Park, sodium, potassium and chloride are all around twice as high as the aquifer average (Table D1.4). This could be due to the proximity of the landfill at Curragh Camp, although Kelly and Fitzsimmons (2002) suggest that the difference might be partly due to the use of water softeners at the source. Transition metal concentrations have been analysed in samples from the three EPA boreholes since 2002. Results from Hare Park borehole only show a rising trend for chromium, nickel and zinc, and high concentrations of barium and boron.

**Table D1.4. Concentration distributions for selected major ions at Hare Park and elsewhere**

| | Na (mg/l) | K (mg/l) | Cl (mg/l) |
|---|---|---|---|
| Hare Park | 25 ± 6 | 1.9 ± 0.4 | 33 ± 9 |
| Rest of the aquifer (not Curragh View) | 8 ± 3 | 0.8 ± 0.4 | 16 ± 5 |

Depth variation

No data are available on depth variations in hydrochemistry.

Temporal variations

Apart from the Hare Park and McDonagh boreholes, there are no sample points that have data from both the 1987-1989 and 1995-2003 sampling periods.

No seasonal variations in groundwater chemistry were observed in the detailed study over the period 1987-1989 although there were occasional fluctuations in water quality. Concentrations at the Curragh View source were seen to rise consistently throughout the period, particularly calcium, sodium, chloride and sulphate (Figure D1.4).

Sulphate concentrations at the Hare Park borehole increased significantly between 1989 and 1995 and more recently have been dropping back to earlier concentrations (Figure D1.5 and Table D1.5). Nevertheless, the sulphate concentration at Hare Park is elevated compared with the aquifer average for the period 1987 to 1989. Also, recent chloride concentrations have been steadily rising (though Na, K, ammonium and nitrate seem stable).

Although Pollardstown Fen is in the discharge area for the aquifer (i.e. down-gradient of Hare Park), there does not appear to have been a similar degree of contamination. This could be due to dilution in the aquifer, by re-circulation of the contaminated water through pumping at the source, or because of slow groundwater velocities in the high porosity aquifer.

**Table D1.5. Sulphate concentration distributions (mean & SD) for different sampling periods**

| | $SO_4$ (mg/l as S) 1987 – 1989 | $SO_4$ (mg/l as S) 1995 – 2003* |
|---|---|---|
| Total aquifer** | 16 ± 6.7 | n/a |
| Pollardstown Fen | n/a | 19 ± 1.1 |
| McDonagh (Curragh Camp) | 14 ± 3.5 | 20 ± 2.0 |
| Hare Park (Curragh Camp) | 30 ± 2.1 | 28 ± 5.8 |

* Hare Park and McDonagh samples for 27 August 1996 are omitted due to anomalous results.

** Not including samples from Hare Park, McDonagh or Pollardstown Fen.

Exclusions

It is clear from the above discussions that the groundwater chemistry of Hare Park borehole no longer reflects natural concentrations and probably did not during the 1987-1989 sampling period. This is may be due to the impact of the nearby landfill.

The origin of the increasing concentrations of major ions and TDS at Curragh View is unknown but the rising trend between 1987 and 1988 suggests that the chemistry was being affected by some anthropogenic activities. Concentrations of all determinands at Curragh View are omitted from further analysis.

## Indicator chemistry

Redox indicators

Sulphate concentrations are available for all sample points and the species has been detected in all samples. Iron and manganese concentrations are only available for the EPA monitoring boreholes and these species have been detected at these three sample points but not in all individual samples. Dissolved oxygen levels are unavailable for the Curragh groundwater body.

Currently, groundwaters at Pollardsdown Fen appear to be more reduced than those at Curragh Camp, since Mn and Fe concentrations are on average higher there, and sulphate concentrations are slightly lower (Table D1.6). However, these minor differences are probably not statistically valid given the high proportion of non-detects at Pollardstown Fen; indeed, the maximum concentrations of both Mn and Fe were detected at the Hare Park borehole. No iron or manganese concentrations are available from the 1987-1989 survey.

Sulphate results from Hare Park and McDonagh were anomalously low in the sample from 27 August 1996. This is perhaps due to their being incorrectly converted to mg/l as $SO_4$, rather than as S, like the rest of the database. These results (sulphate only) are omitted from further analysis.

**Table D1.6. Median concentrations of redox indicators for all samples**

| | Mn (µg/l) | Fe (µg/l) | $SO_4$ (mg/l as S) |
|---|---:|---:|---:|
| Pollardstown Fen | 7.9 | 109 | 18.6 |
| McDonagh (Curragh Camp) | < 2 | < 50 | 19.4 |
| Hare Park (Curragh Camp) | < 2 | < 50 | 24.8 |
| Rest of aquifer | n/a | n/a | 16.8 |

Natural background concentration limits for redox indicators will therefore be calculated based on all the data except:

- no sulphate data from Hare Park will be used, nor
- sulphate data for McDonagh from August 1996.

There are insufficient data to enable construction of a cumulative probability plot for the metallic species. It is assumed that all the concentrations observed at Pollardstown Fen and McDonagh are representative of natural concentrations so the mean of the log values plus two standard deviations are used to compute natural background limits.

For sulphate, there are sufficient data to enable construction of a cumulative frequency plot (Figure D1.6). The plot does show removal of sulphate at lower concentrations for almost half the samples suggesting that redox conditions in the aquifer vary and that there are perhaps two natural distributions of sulphate. A lower limit of sulphate concentrations therefore becomes meaningless as the 5th percentile of the lowest distribution is below the detection limit of sulphate.

Since it is a shallow unconfined aquifer, dissolved oxygen concentrations should be relatively high except, perhaps, beneath peaty areas. The lower dissolved oxygen limit is based on a groundwater with 95% saturation at 15ºC.

**Table D1.7. Natural background concentration limits for redox indicators**

| | Observed Range | Limits | |
|---|---|---|---|
| Dissolved oxygen (mg/l) | n/a | Upper | 9.4 |
| Manganese (µg/l) | < 1 – 69 | Upper | 35.4 |
| Iron (µg/l) | < 50 – 293 | Upper | 1560 |
| Sulphate (mg/l as S) | 4.0 – 42.7 | Lower | n/a |

### Chloride

Chloride concentrations in the aquifer typically lie between 10 and 20 mg/l. The highest concentrations have been identified in the Curragh View borehole (up to 50 mg/l) and in the Hare Park borehole (up to 45 mg/l).

Between 1987 and 1989 there was a consistent pattern in the variation of chloride concentrations across the whole aquifer (Figure D1.7). After period of very stable concentration, they almost doubled during Summer 1988 before returning back to the original concentration. This pattern is not reflected in concentrations of the other major ions in rainwater. It is not known what this impact was due to, but it is assumed to have been anthropogenic. However, the cumulative frequency plot (Figure D1.6) shows two distinct log-normal distributions, suggesting that there are two natural processes contributing to the chloride concentrations.

More recently (1995-2003), chloride concentrations in the Hare Park borehole have been steadily increasing; whereas those in McDonagh and Pollardstown Fen have been, on average, dropping (Figure D1.8). Concentrations at McDonagh and Pollardstown Fen both show long term fluctuations which perhaps relate to trends in annual rainfall.

Table D1.1 suggests that, assuming that chloride is conservative through the soil zone, its concentration in recharge water will be approximately 14.7 mg/l. This is approximately the average value of the early 1988 data and the recent data at McDonagh and Pollardstown Fen, suggesting that these might reflect natural background concentrations. For comparison, the median concentration of natural background samples is 13.5 mg/l.

An natural background concentration limit for chloride will therefore be calculated as the mean plus two standard deviations of the logs of the apparently natural concentrations before March 1988 and those at McDonagh and Pollardstown Fen after 1995 (Table D1.8).

**Table D1.8. Natural background concentration limit for chloride**

| | Observed Range | Limits | |
|---|---|---|---|
| Chloride (mg/l) | 4 – 49 | Upper | 20.7 |

Nitrogen species

Nitrate is present at fairly high concentrations in the groundwater body (median concentration 4.1 mg/l as N). The highest concentrations are found along the axis of the Curragh ridge in recharge areas (Figure D1.9), whereas in the groundwater discharge area around Pollardstown Fen concentrations are relatively low. This could be either because they are less polluted, or perhaps because the nitrate has been reduced. There are no particular trends in nitrate concentrations at any boreholes (Table D1.9).

**Table D1.9. Nitrate concentration distributions (mean & SD) for different sampling periods**

| | $NO_3$ (mg/l as N) 1987 – 1989 | $NO_3$ (mg/l as N) 1995 – 2003 |
|---|---|---|
| Total aquifer* | 4.6 ± 2.9 | n/a |
| Pollardstown Fen | n/a | 2.9 ± 0.1 |
| McDonagh (Curragh Camp) | 6.2 ± 0.1 | 5.2 ± 0.3 |
| Hare Park (Curragh Camp) | 4.2 ± 0.4 | 4.8 ± 0.5 |

* Not including samples from Hare Park, McDonagh or Pollardstown Fen.

The median concentration of ammonium is below the detection limit (of 0.01 mg/l as N) and, when detected, concentrations tend to be only very slightly above the detection limit (max for the groundwater body is 0.03 mg/l as N). Concentrations are too low to show any geographic distribution.

Table D1.1 suggests that, assuming that nitrate is conservative through the soil zone, its concentration in recharge water will be approximately 1.8 mg/l as N. This is a significant fraction of the measured groundwater concentrations but it cannot account for most of the nitrate in groundwater. The ammonium concentration is predicted to be approximately 0.5 mg/l, so it is clear that ammonium is not conservative in the soil zone.

It appears that the groundwaters of the Curragh are contaminated by anthropogenic nitrate both from atmospheric inputs and from direct inputs (probably mainly agriculture). Natural background concentrations cannot therefore be determined for the groundwater body based on measured concentrations. The best estimate is that the upper limit should be based on the estimated infiltration contribution of 1.8 mg/l as N, scaled by the ratio between the 95th percentile and estimated infiltration concentrations of chloride.

It is unlikely that the aquifer is still in its natural state with regards to ammonium concentrations, since it has been shown to be subject to anthropogenic nitrogen inputs. However, concentrations are too low to use for meaningful analysis. The best estimate is that the upper limit should be the lowest detection limit in the data set.

**Table D1.10. Natural background concentration limits for nitrogen species**

| | Observed Range | Limits | |
|---|---|---|---|
| Nitrate (mg/l as N) | 0.5 – 13.5 | Upper | 2.5 |
| Ammonium (mg/l as N) | < 0.005 – 0.03 | Upper | 0.005 |

Electrical Conductivity

Groundwater conductivity varies from 568 to 1073 µS/cm; the highest being determined for Curragh View. These are quite high, but the waters are very hard: calculated hardness values vary from 300 to 750 mg/l as $CaCO_3$. Comparison with Table 6 of the main report suggests that the high conductivity is likely to be entirely due to the high hardness.

Saline intrusion is not a risk at the Curragh so derivation of an natural background limit is meaningless in that context. Since the background concentrations are high due to the hardness of the water, impacts from pollution will not be observed against the natural variation.

An upper limit has been set at the mean concentration plus two standard deviations of the log concentrations.

| | Observed Range | Limits | |
|---|---|---|---|
| Electrical Conductivity (µS/cm) | 568 – 1073 | Upper | 999 |

pH and Alkalinity

pH varies from 6.9 to 8.1 and alkalinity is correspondingly high and relatively constant, at 257 to 423 mg/l as $CaCO_3$. These indicate alkaline conditions typical of carbonate terrains. Risk of acidification is therefore minimal in this very well buffered aquifer and derivation of natural background limits for pH and alkalinity are therefore meaningless in that context.

Lower limits have been set at the mean concentration minus two standard deviations. Log concentrations were used for the alkalinity, pH values were used directly.

| | Observed Range | Limits | |
|---|---|---|---|
| pH | 6.9 – 8.1 | Lower | 6.8 |
| Alkalinity (mg/l as $CaCO_3$) | 257 – 423 | Lower | 298 |

Sulphate

Sulphate concentrations tend to be higher in the Curragh Camp boreholes, as previously discussed, due to the more oxidising conditions in the recharge area. However, since tills are found within the sand and gravel sequence, there is likely to be a natural contribution due to oxidation of sulphides.

Table D1.1 suggests that, assuming that sulphate in rainfall is conservative through the soil zone, its concentration in recharge water will be approximately 2.5 mg/l as S. This is a minor fraction of the measured groundwater concentrations.

The cumulative frequency plot for sulphate (Figure D1.6) shows removal of sulphate at lower concentrations for almost half the samples. This suggests that redox conditions in the aquifer vary and that there are perhaps two natural distributions of sulphate. If this is so, the 95th percentile concentration of the distribution of higher concentrations (excluding Hare Park and Curragh View) can be used to define the upper limit of background conditions (30 mg/l as S). The natural background concentration is therefore calculated by subtracting the anthropogenic atmospheric input (Table D1.11).

**Table D1.11. Natural background concentration limit for sulphate**

| | Observed Range | Limits | |
|---|---|---|---|
| Sulphate (mg/l as S) | 4.0 – 42.7 | Upper | 27.5 |

Phosphate

The median concentration of phosphate in the aquifer is 0.005 mg/l as P; unusually for groundwater there are very few non-detect results and phosphate appears to be ubiquitous. The cumulative frequency plot suggests that there are perhaps two log normal distributions of phosphate concentrations in the aquifer, but does not suggest whether or not either is anthropogenic. It is notable that all non-detects, and most of the lowest concentrations, have been from more recent (EPA) results, possibly due to improved analytical techniques.

It is not possible at this stage to determine whether the phosphate concentrations reflect ubiquitous contamination, or an unusually high background concentration. It is assumed that, as with nitrate, the aquifer is widely contaminated. A natural background concentration limit cannot therefore be set, but the best estimate would be the lowest measured value (Table D1.12).

**Table D1.12. Natural background concentration limit for phosphate**

| | Observed Range | Limits | |
|---|---|---|---|
| Phosphate (mg/l as P) | 0.0013 – 0.217 | Upper | 0.0013 |

Metals

Heavy metals including zinc, lead, cadmium and arsenic have only been analysed since 2002. Apart from one very low lead concentration in 2002, none of the metals apart from zinc have been detected.

The highest zinc concentrations occur in the samples from the Curragh Camp boreholes. It has been found at concentrations well in excess of 100 µg/l, whereas concentrations at Pollardstown Fen do not exceed 2 µg/l. This may be due to the influence of the nearby landfill. Although there are only three measurements the natural background limit is determined as the mean concentration plus two standard deviations of the log concentrations at Pollardstown Fen (Table D1.13)

**Table D1.13. Natural background concentration limits for heavy metals**

| | Observed Range* | Limits | |
|---|---|---|---|
| Cadmium (µg/l) | < 0.1 | Upper | 0.1 |
| Lead (µg/l) | < 1 – 2.9 | Upper | 1 |
| Arsenic (µg/l) | < 1 | Upper | 1 |
| Zinc (µg/l) | < 1 - 3261 | Upper | 4.7 |

* for the whole groundwater body

Natural background groundwater quality

The data available are extremely limited both in terms of geographical and temporal spread. Any conclusions are therefore very tentative at this stage. Additionally, there are no data that pre-date the intensification of agriculture in 1973, so the impact of increased agricultural production on recharge to groundwater cannot be assessed. The Table D1. below summarises the proposed natural background limits for indicator species.

**Table D1.14. Natural background concentration limits for indicator species**

| | Observed Range | Limits | |
|---|---|---|---|
| Dissolved oxygen (mg/l) | n/a | Upper | 9.4 |
| Manganese (µg/l) | < 1 – 69 | Upper | 35.4 |
| Iron (µg/l) | < 50 – 293 | Upper | 1560 |
| Chloride (mg/l) | 4 – 49 | Upper | 20.7 |
| Nitrate (mg/l as N) | 0.5 – 13.5 | Upper | 2.5 |
| Ammonium (mg/l as N) | < 0.005 – 0.03 | Upper | 0.005 |
| Electrical conductivity (µS/cm) | 568 – 1073 | Upper | 999 |
| pH | 6.9 – 8.1 | Lower | 6.8 |
| Alkalinity (mg/l as $CaCO_3$) | 257 – 423 | Lower | 298 |
| Sulphate (mg/l as S) | 4.0 – 42.7 | Upper | 27.5 |
| Sulphate (mg/l as S) | 4.0 – 42.7 | Lower | n/a |
| Phosphate (mg/l as P) | 0.0013 – 0.217 | Upper | 0.0013 |
| Cadmium (µg/l) | < 0.1 | Upper | 0.1 |
| Lead (µg/l) | < 1 – 2.9 | Upper | 1 |
| Arsenic (µg/l) | < 1 | Upper | 1 |
| Zinc (µg/l) | < 1 - 3261 | Upper | 4.7 |

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# Figure s

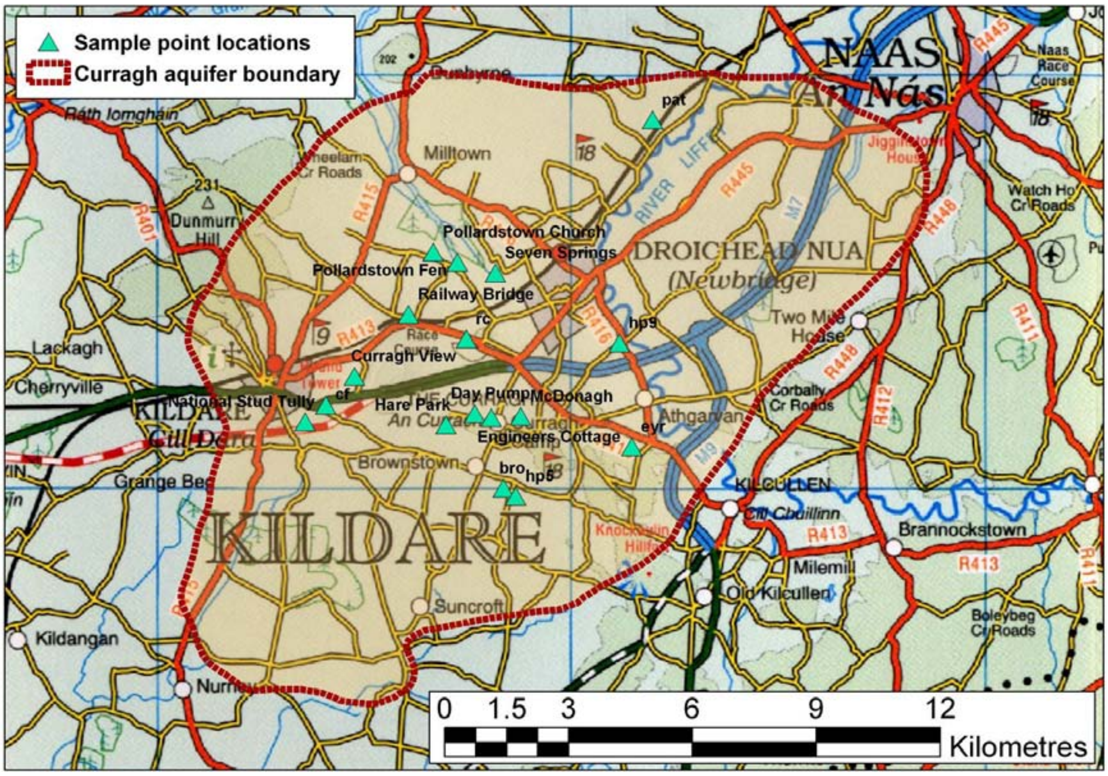

**Figure D1.1. Location of Curragh groundwater body and sample points**

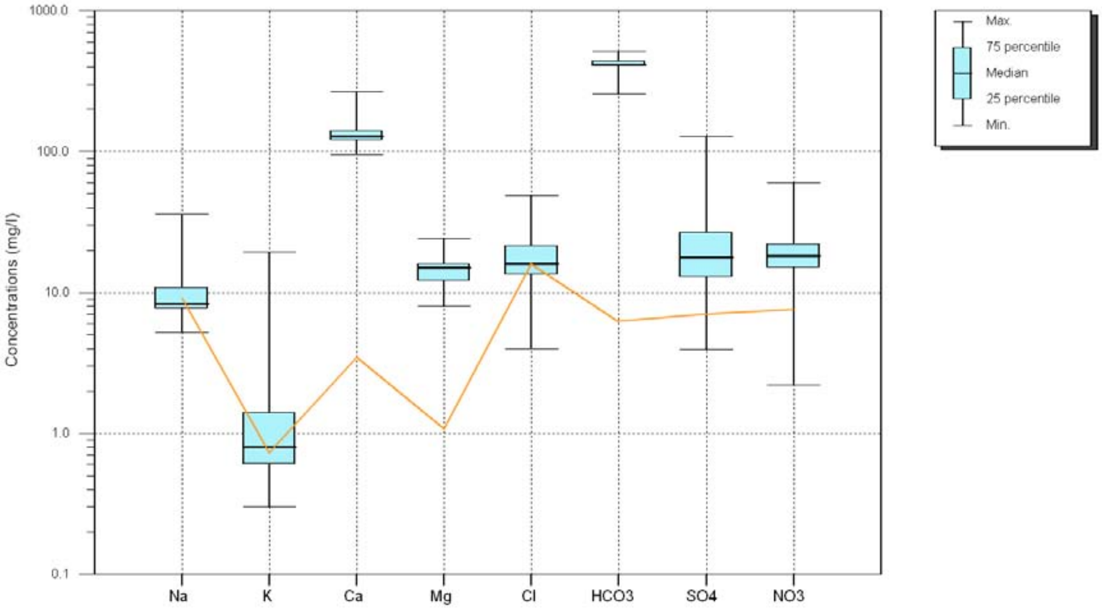

**Figure D1.2. Box and whisker plot of total major ion concentrations. Orange line shows rainfall composition normalised to median groundwater chloride concentration.**

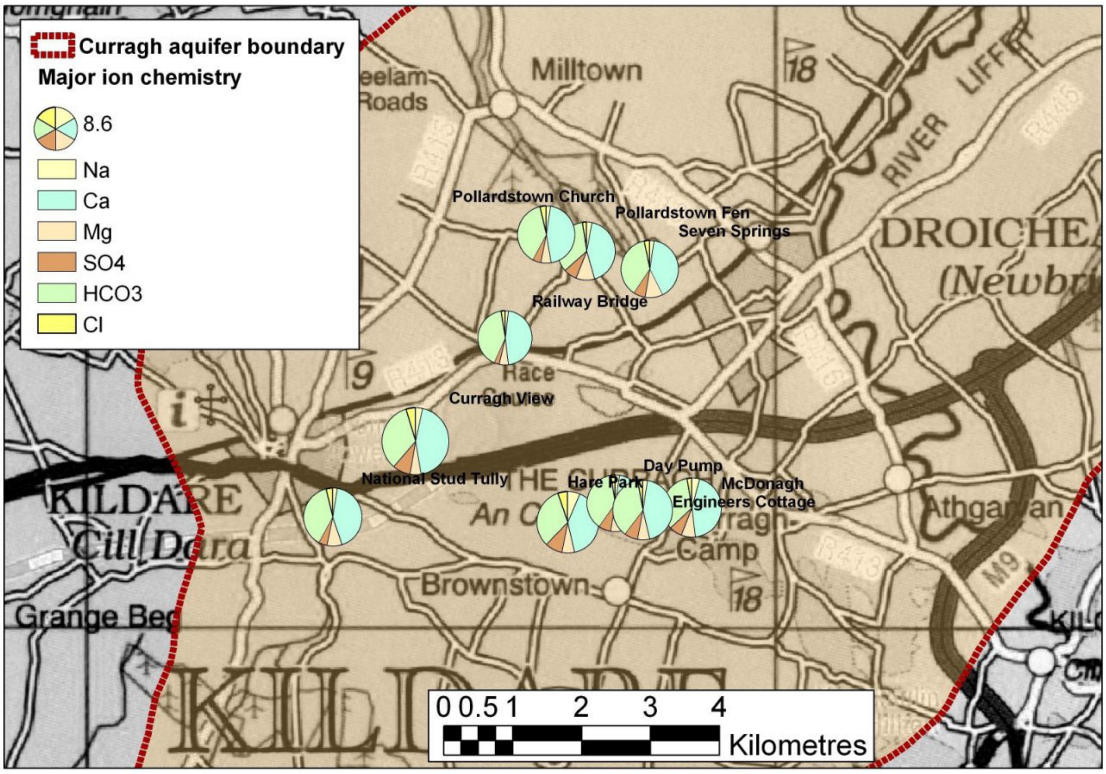

**Figure D1.3. Major ion chemistry. Symbols scaled according to TDS (meq/l)**

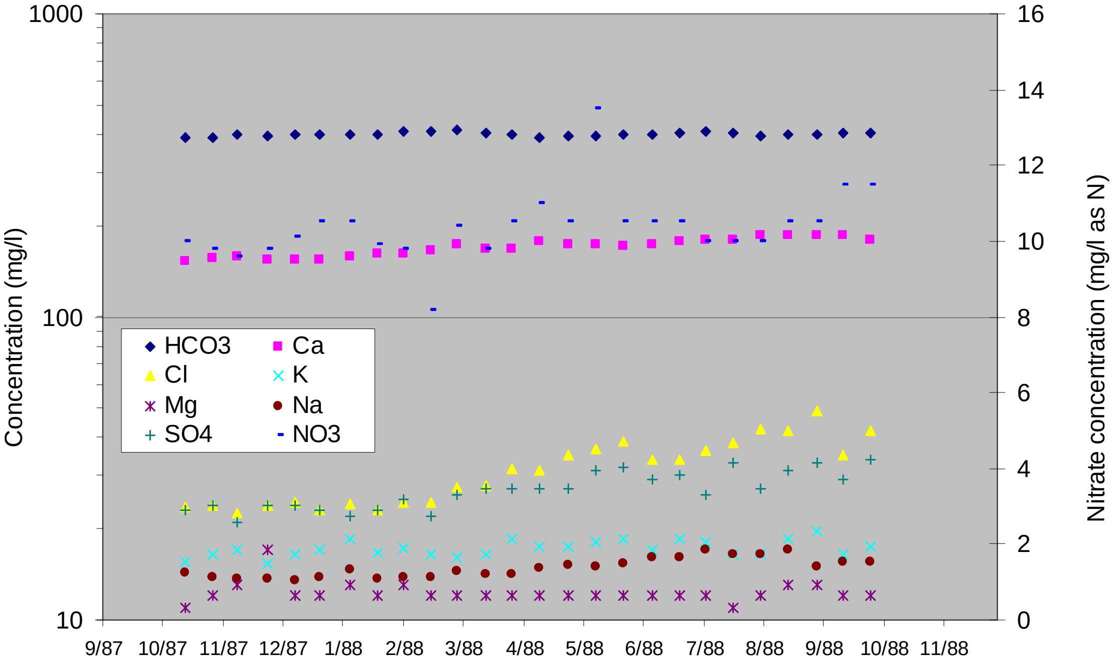

**Figure D1.4. Change in major ion chemistry at Curragh View borehole**

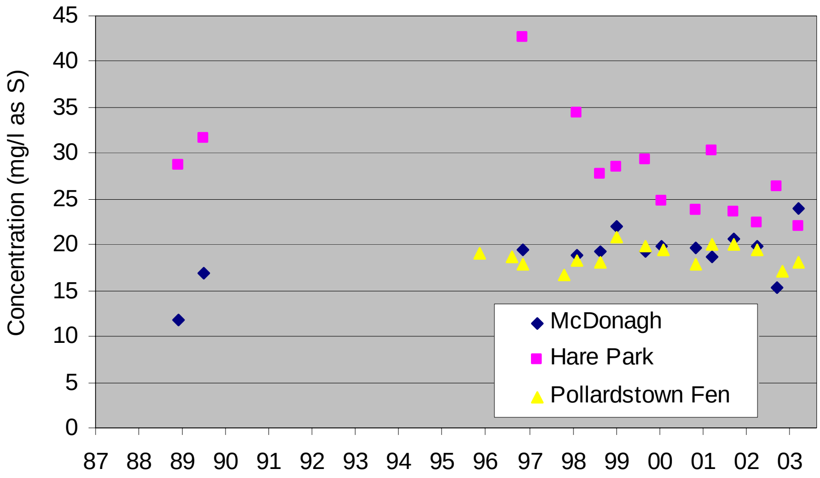

**Figure D1.5. Variation in groundwater sulphate concentrations**

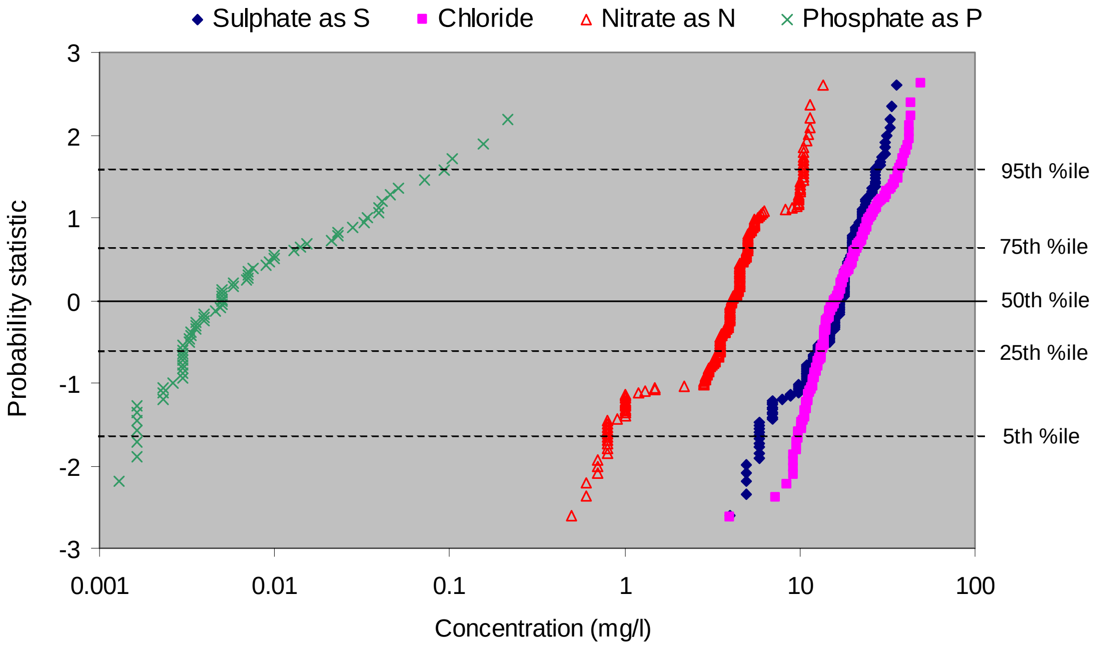

**Figure D1.6. Cumulative frequency plot for anion species**

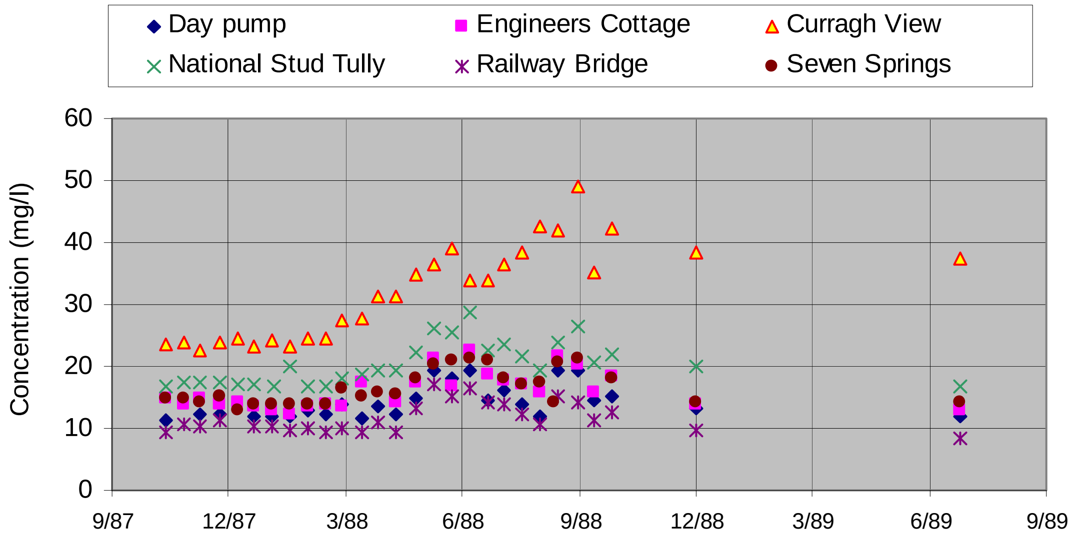

**Figure D1.7. Chloride concentrations 1987 - 1989**

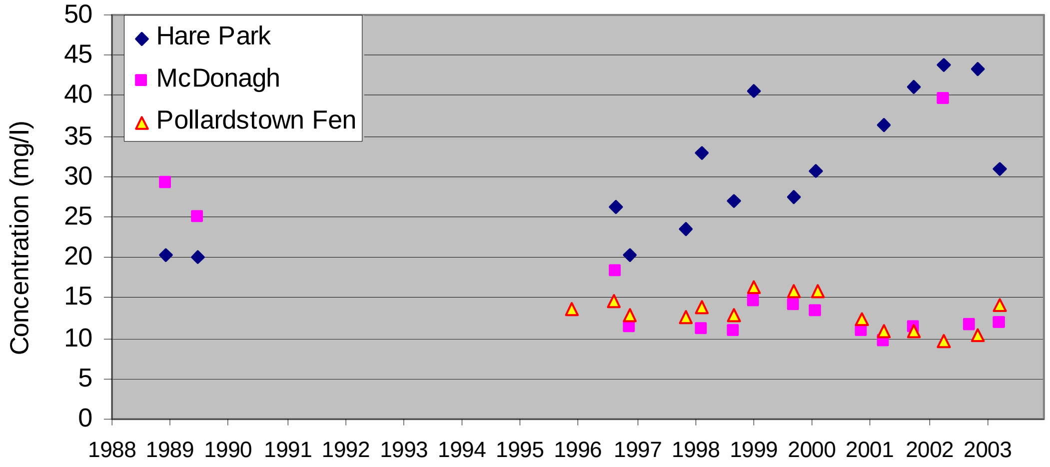

**Figure D1.8. Chloride concentrations 1988 - 2003**

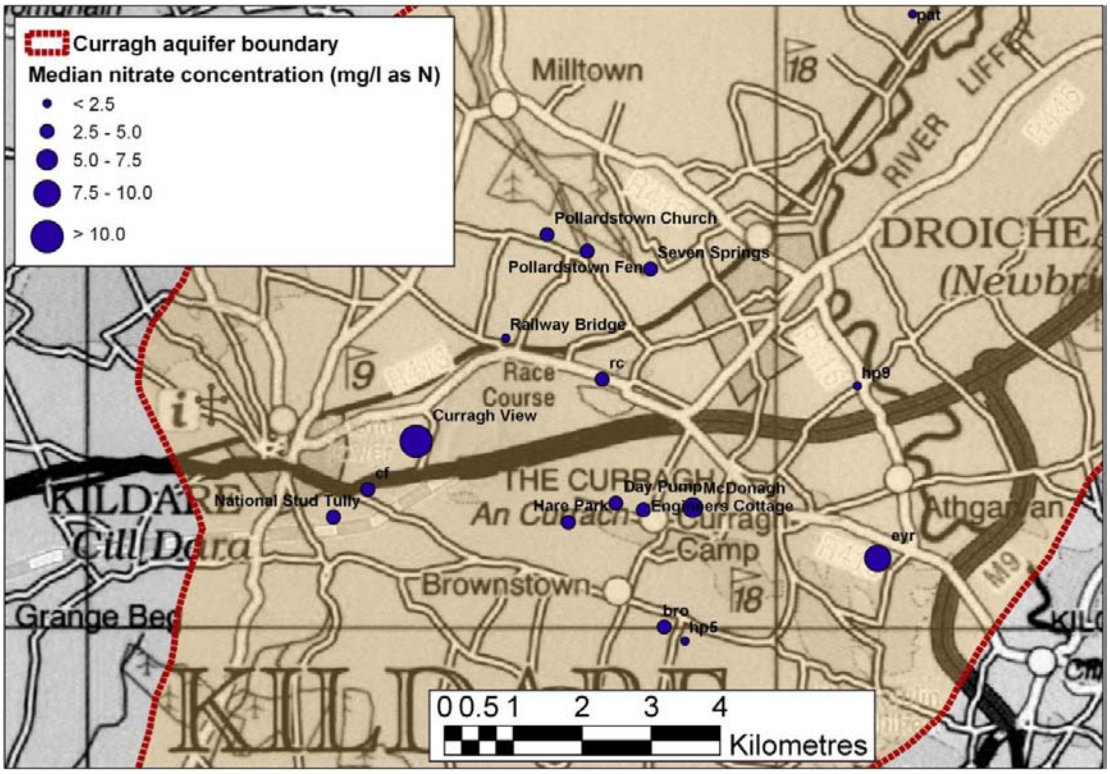

**Figure D1.9. Median nitrate concentrations**

## *The Wexford Limestone (Unit SE3)*

### Study Area

Location & boundaries

The Wexford Carboniferous Limestone aquifer comprises a thin, southward dipping limestone band, covering approximately 120 km$^2$, stretching across the Wexford peninsula to the coast on the east and south-west sides (the Irish Sea and the Atlantic Ocean respectively) (Figure D2.1). It typically consists of shallow water limestones and oolites, with micrites and dolomites, unconformably overlying Precambrian strata. Locally the strata comprise red fluviatile sandstones and shales, grading into shallow water oolitic limestones. The limestone forms part of the Limerick Province (Philcox, 1984), which is bounded to the south by the South Munster Basin and extends northwards into the Irish Midlands. The aquifer is bounded to the north by a thin band of Devonian strata marking the transition between the terrestrial Old Red Sandstone and the marine Carboniferous Limestone. North of this, crystalline Precambrian rocks crop out. To the south the Carboniferous Limestone is faulted against the Precambrian Rosslare complex.

Most of the aquifer is covered with Glacial Till, with a thickness of 5 to 15 m. It varies in texture from clay to loam and contains calcareous clay (‘marl’) horizons. Borehole logging has shown that the marl is interbedded with thick gravel lenses (Cullen, 1978), and between Mayglass and Killinick there are patchy gravel deposits, comprising shale, schist and quartz fragments.

Two main watercourses (un-named on map) traverse the groundwater body; both enter from the north. One flows east to Rosslare and the other west, discharging to the Irish Sea at Duncormick. It is likely that these rivers obtain a portion of their baseflow from the aquifer, although this may be limited by the occurrence of thick low permeability superficial deposits.

Gleysols overlie the majority of the Wexford limestone. These are soils in which vertical drainage is impeded, and have developed under permanent or intermittent water logging. The water table in such soils is likely to be near the surface. Such soils have a poor physical structure and are not generally suitable for cultivation or intensive grassland farming. The land is therefore classified as marginally suitable arable land.

Hydrogeology

The aquifer is mainly confined by the low permeability Till. Recharge and discharge, to and from the aquifer, are believed to occur mainly via the gravel deposits, and, at a slower rate through the less clayey Tills, in areas of good soil drainage. Where the limestone succession is exposed, recharge occurs to the aquifer along several streams cutting through the region (Cullen, 1978), or directly via infiltration.

No information is available concerning the primary permeability of the formation in County Wexford, although it is expected that, due to the semi-karstic nature of the aquifer, the majority of flow is fissure-related. Existing groundwater exploitation in the Wexford aquifer is from the micrite and dolomite units, and wells in these strata are high yielding. Transmissivity values of between 22 and 600 m$^2$/day, and an unconfined storage of $10^{-3}$ have been derived from pumping tests (Cullen, 1978). Hydrograph data indicate that groundwater levels in the overburden are slightly higher than in the limestone.

Regional groundwater flow directions show that groundwater flow is from the north towards the south-east and south-west.

Intensive groundwater abstraction from the aquifer started in 1978 from the three boreholes that are on the EPA monitoring network.

Rainfall and recharge

The nearest rainfall chemistry monitoring station to the Wexford Limestone groundwater body is Rosslare. Average rainfall statistics for 1992 – 1994 are presented in Table D2.15. No data on recharge to the limestone aquifer are available. An estimate of effective precipitation of 50% of the rainfall is therefore used for estimating atmospheric inputs to the aquifer.

**Table D2.15. Rainfall statistics and quality**

| **Station** | **Rain (mm/a)** | **$SO_4$ (mg/l S)** | **Cl (mg/l)** | **$NO_3$ (mg/l N)** | **$NH_4$ (mg/l N)** |
|---|---|---|---|---|---|
| Rosslare | 958 | 2.09 | 23.58 | 0.61 | 0.41 |
| Recharge depth/conc. | 480 | 4.18 | 47.16 | 1.22 | 0.82 |

## Hydrochemistry

Sample Locations

Because hydrochemical data from the Wexford limestone are limited, confidence in any interpretation is therefore limited. No more than 41 analyses were available for any single chemical species and almost all of these were from three sources with records held by the EPA (Table D2.2 and Figure D2.1). Data for 24 sampling points in 1978 (12 limestone, 12 superficial) (Cullen, 1978) contain only one analysis for each parameter. As such, the majority of data are largely from three EPA sources over the period 1993 to 2003. This means that no historical data prior to the intensification of agriculture in the early 1970s are available.

The distribution of the locations used in the 1978 sample round was broad and covered both recharge and discharge zones and areas of varying land use. The three points currently available are less representative, all lying in the north eastern half of the aquifer, in or near a discharge zone adjacent to a river running north west to south east across the Carboniferous Limestone. These limitations may be compensated for by the fact that the three monitoring points are large abstraction wells which sample a relatively large part of the aquifer.

Any difference in concentrations between the 1978 samples and the 1993-2003 samples may be due to hydrogeological changes in the aquifer due to intense abstraction that started in 1978.

**Table D2.16. Main sample point locations and dates**

| Sample Point | Source | Samples | Period |
|---|---|---|---|
| Busherstown 3 | EPA | 10 | Jun 1993 – Feb 2003 |
| Orristown | EPA | 10 | Jun 1993 – Feb 2003 |
| Rathmacknee | EPA | 9 | Jun 1993 – Oct 2002 |
| 42/108 | Cullen (1978) | 1 | Jan 1978 |
| 42/124 | Cullen (1978) | 1 | Jan 1978 |
| 42/173 | Cullen (1978) | 1 | Jan 1978 |
| 42/175 | Cullen (1978) | 1 | Jan 1978 |
| 46/1 | Cullen (1978) | 1 | Jan 1978 |
| 46/3 | Cullen (1978) | 1 | Jan 1978 |
| 47/32 | Cullen (1978) | 1 | Jan 1978 |
| 47/45 | Cullen (1978) | 1 | Jan 1978 |
| 47/53 | Cullen (1978) | 1 | Jan 1978 |
| 47/55 | Cullen (1978) | 1 | Jan 1978 |
| 47/76 | Cullen (1978) | 1 | Jan 1978 |
| 47/79 | Cullen (1978) | 1 | Jan 1978 |

### Major ion chemistry

Calcium bicarbonate, reflecting the limestone host aquifer, dominates the Wexford groundwater body chemistry (Figure D2.2). Sulphate and chloride occur as minor anionic components. Magnesium is more prevalent, as a major cation component, consistent with the dolomitic nature of the limestone. Neither sodium nor potassium is present at significant concentrations.

A box and whisker plot is presented in Figure D3.3. It has been assumed that the median concentration of chloride in groundwater originates from rainfall and all other determinands have been normalised against this. The plot shows that significant amounts of calcium and magnesium originate from sources other than rainfall, consistent with the dolomitic limestone nature of the aquifer. This is also the case for sulphate, discussed further below. Factors affecting nitrate concentrations are also discussed below.

### Regional variation

There are no systematic variations in major ion chemistry across the aquifer. Chemistry does not vary greatly through the aquifer. Calcium and magnesium levels are similar in the drift and limestone, suggesting that calcite saturation is achieved in the drift before contact with the dolomitised limestone

### Depth variation

No data are available on depth variations in hydrochemistry within the limestone.

### Temporal variation

The only significant temporal difference appears to be an increase in average sulphate concentrations between the 1978 data and the more recent data from 1993 to 2003. However, the separation of data makes it difficult to draw any trends. It is thought that the groundwater abstractions may be drawing more recharge through the Tills, which will contain a certain proportion of pyrite.

**Indicator chemistry**

Redox indicators

Dissolved oxygen levels are unavailable for the Wexford groundwater body. Since the aquifer is confined by Glacial Till, concentrations of dissolved oxygen may be low, as reducing conditions are likely to be present.

Sulphate has been detected in all except one sample; iron and manganese are unavailable for the 1978 sampling period, but manganese has been detected in all samples between 1993 and 2003 and iron has been detected at the Busherstown sample point.

**Table D2.17. Median concentrations of redox indicators (1993 – 2003)**

| | Mn (µg/l) | Fe (µg/l) | $SO_4$ (mg/l as S) |
|---|---|---|---|
| Busherstown 3 | 203 | 88 | 20.8 |
| Orristown | 255 | <50 | 22 |
| Rathmacknee | 503 | <50 | 22 |

In groundwater sampled from the limestone unit in 1978, the majority of sulphate concentrations are below 4 mg/l as S. In groundwater from the overlying superficial deposits, sulphate concentrations are significantly higher; the majority lie within the range of 5 – 30 mg/l as S. Such low concentrations within the aquifer compared to the Drift suggest that limestone groundwater was reduced. Concentrations of sulphate in the limestone for the sampling period 1993 – 2003 generally lie within the range of 19 – 25 mg/l as S. Iron concentrations are generally low, only being detected in the Busherstown borehole. This sample point lies at the northern limit of the groundwater body within the transitional zone between the underlying Devonian Old Red Sandstone and the Carboniferous Limestone.

Manganese concentrations are high in all three EPA monitoring points, and have generally increased over the monitored period (Figure D2.4). It is likely that the manganese is being released to groundwater when manganese oxides are reduced. The cause of this reduction is uncertain. Ammonium concentrations have generally increased a little over the monitored period indicating that oxidation of diffuse ammonium pollution is not the cause and that it may be a result of the natural oxidation of the organic matter in the aquifer matrix.

Nitrate is present in moderate concentrations in the groundwater body prior to 1993. All samples from 1993 – 2003 have low concentrations of nitrate (Figure D2.5) with many below the limit of detection. Although concentrations are currently low, this does not preclude the possibility of earlier pollution, now removed by reduction in confined conditions.

Generally speaking nitrates are low and manganese is correspondingly high, indicating reducing groundwater conditions, probably due to natural oxidation of organics. Very reducing conditions have not yet been reached as indicated by the low iron (detected only in the Busherstown borehole, located in the part of the aquifer most confined by drift) and relatively high sulphate concentrations (lowest in the Busherstown borehole).

Where large numbers of non-detect values are given for a determinand average values calculated can be biased by the non-detect multiplier used. Where this is a potential issue (iron, nitrate and ammonium), the AM0/AM100 ratio (Section 4.5.2 of the main report) has been calculated. In these three cases the ratio is greater than 0.6 and therefore the data are considered to be relatively unbiased.

Natural background concentration limits for dissolved oxygen have not been set due to the lack of data. Natural background concentration limits for the redox indicators, manganese, iron and sulphate, have been set using the mean plus (minus for sulphate) two standard deviations of the log concentrations. One very low outlier for manganese was removed prior to computing the limit.

The post-1993 (i.e. EPA monitoring) data are used alone to compute limits for redox indicators as these appear to sample more oxidised groundwaters. It is these waters that are being protected by the definition of a natural background limit, rather than the naturally reduced waters sampled in 1978.

**Table D2.18. Natural background concentration limits for redox indicators**

| | **Observed Range*** | **Limits** | |
|---|---|---|---|
| Dissolved oxygen (mg/l) | n/a | n/a | n/a |
| Manganese (µg/l) | <2 – 524 | Upper | 797 |
| Iron (µg/l) | <50 – 209 | Upper | 139 |
| Sulphate (mg/l as S) | <0.33 – 27.4 | Lower | 18.5 |

* for the whole groundwater body

<u>Chloride</u>

Chloride values range between 19 and 57 mg/l, with a median of 39 mg/l. Chloride concentrations show a general decline at Rathmacknee from 40 mg/l in 1993 to 34 mg/l in 2002, although no clear trends can be discerned at Busherstown 3 and Orristown (Figure D2.5). Elevated chloride trends are not consistent.

The atmospheric contribution of chloride to groundwater, assuming it is conservative through the soil zone, is calculated as 47.2 mg/l (Table D2.15). When the median concentration of chloride in the Wexford aquifer is considered against the average annual concentration of chloride in rainfall, the contribution of rainfall to effective precipitation is calculated as 60%. Concentrations in the drift, recorded in 1978, are significantly higher than those in the main aquifer, ranging between 27 and 160 mg/l.

When examined on a cumulative frequency plot (Figure D2.6), chloride concentrations exhibit a positive skew. Six samples from the 1978 sampling period show deviation from the log-normal distribution, which may reflect temporary point source pollution. The value of the 95th percentile on the cumulative frequency plot has been taken as the upper concentration limit for chloride.

**Table D2.19. Natural background concentration limit for chloride**

| | **Observed Range *** | **Limit** | |
|---|---|---|---|
| Chloride (mg/l) | 19 - 57 | Upper | 44 |

* for the whole groundwater body

<u>Nitrogen species</u>

Ammonium concentrations are very low; all concentrations are within an order of magnitude of the detection limit of 0.01 mg/l, although a rising ammonium trend is observed in groundwater from Rathmacknee (Figure D2.7).

There are a number of obvious high ammonium outliers, at concentrations above 0.05 mg/l as N, in groundwater sampled from Rathmacknee. If these are eliminated, the natural background limit can be calculated using the mean plus two standard deviations of the log concentrations of the remaining data (Table D2.5).

Low nitrate concentrations recorded in the limestone unit indicate reduced groundwaters (Figure D2.8). In groundwater sampled from the overlying superficial deposits, nitrate concentrations are fairly high; the majority lie within the range 1.2 to 6.7 mg/l as N. Any calculated limit for nitrate for groundwater in the limestone should therefore be lower, due to the naturally reduced conditions, than that calculated for unconfined areas of the groundwater body.

The atmospheric contribution of nitrate can be calculated as 1.22 mg/l as N (Table D2.15). This is greater than the majority of groundwater concentrations measured in the limestone. This cannot be applied as an upper limit to reducing groundwaters under confined conditions. Even confined groundwaters with diffuse nitrate pollution may exhibit nitrate concentrations less than this limit. Consideration should therefore be given to the mapping of confined and unconfined areas of the limestone and it is considered that nitrate in groundwater should remain below the rainfall concentration in unconfined areas.

The best estimate is that the upper limit should be based on the estimated infiltration contribution of 1.22 mg/l as N, scaled by the ratio between the 95th percentile and estimated infiltration concentrations of chloride.

**Table D2.20 Natural background concentration limits for nitrogen species**

| | **Observed Range*** | **Limits** | |
|---|---|---|---|
| Nitrate (mg/l as N) | <0.0023 – 6.946 | Upper | 1.38 |
| Ammonium (mg/l as N) | <0.003 – 0.073 | Upper | 0.18 |

* for the whole groundwater body

pH and Alkalinity

pH varies from 7.2 to 7.8 and the alkalinity is correspondingly high, at 268 to 568 mg/l as $CaCO_3$. These indicate alkaline conditions typical of carbonate terrains. Risk of acidification is therefore minimal in this well buffered aquifer and derivation of natural background limits is meaningless in that context.

Lower limits have been set at the mean concentration minus two standard deviations. Log concentrations were used for the alkalinity, pH values were used directly.

| | Observed Range | Limits | |
|---|---|---|---|
| pH | 7.2 – 7.8 | Lower | 7.2 |
| Alkalinity (mg/l as $CaCO_3$) | 268 – 568 | Lower | 271 |

Electrical Conductivity

Groundwater conductivity varies from 661 to 739 µS/cm. These are quite high, but the waters are very hard: hardness values tend to be around 320 mg/l as $CaCO_3$ (Main report: Table 6). As the Wexford aquifer is bounded by both the Irish Sea and the Atlantic Ocean, and contains several large groundwater abstractions, saline intrusion is a potential risk.

When examined on a cumulative frequency plot (Figure D2.9), the data exhibit a good fit to a log-normal distribution, with only three points showing deviation. This suggests that that little saline mixing or pollution has yet occurred. Chloride concentrations are also not particularly high for the groundwater body. The upper limit value has been set at the 95th percentile value.

| | **Observed Range** | **Limit** |
|---|---|---|

| | | | |
|---|---|---|---|
| Electrical Conductivity (µS/cm) | 661 – 739 | Upper | 700 |

Sulphate

Sulphate concentrations are slightly higher in the Orristown and Rathmacknee boreholes. Potassium concentrations do not vary with sulphate, and are approximately consistent around the median of 1.8 mg/l, suggesting that variation in these chemicals is not necessarily derived from fertiliser use.

The atmospheric contribution of sulphate can be calculated as 4.18 mg/l as S (Table D2.15). This is a small fraction of the majority of measured groundwater concentrations and indicate that there is significant additional sulphate input to the system.

When examined on a cumulative frequency plot (Figure D2.10), the recent data for the Busherstown 3, Orristown and Rathmacknee boreholes exhibit a log-normal distribution and the 95th percentile concentration has been taken as the upper concentration limit.

**Table D2.21. Natural background concentration limit for sulphate**

| | Observed Range | Limit | |
|---|---|---|---|
| Sulphate (mg/l as S) | 19.3 – 27.4 | Upper | 25.8 |

Phosphate

Most phosphate concentrations vary about the detection limit of 0.02 mg/l as P. Concentrations are therefore too low to use for meaningful analysis. The best estimate is that the natural background upper limit should, at present, be the detection limit.

**Table D2.22. Natural background concentration limit for phosphate**

| | **Observed Range** | **Limit** | |
|---|---|---|---|
| Phosphate (mg/l as P) | < 0.02 | Upper | 0.02 |

Metals

There are limited data available between 1993 and 1997 for heavy metals in the Wexford Aquifer. All data for cadmium, chromium and arsenic were below the detection limit and therefore upper concentration limits for these species have been set at the current limits of detection.

Historically lead and zinc were mined in the Wexford area. Due to the limited data the upper limit values for these metals have been set at the mean plus two standard deviations of the log concentrations.

**Table D2.23. Natural background concentration limits for heavy metals**

| | **Observed Range** | **Limits** | |
|---|---|---|---|
| Cadmium (µg/l) | < 0.1 | Upper | 0.1 |
| Arsenic (µg/l) | n/a | Upper | 1 |
| Lead (µg/l) | 1 – 2 | Upper | 3.5 |
| Mercury (µg/l) | n/a | Upper | 0.1 |
| Zinc (µg/l) | 6 – 85 | Upper | 554 |

Natural background groundwater quality

The data available are limited both in terms of geographical and temporal spread. Any conclusions are therefore very tentative at this stage. Additionally, although there are some historical data for 1978, there are no data that pre-date the intensification of agriculture in 1973, so the impact of increased agricultural production on recharge to groundwater cannot be assessed.

Groundwater is reducing and appears to become slightly more so in a northerly direction, where it is under increasingly confined conditions.

**Table D2.24 Natural background concentration limits for indicator species**

| | **Observed Range** | **Limits** | |
|---|---|---|---|
| Dissolved oxygen (mg/l) | n/a | n/a | n/a |
| Manganese (µg/l) | <2 – 524 | Upper | 797 |
| Iron (µg/l) | <50 – 209 | Upper | 139 |
| Nitrate (mg/l as N) | <0.0023 – 6.946 | Upper | 1.38 |
| Ammonium (mg/l as N) | <0.003 – 0.073 | Upper | 0.18 |
| Electrical conductivity (µS/cm) | 661 – 739 | Upper | 700 |
| pH | 7.2 – 7.8 | Lower | 7.2 |
| Alkalinity (mg/l as $CaCO_3$) | 268 – 568 | Lower | 271 |
| Chloride (mg/l) | 19 – 57 | Upper | 44 |
| Sulphate (mg/l as S) | 19.3 – 27.4 | Upper | 25.8 |
| Sulphate (mg/l as S) | <0.33 – 27.4 | Lower | 18.5 |
| Phosphate (mg/l as P) | < 0.02 | Upper | 0.02 |
| Cadmium (µg/l) | < 0.1 | Upper | 0.1 |
| Arsenic (µg/l) | n/a | Upper | 1 |
| Lead (µg/l) | 1 – 2 | Upper | 3.5 |
| Mercury (µg/l) | n/a | Upper | 0.1 |
| Zinc (µg/l) | 6 – 85 | Upper | 554 |

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**Philcox, M. E. 1984.** Lower Carboniferous Lithostratigraphy of the Irish Midlands. Irish Association for Economic Geology, Dublin, 89 pp.

## FIGURES

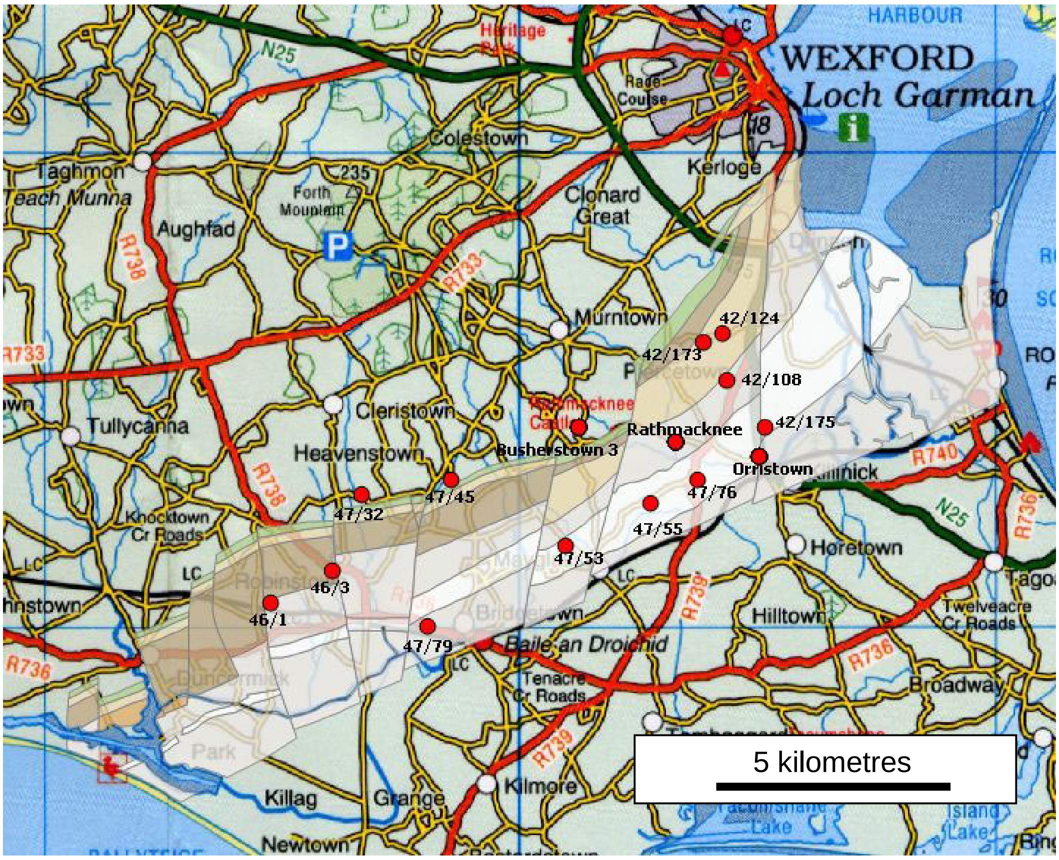

**Figure D2.1 Outcrop location and sampling points within the Wexford Limestone aquifer**

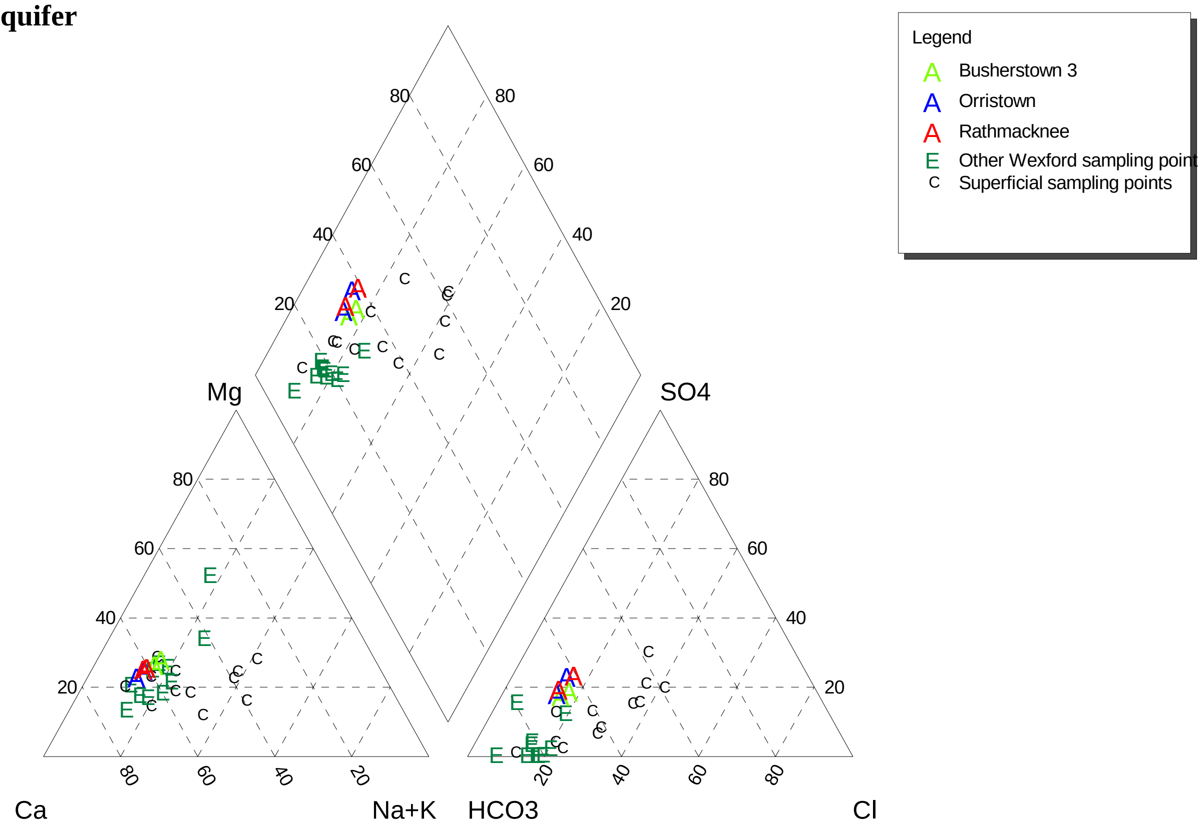

**Figure D2.2. Piper plot for the Wexford Limestone**

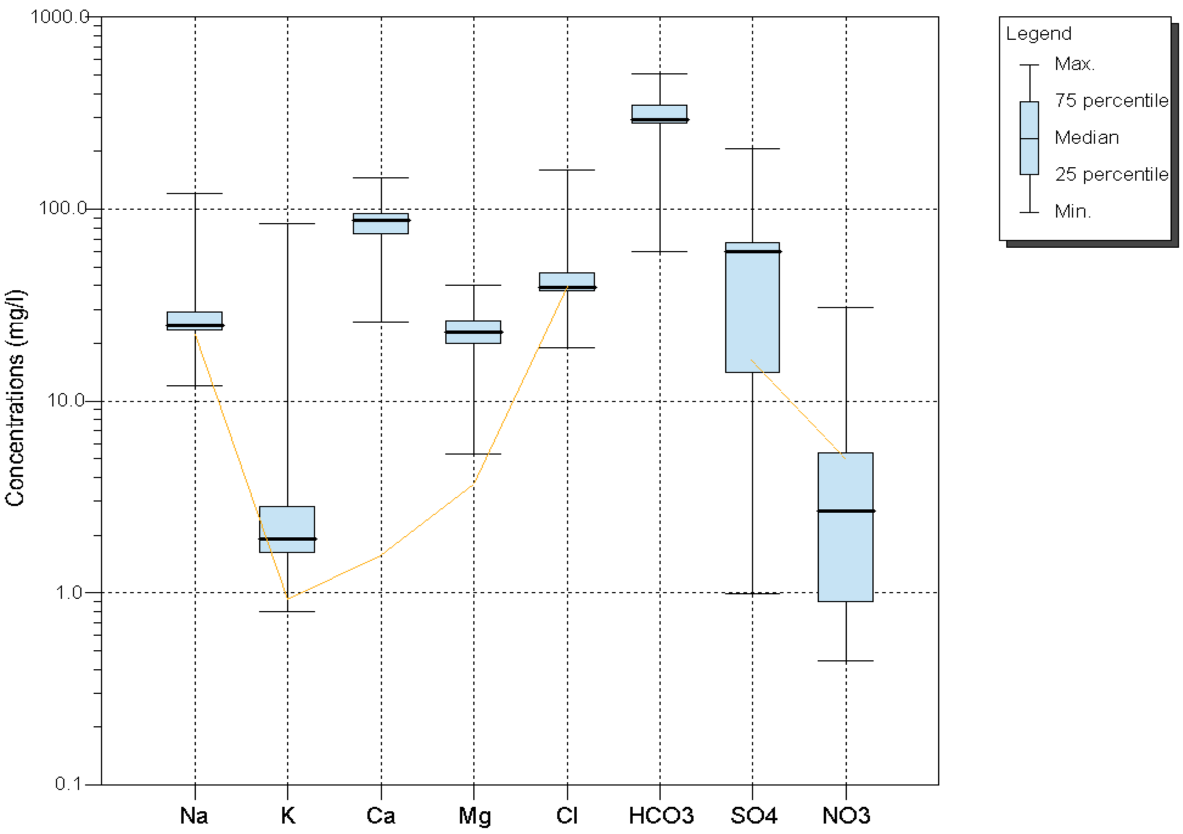

**Figure D2.3. Box and whisker plot for total major ion concentrations within the Wexford Limestone aquifer. Orange line shows rainfall composition normalised to median groundwater chloride concentration. Note: alkalinity is given as a negative number so is not shown on the diagram.**

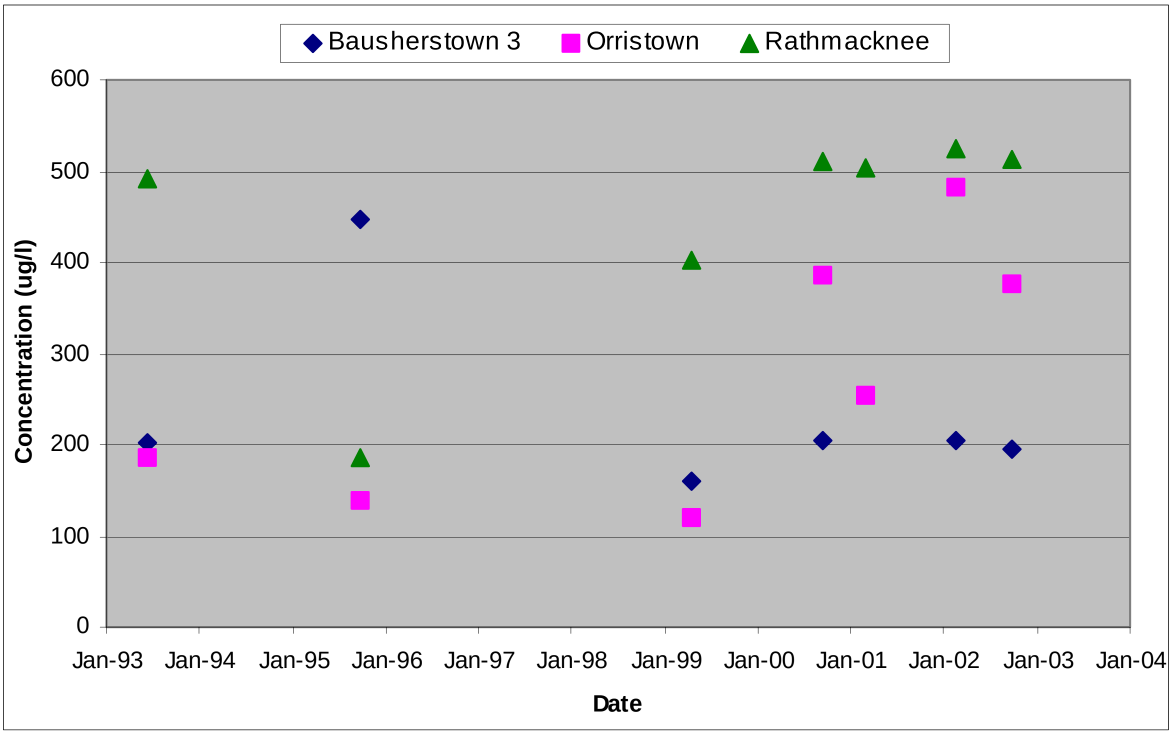

**Figure D2.4. Variations in manganese concentrations with time**

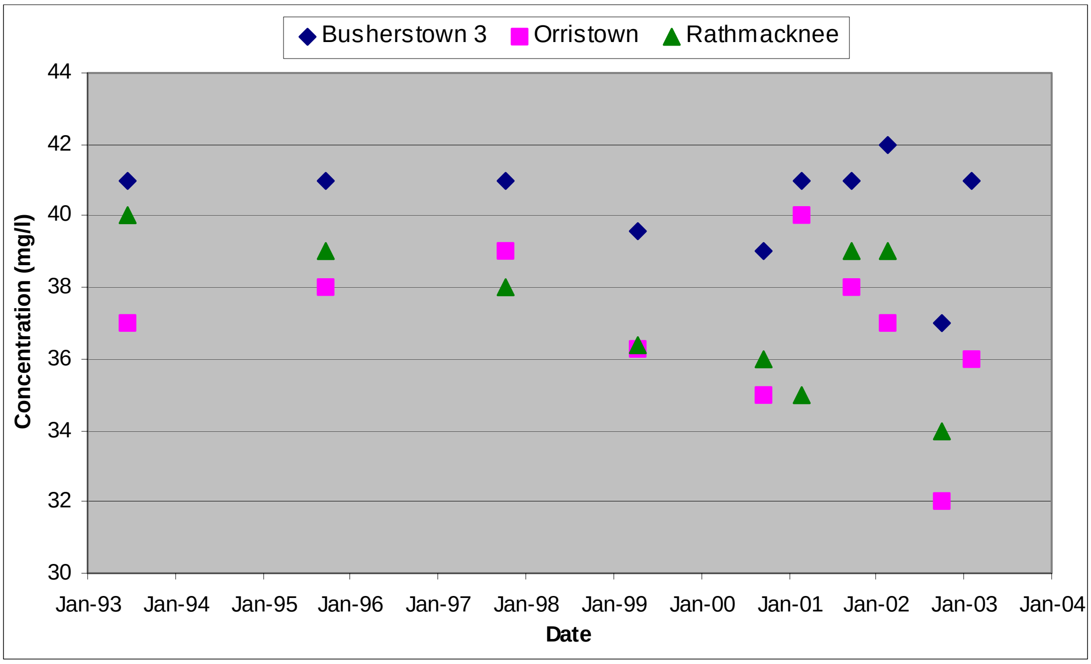

**Figure D2.5. Variations in chloride concentrations with time**

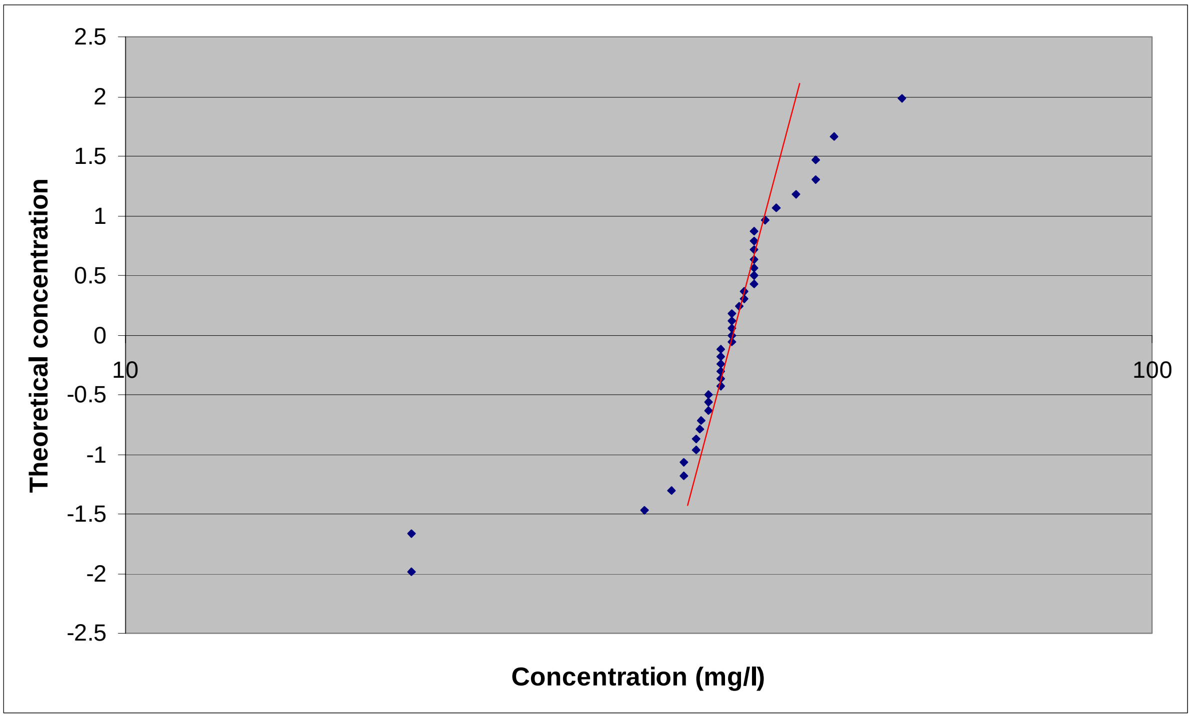

**Figure D2.6. Cumulative frequency plot of chloride concentration in the Wexford aquifer**

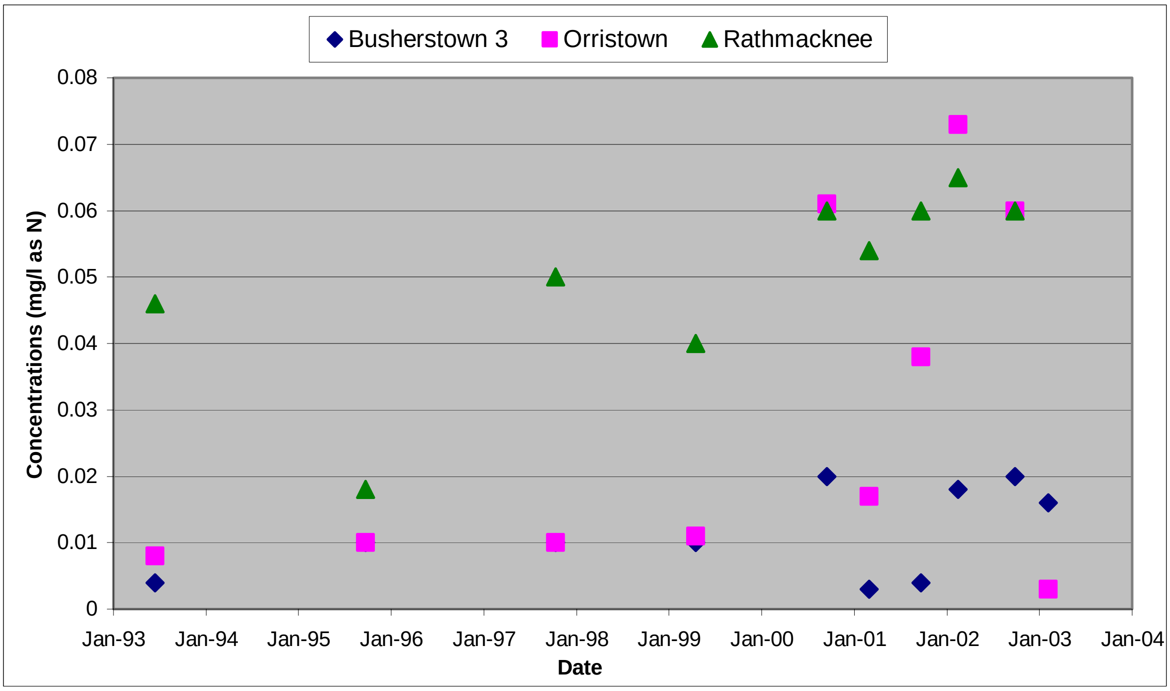

**Figure D2.7. Variations in ammonium concentrations with time**

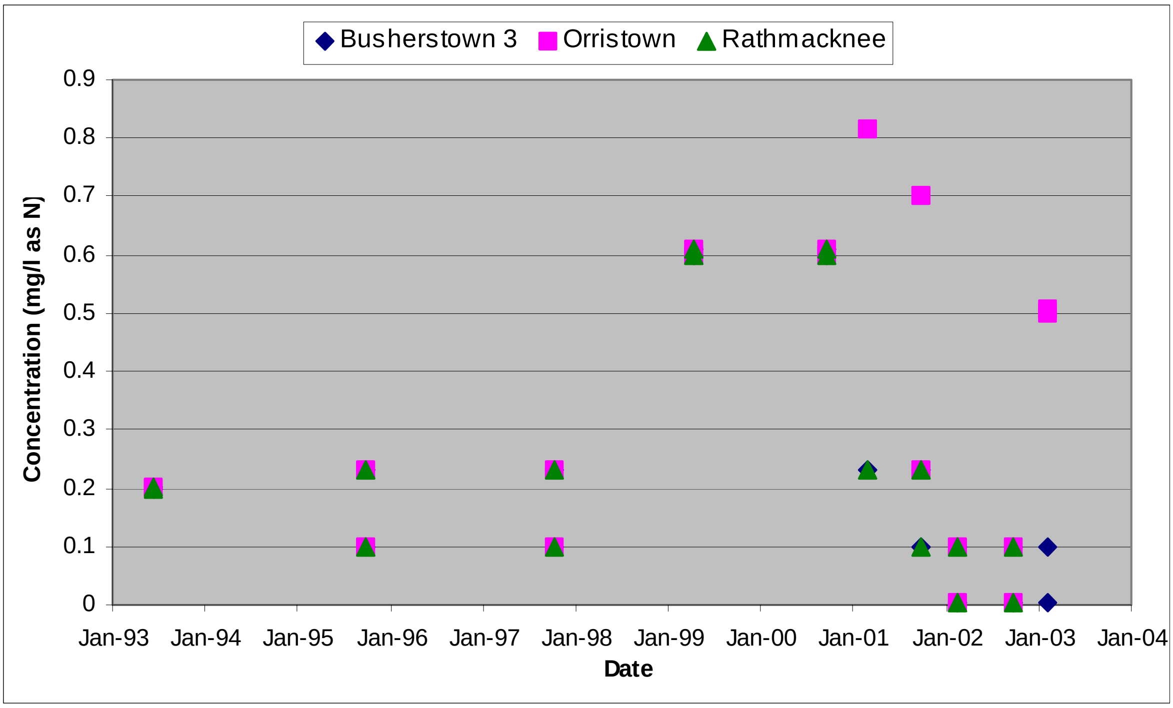

**Figure D2.8. Variation in nitrate concentrations with time**

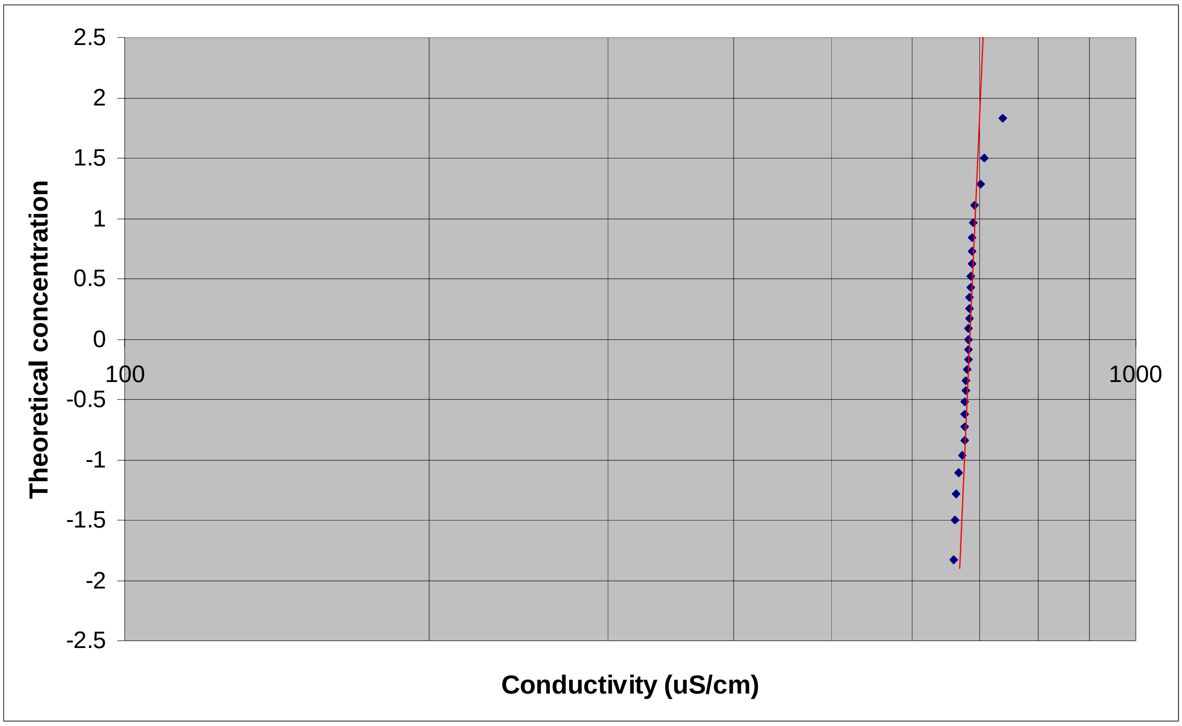

**Figure D2.9 Cumulative frequency plot of electrical conductivity in the Wexford aquifer**

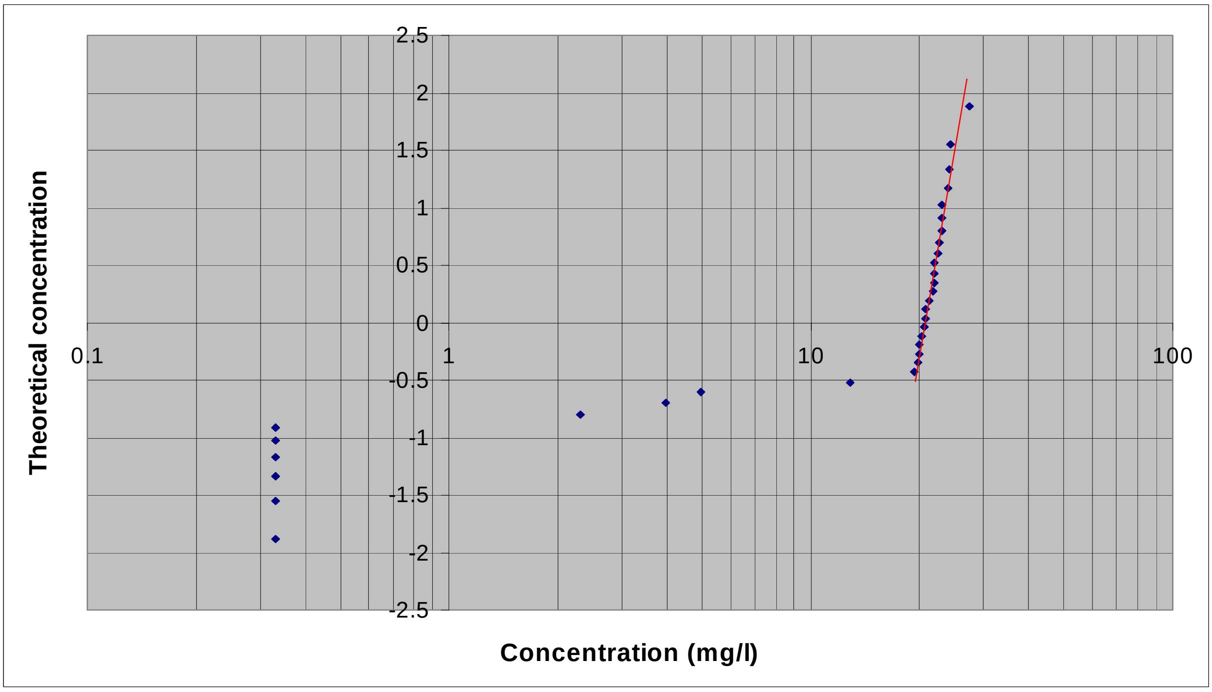

**Figure D2.10 Cumulative frequency plot of sulphate concentration in the Wexford aquifer**

## *The Devonian Old Red Sandstone*

### Study Area

Location & boundaries

The Devonian Old Red Sandstone (ORS) system in the South East River Basin District (SERBD) comprises a number of groundwater bodies that are geologically continuous. However, they are subdivided on the basis of surface water catchment boundaries as approximations of groundwater divides. Its outcrop within the SERBD is approximately 1160 km$^2$ in area.

Some of the defined groundwater bodies contain no groundwater sampling points, the rest very few. On this basis, the characterisation of natural background limits for individual groundwater bodies would be problematical due to the lack of data. The Old Red Sandstone groundwater bodies within the SERBD have therefore been grouped together and the data from sampling points aggregated to provide sufficient data to enable characterisation of natural background limits for the whole unit.

As shown on Figure D3.1, the majority of the ORS outcrop occurs in the south in County Waterford and the southern part of County Kilkenny and is exposed from Kilworth and the Knockmealdown Mountains in the west to the Comeragh Mountains in the east. A north east trending band approximately 80 km in length forms the southern margin of a Silurian and Devonian inlier comprising the Galty, the Slievenamon and Slieve Phelim Mountains. The ORS consists predominantly of coarse-grained sandstones, mudstones and conglomerate bands.

The western limit of the group of groundwater bodies coincides with the boundary of the SERBD, which is a surface water divide, which has been assumed to coincide with the groundwater divide. The southern part of the group of groundwater bodies falls within the eastern part of the Munster Basin, in which the Old Red Sandstone is approximately 1000 m thick at the north and eastern boundaries, and thickens to the south and west (Graham, 2001). These strata unconformably overlie Silurian Quartzites. The northern ORS outcrops thin rapidly from County Tipperary into County Laois

The predominant drift deposit seen in the area is the limestone-clast dominated Glacial Till. The southern depositional limit of this approximately coincides with the foot of the steep northern escarpments of the Galty, Comeragh and Knockmealdown Mountains, such that the majority the Old Red Sandstone is unconfined and relatively drift-free.

The land supported by the ORS is of mixed arable suitability. The upland mountainous regions with thin soil cover support minimal agriculture, however the lowland areas, with loamy soil cover can be highly suitable for arable farming (Diamond and Shanley, 1998). The Suir Valley runs through the centre of Kilkenny, and is one such fertile area. The central river plain of the Suir comprises predominantly grey brown podzolics with a transition to acid brown earths downstream from Clonmel to Waterford Harbour. To the north west and south of the catchment, the mountainous areas host peats and bare rock with brown podzolics changing to gleys at lower levels. In the north eastern area there is significant peat cover.

The River Barrow and the River Suir are the principal watercourses that traverse ORS outcrop. However, neither traverses significant stretches of the aquifer so contributions to their baseflow are likely to be small. Baseflow contributions from the ORS to smaller rivers such as the Blackwater River, which traverse the ORS and form tributaries to the principal watercourses, are likely to be more significant.

Agricultural sources make up 57% of the pollution load in the River Suir (pollutants not specified), and of this, 71% is from diffuse sources (MCOS, 2002). Water quality appeared to deteriorate in the Suir catchment during the lifetime of the MCOS (2002) study (2000 –2001).

Hydrogeology

The Old Red Sandstone was deposited in non-marine clastic environment and contains a high percentage of fine-grained material, including mud and siltstones. Its primary permeability is therefore negligible. The unit is however considered to be a moderately productive aquifer in areas where intense folding and faulting provides some very local zones of secondary permeability. In addition, the basal contact of the ORS with lower Palaeozoic strata forms a high permeability zone at depth (Daly *et al*. 2001).

The aquifer is predominantly unconfined, with the average water table less than 15 m below ground surface. Where superficial sand and gravel deposits exist, the ORS is generally in hydraulic continuity with them and where Glacial Till overlies the bedrock, confined conditions may result. Confined conditions also occur at the centre of synclines where the formation is found at depth and artesian conditions have been recorded (Daly *et al*. 2001). Pockets of confined groundwater may also exist where low permeability mudstones and siltstones occur. The Cloran and Thomastown sample points may be monitoring ORS confined under Glacial Till, however there are insufficient water level data to confirm this.

The topmost unit of the Old Red Sandstone is the Kiltorcan Formation in which the deepest groundwater flows are likely to occur. Its permeability depends upon the proportion of sandstone present, the thickness of the individual sandstone units and their degree of interconnection. These strata are relatively susceptible to surface weathering and, where this has occurred, intergranular permeability will be increased. This weathered zone may be up to 15 m in places (Daly, 1992) underlain by up to 30 m of well fractured bedrock and a poorly fractured zone, up to a further 60 m in thickness.

Extensive work carried out on this aquifer in the Nore Basin indicates that transmissivities of up to 500 $m^2$/day are common, and the public water supply at Thomastown yields 1000 $m^3$/day (Daly *et al*. 2001). Specific yield is normally about 2% although near the surface it can be as high as 5% (Daly, 1988). Dry weather flows for the Blackwater River catchment upstream of Mullinavat, which is almost entirely underlain by the ORS are very low, which suggests that the aquifer has a low storage capacity as these flow quantities are low during summer months.

The overall groundwater flow direction is likely to be southward to the sea. However, groundwater will also discharge to the Rivers Suir and Barrow and their tributaries, resulting in some local variations in the direction of groundwater flow.

Annual rainfall in Kilkenny for the period from 1961 to 1990 ranged from 820 mm to 1100 mm, between the mid-Kilkenny lowlands and the uplands in the south of the county (Fitzgerald and Forrestal, 1996). Annual rainfall in the south Tipperary uplands varies from between 1000 mm in the east to 1800 mm in the west and south. Lowland areas receive less than 1000 mm per annum. The effective rainfall for south Tipperary is estimated by Fitzgerald and Forrestal (1996) as 535-575 mm/year and 525-1325 mm/year for the lowlands and uplands respectively.

Rainfall and recharge

The closest rainfall chemistry monitoring station to the group of groundwater bodies is at Cork Airport; average rainfall statistics for 1992-1994 are presented in Table D3.25. The highest effective rainfall value for the lowlands (575 mm/a) is used to estimate solute concentrations in infiltration, assuming that the species are conservative through the soil zone.

Because Cork is on the south coast, a sea water influence on the rainfall chemistry and concentrations may be higher than appropriate for the entire ORS groundwater body. The Kinnity monitoring station is located inland, to the north of the groundwater body, and the marine influence on rainfall chemistry will therefore be less. The data for the two stations have therefore been averaged to obtain representative concentrations for the groundwater body as a whole.

**Table D3.25. Rainfall statistics and quality**

| Station | Rain (mm/a) | $SO_4$ (mg/l S) | Cl (mg/l) | $NO_3$ (mg/l N) | $NH_4$ (mg/l N) |
|---|---|---|---|---|---|
| Cork Airport | 1266 | 0.88 | 6.82 | 0.27 | 0.29 |
| Kinnity | 904 | 0.78 | 6.68 | 0.12 | 0.07 |
| Average value | 1085 | 0.83 | 6.75 | 0.195 | 0.18 |
| Recharge depth/conc. | 575 | 1.57 | 12.74 | 0.37 | 0.34 |

Aquifer mineralogy

In the absence of specific references to the mineralogy of the Old Red Sandstone in Ireland, it is suggested that the composition will depend upon and reflect the source rocks and the products of diagenesis. Iron oxides are ubiquitous in the ORS, giving it the characteristic red pigmentation. These are thought to have formed via dehydration of ferric hydroxides (FeOOH) in the dryer and hotter post depositional environment of the ORS.

General fining up sequences are seen in the ORS outcrop and also a fining towards the centre of the Munster Basin in the south. Marginal sediments are generally locally derived from the Silurian sediments of the Comeragh Mountains and the Waterford Volcanic Belt, however the bulk are thought to be derived from volcanic basement rocks in the north and west of Ireland (Graham, 1983; Price, 1986).

In the east of the Munster Basin, sediments were deposited from the north, and are dominated by vein quartz and quartzite. In Tipperary the Upper ORS is dolomitised in places, commonly with a soluble dolomitic or calcareous cement and containing easily weathered feldspars.

Lead concentrations within the ORS are known to be naturally high in the Silvermines area of Tipperary (EPA, 2002), in Old Red Sandstone are just adjacent to the SERBD. The aquifer characteristics seen are therefore likely to apply to the Tipperary ORS and perhaps to the remainder of the ORS within the SERBD, which have been subject to the same orogenic and diagenetic processes. Mean soil concentrations in the Silvermines area were found to be significantly elevated, at 782 mg/kg (EPA, 2002). For comparison, the mean soil lead concentrations across rural areas of Ireland range from 17.6 mg/kg to 38.1 mg/kg (EPA, 2002).

## Hydrochemistry

Sample Locations

As discussed in Section 4.4.1 in the Main Report, the spatial distribution of monitoring points is a key factor in obtaining data representative of the entire aquifer. The seven monitoring points available for the Old Red Sandstone are suitably distributed across the aquifer and provide adequate coverage of the aquifer to allow regional hydrochemical variations to come to light. However, without detailed hydrogeological information it is difficult to determine which points are located in recharge and discharge zones.

There are a limited number of sample points and associated hydrochemical data available for the ORS and therefore a degree of uncertainty exists in the interpretation of these data. Data are available for seven groundwater monitoring points within the period October 1991 to February 2003. No one location has data for every year and some have very limited time series data. Given the recent dates for which data are available, historic information regarding groundwater quality prior to the intensification of agriculture in 1973 could not be obtained. Ionic balances are in general, good, however, several of the recent samples from the EPA database have ionic balance errors greater than ±10%.

The seven sample points and the dates for which data are available are listed in Table D3.26, locations are shown on Figure D3.1.

**Table D3.26. Sample point locations and dates**

| Name | No. of sampling events | Period |
|---|---|---|
| Grange | 9 | June 1993 – Sept 2001 |
| Poulavanogue | 8 | June 1993 – Feb 2003 |
| Cloran | 7 | Oct 1991 – Oct 2000 |
| Thomastown WS | 7 | Nov 1993 – Feb 2003 |
| Ironmills | 8 | May 1993 – Feb 2003 |
| Drombane WS | 3 | Sept 1993 – Nov 1999 |
| Knock GWS | 2 | Sept 1993 – Jan 1996 |

### General

The predominance of limestone and limestone-derived subsoils in south Tipperary results in a groundwater rich in calcium bicarbonate (Figure D3.2). In areas underlain by Silurian rocks and where no limestone is present, sodium chloride rich groundwaters have also been identified.

A box and whisker plot showing the distribution of concentrations of major ions in the groundwater is presented in Figure D3.3. The rainfall contribution to infiltration is superimposed. It is assumed that the median chloride concentration in groundwater is entirely derived from rainfall. The other determinands have been normalised to show their proportional contribution to infiltration. All sodium in the groundwater appears to be derived from rainfall. The predicted infiltration concentration of potassium passes through the minimum concentration for groundwater, indicating that there are other sources of potassium in addition to rainfall, such weathering of silicate minerals, or application of agricultural fertilisers.

In the Galtee and Slievenamon areas groundwater displays low total hardness values which indicate that the subsoils overlying the Old Red Sandstone contain little carbonate minerals. Groundwaters in the Slieveardagh Uplands area are also relatively soft. Daly *et al.* (2001) suggests that lithology is a dominant factor in controlling the Mg/Ca ratio of groundwaters. The presence of dolomite commonly results in increased Mg concentrations.

Surface water quality in the study area is good: a survey of dangerous substances in surface freshwaters (EPA, 2001) included analysis of the waters of the Rivers Barrow, Suir, Nore and Blackwater. All measured parameters, which included a comprehensive list of metals, pesticides and VOCs, were well below the EQS/WQS proposed by the EPA, with the exception of barium. Barium was found to be considerably elevated in all these watercourses, except for the River Blackwater, and is thought to be due to the natural geology of the region, and the mineralogy of the strata (EPA, 2001). A survey of pesticides in Irish drinking water supplies (EPA, 1995) showed no detectable levels of pesticides in supplies from this groundwater body.

### ORS sample data

The alkalinity of the sampled groundwater varies across the groundwater body. The northern and eastern sample points of Knock, Ironmills, Drombane and Thomastown all show alkalinities between 200 and 300 mg/l $HCO_3$, whereas those in the central part of the study area are much less alkaline, with median concentrations of 126, 25 and 8 mg/l $HCO_3$ at Grange, Polavanogue and Cloran respectively. The water is also notably softer in Cloran and Polavanogue and has a lower electrical conductivity.

Concentrations of the metals analysed (iron, manganese, potassium, sodium, calcium and magnesium) are typically low across the study area. The Grange borehole in the south commonly exhibits the highest concentrations. Magnesium and calcium concentrations are lowest at Poulavanogue, where the water is softest.

Depth variation

There are no data available pertaining to the depth of samples and the potential variation in hydrochemistry with depth.

Temporal variations

Time series data for nitrate (Figure D3.4) show relatively constant concentrations over the monitored period, with the exception of the Grange borehole, which shows a significant overall decrease from over 20 mg/l as N in 1993 to less than 5 mg/l as N in 2001.

Sulphate concentrations are also fairly constant (Figure D3.5), again with the exception of the Grange borehole which shows a significant decrease.

Concentrations of iron (Figure D3.6) show a general increase with time, with the Grange borehole showing a significant increase in the most recent measurements. There is no clear trend in the manganese concentrations (Figure D3.6), although again a rapid increase is seen in recent measurements at the Grange borehole.

Concentrations of ammonium (Figure D3.7) are typically low throughout the monitored period, with intermittent peaks possibly due to point sources of pollution. However, at these low concentrations they may be due to data quality issues.

An overall decrease in chloride concentrations (Figure D3.8) is seen in both the Ironmill and Grange boreholes over the monitored period, although they remain at concentrations higher than all the other sites, which have stayed relatively constant over time.

From these data it appears that the Grange borehole may have been subject to contamination during the early part of the monitored period and concentrations of a number of determinands remain elevated in the most recent records. Data for the Grange borehole will therefore be omitted from further analysis of the natural background condition.

### Indicator chemistry

Redox Indicators

Dissolved oxygen concentrations are not available for the ORS. Given its generally unconfined nature relatively high values would be expected, except where it is confined by Glacial Till, or where the aquifer occurs at depth.

From the limited data available it appears that, broadly speaking, groundwater is most reduced at Cloran, where the lowest nitrate and sulphate concentrations, and relatively high manganese and iron concentrations are observed. However at the Grange borehole a change in the oxidation state of the groundwater has taken place over the monitored period, with it becoming increasingly reduced since monitoring began in 1993 (Figures D3.4 to D3.7). This indicates that pollution to groundwater may have occurred; therefore in calculating natural background concentration limits for the groundwater body, data from this location will be omitted.

Where large numbers of non-detect values are given for a determinand, calculated average values can be biased by the choice of non-detect multiplier. Where this is possible, the AM0/AM100 ratio has been calculated for manganese and iron. In all these cases the ratio is lower than 0.6 and therefore conclusions drawn from the data can only be tentative. There are insufficient data to construct a cumulative probability plot and therefore the mean plus two standard deviations of the log concentration will be used to calculate the natural background limit values, using data from the sample points that are considered to be at natural background quality. There are too few values for manganese to provide a reliable value, therefore a limit has not bee derived.

Although sulphate can be used as a semi-quantitative indicator for the redox state of the groundwater in the study area, the natural concentrations of sulphate in the aquifer are very low and therefore an upper concentration limit only will be set.

The concentration limit for dissolved oxygen, for which there are no data, has been based on 95% saturation of groundwater at 15ºC. The calculated natural background concentration limits are presented in Table D3.27.

**Table D3.27. Natural background concentration limits for redox indicators**

| | Observed Range* | Limit | |
|---|---|---|---|
| Dissolved Oxygen (mg/l) | n/a | Upper | 9.4 |
| Manganese (µg/l) | <1 – 7 | Upper | n/a |
| Iron (µg/l) | < 50 – 105.1 | Upper | 91 |
| Sulphate (mg/l as S) | 1 – 16 | Lower | n/a |

*for the entire groundwater body, with the exception of Grange borehole data.

Chloride

With the exception of the Grange borehole and Thomastown, chloride values are typically less than 20 mg/l across the study area.

The atmospheric contribution of chloride to groundwater given in Table D3.25 is 12.74 mg/l. This is a significant fraction of the measured chloride concentrations in groundwater and this suggests that groundwaters in the study area are at natural background concentrations with respect to anthropogenic chloride.

The reasons for the elevated concentrations at Grange and Thomastown are uncertain. These data have been excluded from further analysis and a natural background concentration limit calculated using the mean plus two standard deviations of the log concentrations for the remaining data.

**Table D3.28. Natural background concentration limits for chloride**

| | Observed Range* | Limit | |
|---|---|---|---|
| Chloride (mg/l) | 9 – 21 | Upper | 22.1 |

*for entire groundwater body, with the exception of Grange and Thomastown.

Nitrogen species

In general nitrate concentrations in the aquifer are fairly high, although the Drinking Water Standard (50 mg/l as $NO_3$) is not exceeded at any location. An atmospheric contribution of nitrate to groundwater of 0.37 mg/l as N is calculated in Table D3.25. Whilst this is a fraction of the measured nitrate concentrations in groundwater, the main fraction of nitrogen remains unaccounted for. It is therefore likely that the groundwaters of this study area are polluted by anthropogenic nitrate both from the atmosphere and from direct inputs such as agriculture. Ammonium concentrations are generally low, the highest (0.06 mg/l as N) is seen in the central area of ORS outcrop at Cloran.

The decrease in nitrate concentrations at the Grange borehole is consistent with the increasingly reduced conditions seen at this location. Elsewhere no significant trends are seen in the nitrate or ammonium time series data.

Due to existing contamination, natural background concentration limits for nitrate cannot be calculated. Instead, it is suggested that groundwater concentrations should not exceed that of the infiltration, calculated in Table D3.25 as 0.37 mg/l as N, scaled by the ratio between the 95th percentile and estimated infiltration concentrations of chloride.

It is unlikely that the aquifer is still in its natural state with regards to ammonium concentrations, since it has been shown to be subject to anthropogenic nitrogen inputs. However, concentrations are too low to use for meaningful analysis. The best estimate is that the natural background limit should currently be the detection limit.

**Table D3.29. Natural background concentration limits for nitrogen species**

| | Observed Range | Limit | |
|---|---|---|---|
| Nitrate (mg/l as N) | < 0.1 – 7.4 | Upper | 1.21 |
| Ammonium (mg/l as N) | < 0.003 – 0.38 | Upper | 0.003 |

Electrical Conductivity

Electrical conductivity of the groundwater varies widely and is lowest in the central part of the study area, where the water is also softest. The Grange borehole is the only site at potential risk from saline intrusion, however the groundwater chemistry indicates that this is not occurring at present and the highest electrical conductivity values are actually recorded at Thomastown.

Because saline intrusion is a risk in this aquifer, an upper concentration limit has been set, based on the mean plus two standard deviations of the log conductivity, excluding the highest values recorded at Thomastown.

**Table D3.30. Natural background upper limit for electrical conductivity**

| | Observed Range | Limit | |
|---|---|---|---|
| Electrical conductivity (µS/cm) | 49 – 798 | Upper | 1675 |

pH and alkalinity

pH measurements range from 6 to 7.4 with the lowest values occurring in the central area (at Cloran, Poulavanogue and Grange), where correspondingly lower alkalinity is also recorded. These lower values tend to occur where drift cover is absent or limited, such that the $CaCO_3$ that occurs in the drift is not available to buffer the groundwater and acidification is therefore a risk. In order to calculate a lower limit value for pH, the mean minus two standard deviations has been computed. The result, pH 5.66, lies approximately at the value for natural background rainwater (pH 5.6) (Section 4.7.1).

As described previously, alkalinity does vary significantly across the aquifer. A lower natural background limit value has been set in order to detect acidification if it occurs. Data for Cloran and Poulavanogue have been excluded due to their naturally low alkalinities – these concentrations are already below the 12.3 mg/l $HCO_3$ limit that is required to buffer against acidification (main report Section 4.7.1). This value was derived for Dublin Airport, where atmospheric deposition of anthropogenic sulphate and nitrate is known to occur, and will be a conservative estimate for the ORS aquifer in general.

The mean minus two standard deviations of the log concentrations of the remaining samples has been used to give a lower concentration limit. Clearly the groundwaters at Cloran and Poulavanogue are at significantly greater risk of acidification than the rest of the aquifer.

**Table D3.31. Natural background lower limit for pH and alkalinity**

| | Observed Range | Limit | |
|---|---|---|---|
| pH | 6 – 7.4 | Lower | 5.66 |
| Alkalinity (mg/l as $CaCO_3$)* | 112 – 390* | Lower | 108 |

*for entire groundwater body, with the exception of Cloran and Poulavanogue.

Sulphate

Sulphate has been detected at all sample locations except Knock, where no analysis has been carried out. Significantly elevated concentrations are not seen at any of the locations, although those at Grange and Thomastown WS are higher than the other five. Table D3.25 gives an atmospheric contribution of sulphate to groundwater of 1.57 mg/l. This is a significant fraction of the measured sulphate concentrations in groundwater, but some sulphate remains unaccounted for and is likely to be anthropogenic.

The highest sulphate concentrations are observed at the Grange borehole, and the decreasing trend seen is also observed in potassium concentrations for the site. This suggests that agricultural fertiliser may be the source of this contamination.

Due to existing contamination, natural background concentration limits for sulphate cannot be calculated. Instead, it is suggested that groundwater concentrations should not exceed that of the infiltration, calculated in Table D3.25 as 1.57 mg/l as S, scaled by the ratio between the 95th percentile and estimated infiltration concentrations of chloride.

**Table D3.32. Natural background concentration limit for sulphate**

| | Observed Range* | Limit | |
|---|---|---|---|
| Sulphate (mg/l as S) | 1 - 16 | Upper | 2.72 |

*for entire groundwater body, with the exception of Grange borehole data.

Phosphate

No hydrochemical data for phosphate were available for this groundwater body. Phosphate is not expected to occur naturally in this aquifer at any significant concentrations and therefore the natural background concentration limit has been set at the current EPA limit of detection.

**Table D3.33. Natural background concentration limits for phosphate**

| | Observed Range | Limit | |
|---|---|---|---|
| Phosphate (mg/l as P) | n/a | Upper | 0.02 |

Metals

No data for heavy metals were available for this groundwater body. Therefore, with the exception of lead, the natural background concentration limits have been set at the respective current EPA detection limits.

Due to the naturally high concentrations of lead in the ORS, concentrations in groundwater are expected to be above the detection limit (although lead is sparsely soluble). As no data are available for the study area it has not been possible to define a natural background concentration limit. When data become available the spatial distribution of the concentrations should be analysed, as groundwater concentrations are expected to depend upon the degree of mineralisation and diagenesis that has occurred locally. One upper concentration limit may not be applicable to the entire study area if the lead mineralisation is localised.

**Table D3.34. Natural background concentration limits for heavy metals.**

| | **Observed Range** | **Limit** | |
|---|---|---|---|
| Cadmium (µg/l) | n/a | Upper | 0.1 |
| Lead (µg/l) | n/a | Upper | 1* |
| Arsenic (µg/l) | n/a | Upper | 1 |
| Mercury (µg/l) | n/a | Upper | 0.1 |
| Zinc (µg/l) | n/a | Upper | 1 |

* Natural background concentrations are likely to be higher than the analytical detection limit, but there are no data to determine what the limit might be.

**Summary**

Natural background groundwater quality

Due to the limited temporal and spatial distribution of the data available for this groundwater body tentative conclusions only can be made. Due to the absence of data prior to 1991 the impact on groundwater of agricultural intensification in 1973, cannot be assessed. Proposed natural background concentration limits for indicator species are tabulated below.

**Table D3.35. Natural background concentration limits for indicator species**

| | Observed Range | **Limit** | |
|---|---|---|---|
| Dissolved Oxygen (mg/l) | n/a | Upper | 9.4 |
| Manganese (µg/l) | <1 – 7 | Upper | n/a |
| Iron (µg/l) | < 50 – 105.1 | Upper | 91 |
| Chloride (mg/l) | 9 – 21 | Upper | 22.1 |
| Nitrate (mg/l as N) | < 0.1 – 7.4 | Upper | 1.21 |
| Ammonium (mg/l as N) | < 0.003 – 0.38 | Upper | 0.003 |
| Electrical Conductivity (µS/cm) | 49 – 798 | Upper | 1675 |
| pH | 6 – 7.4 | Lower | 5.66 |
| Alkalinity (mg/l as $HCO_3$) | 112 – 390***** | Lower | 108 |
| Sulphate (mg/l as S) | 1 – 19 | Lower | n/a |
| Sulphate (mg/l as S) | 1 - 16 | Upper | 2.72 |
| Phosphate (mg/l as P) | n/a | Upper | 0.02 |
| Cadmium (µg/l) | n/a | Upper | 0.1 |
| Lead (µg/l) | n/a | Upper | 1 |
| Arsenic (µg/l) | n/a | Upper | 1 |
| Mercury (µg/l) | n/a | Upper | 0.1 |
| Zinc (µg/l) | n/a | Upper | 1 |

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Figures

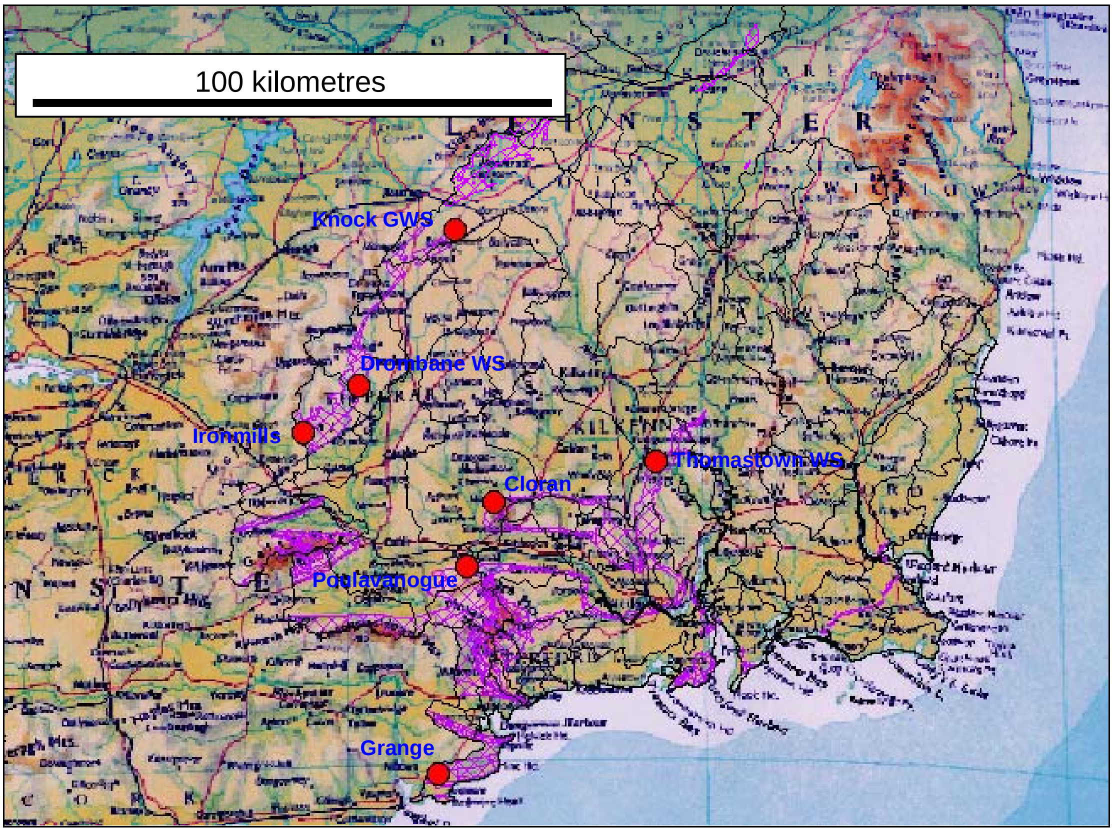

**Figure D3.10: Outcrop location and monitoring points**

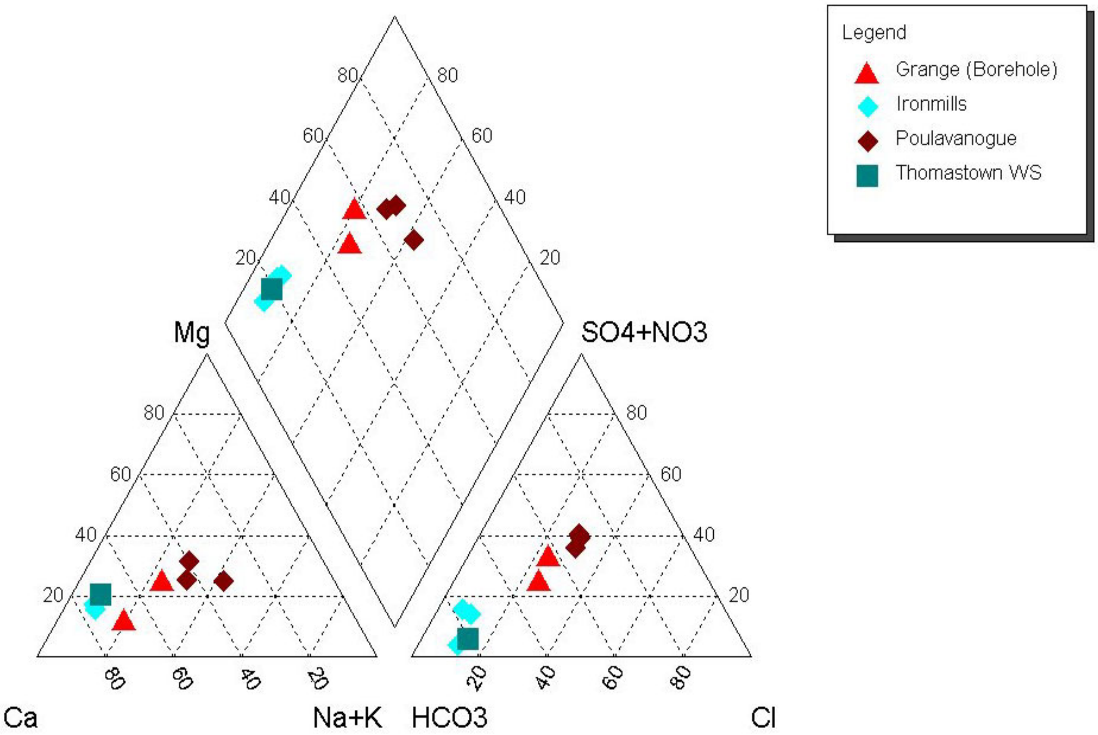

**Figure D3.11: Piper plot for Old Red Sandstone**

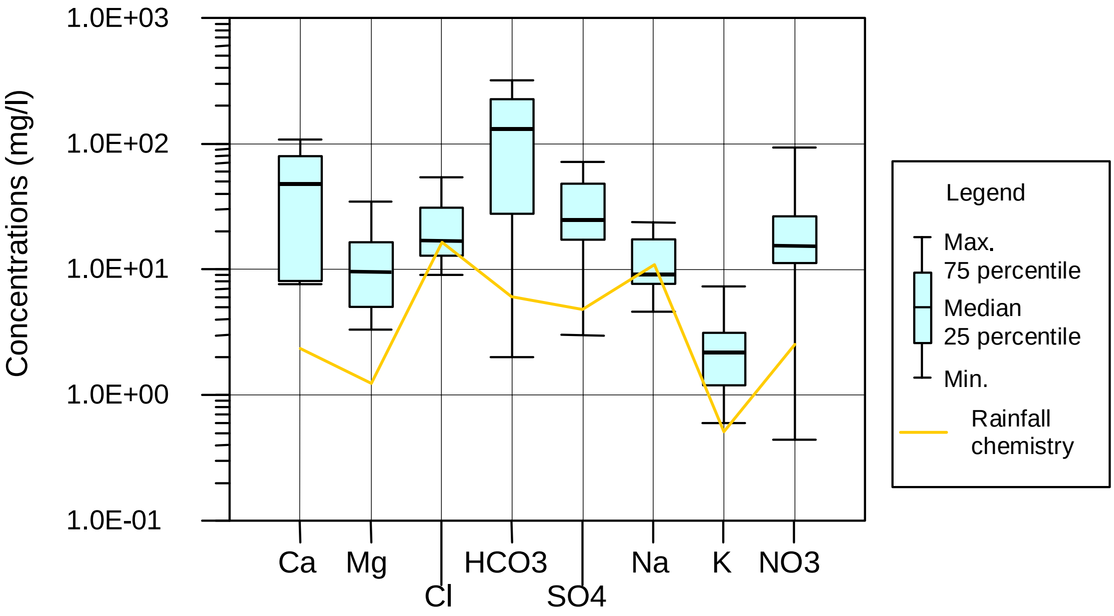

Figure D3.12: Box and Whisker plot, with local rainfall concentrations

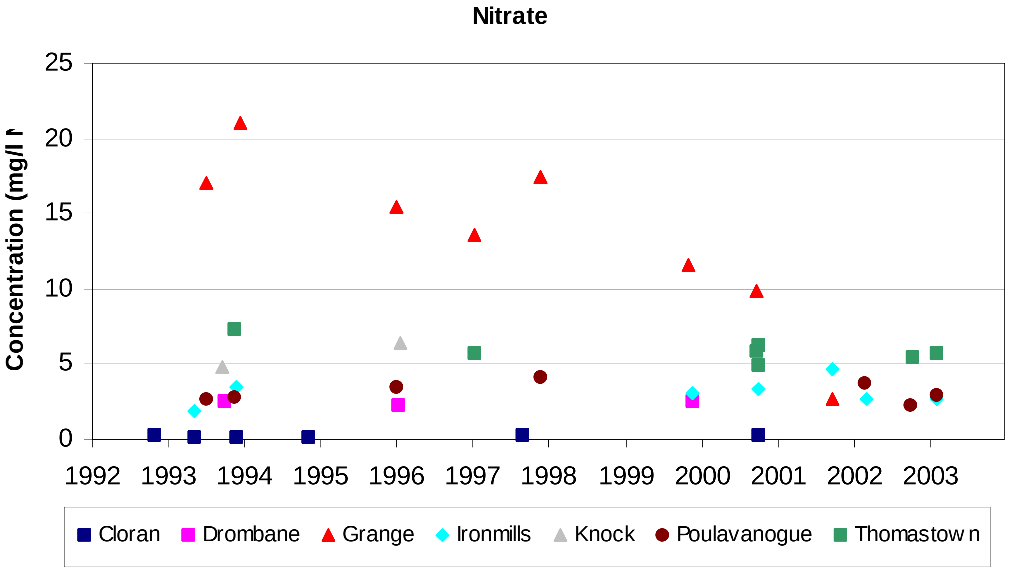

Figure D3.13: Variations in nitrate concentrations with time

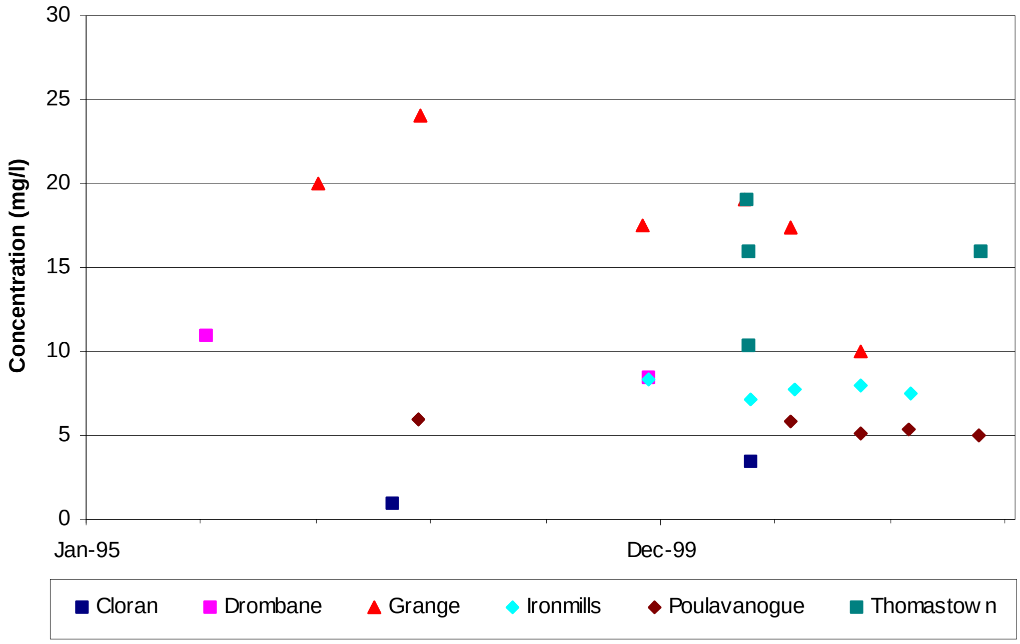

Figure D3.14: Variations in sulphate concentrations with time

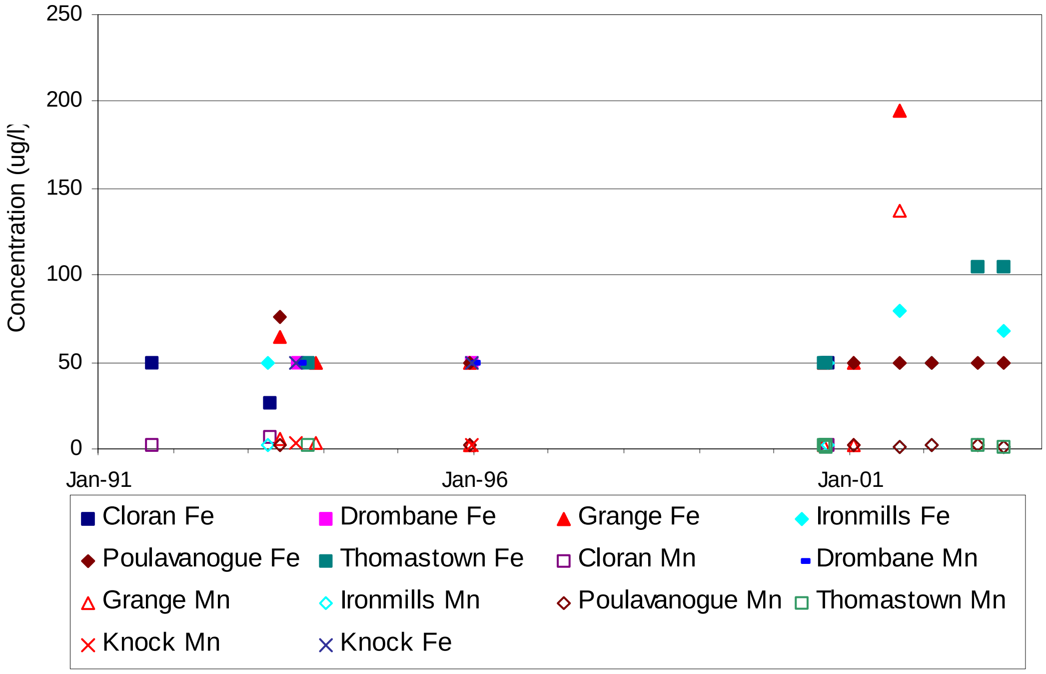

Figure D3.15: Variations in iron and manganese concentrations with time

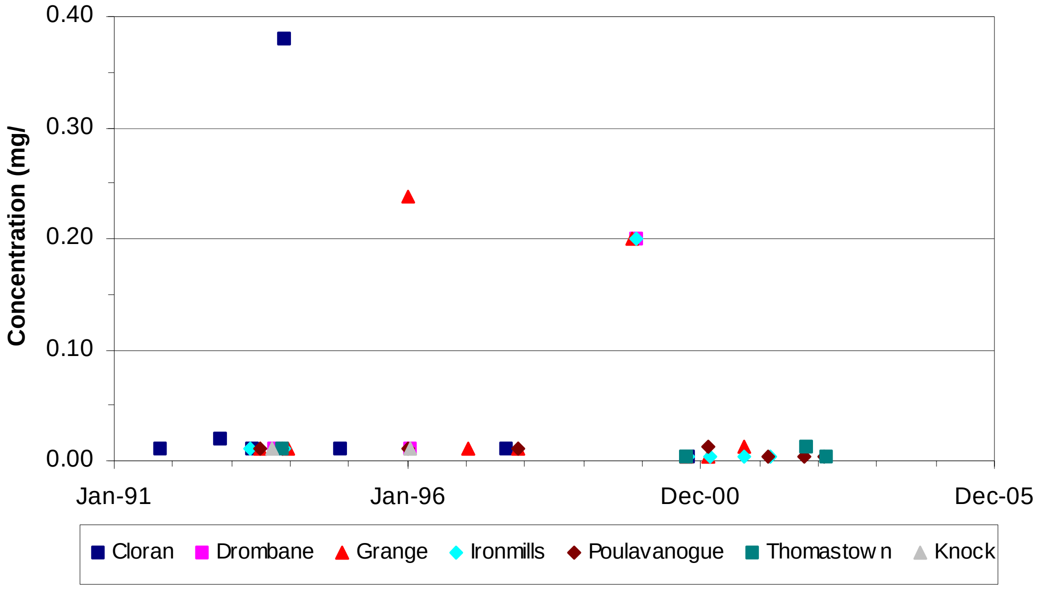

Figure D3.16: Variations in ammonium concentrations with time

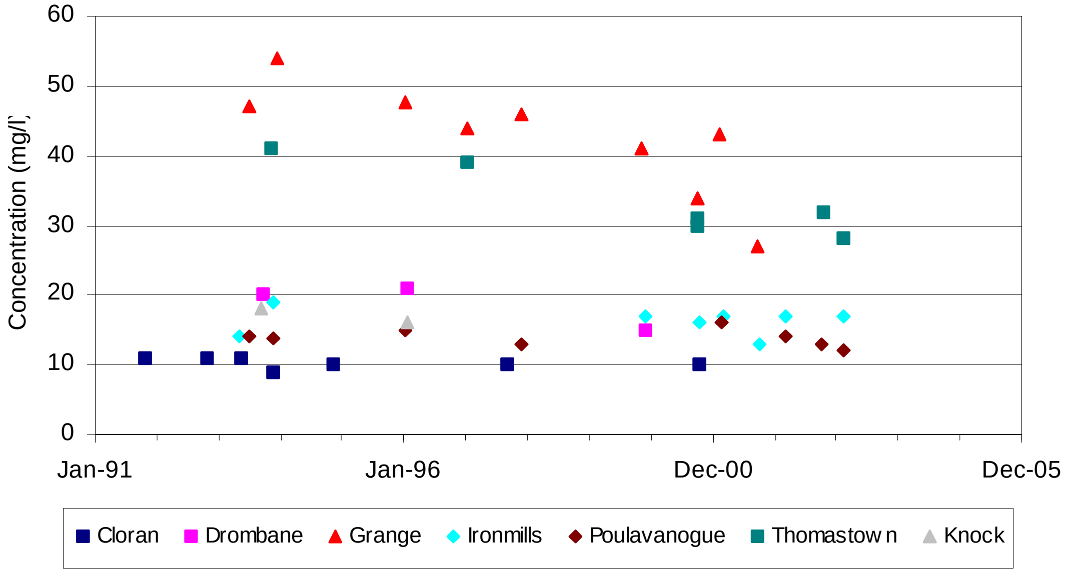

Figure D3.17: Variations in chloride concentrations with time

# *Appendix D4: The Calp Limestone*

## Study Area

Location & boundaries

The Middle Carboniferous Calp Limestone system in the South East River Basin District (SERBD) comprises a number of groundwater bodies that are, in the main, geologically continuous. However, they are subdivided on the basis of surface water catchment boundaries as approximations of groundwater divides. Its outcrop within the SERBD is approximately 790 km$^2$ in area.

Some of the defined groundwater bodies contain no groundwater sampling points, the rest contain very few. On this basis, the characterisation of natural background limits for individual groundwater bodies would be problematical due to the lack of data. The Calp Limestone groundwater bodies within the SERBD have therefore been grouped together and the data from sampling points aggregated to provide sufficient data to enable characterisation of natural background limits for the whole unit.

The outcrop of the Calp Limestones stretches from County Tipperary in the west of the SERBD in a broad north east trending band to County Kildare in the north of the SERBD. The Calp Limestones vary in geology across their outcrop and are differentiated into a number of distinct formations within each county depending on their depositional environment.

The Lower Carboniferous of this area is characterised by a marine transgression across the Devonian Old Red Sandstone, producing a temporal change between shelf and basinal deposits during the Carboniferous, as summarised in Table D4.1. The Calp Limestone was deposited during the Visean period producing a wide variety of deposits. In County Kilkenny the geology typically comprises a shaley, oolitic limestone characteristic of more open water conditions with some degree of turbulence. In County Kildare the limestones have been recorded as being dark grey to black in colour with a component of clay, indicative of deeper water deposition with prevailing reducing conditions.

**Table D4.1. Summarised geological succession through the Carboniferous**

| **Age** | | **Depositional Environment** |
|---|---|---|
| Upper Carboniferous | Westphalian | Deposition exceeded sea floor subsidence producing terrestrial and coal deposits |
| | Namurian | Deep water conditions with turbidite deposits |
| Lower Carboniferous | Visean | A range of depositional environments followed by an unconformity |
| | Courceyan | Transgressive phase with characteristically shallow, turbulent water deposits |

Daly (1985) classifies the land use within the area as being of mixed arable suitability. Mountainous, upland areas are less suitable due to a thin, poorly drained soil cover, whereas lowland regions in southern County Tipperary and central County Kilkenny have a generally thicker, more nutrient rich, well drained soil cover (Flynn *et al*, 2001).

The three main rivers present within the study area are the Suir, Nore and Barrow, all of which flow in a generally southerly direction. The River Nore joins the River Barrow approximately 30 km north from the south coast. The River Suir flows in an easterly direction along the Comeragh Mountains foothills and joins the River Barrow 15 km south of the Nore and Barrow confluence (Figure D4.1). All three rivers cross the Calp Limestone perpendicular to the prevailing aquifer orientation apart from in the south of the study area where the River Suir runs parallel with the limestone while flowing in an easterly direction.

The confluences between the River Nore and Burrow, and the Suir and Burrow do not occur in the proximity of the Calp aquifer.

The Ballyadams Formation, a pale grey, thick bedded, coarse grained, crinoidal limestone, overlies the Calp Limestone and provides a significant amount of baseflow to local rivers within County Tipperary (Flynn *et al*, 2001). It is expected that this formation is in hydraulic continuity with the underlying Calp limestone due to the extreme karstification.

## Hydrogeology

The Calp Limestones consist of a shaley, clay limestone, therefore the primary porosity will be fairly low. The limestones are likely to have a secondary porosity and permeability caused by faulting, dolomitisation and karstification. These features are most prominent in the upper 10 to 20 m of the aquifer due to water movement, weathering and general geological conditions (Flynn *et al*, 2001).

The water table is generally within 10 m of the ground surface and roughly mirrors the surface topography, with an annual fluctuation less than 5 m (Flynn *et al*, 2001).

The majority of groundwater flow occurs in the upper weathered zone within the aquifer where faults and fractures are concentrated. The heterogeneity of the aquifer means groundwater throughput is low and localised, often with short flow paths. Transmissivity values measured in the Calp Limestone in County Kildare range between 10 to 20 $m^2$/day (Kelly and Fitzsimons, 2002) and variable yields have been obtained across the study area.

The limestones are predominantly unconfined over the study area and may be in hydraulic continuity with overlying gravel deposits, where present.

The Calp Limestone within the Counties of Kilkenny and Kildare has been classified as a locally important aquifer which is moderately productive only in local zones (Buckley and Fitzsimons, 2002; Kelly and Fitzsimons, 2002). Dolomitisation may locally increase yields within the limestone aquifer.

In County Kildare there are a number of warm springs issuing groundwater from the Calp Limestone at temperatures between 13° and 25°C, which are significantly above the normal values expected for Irish groundwater. It is thought that this groundwater comes from a deep source, possibly associated with deep faults (Kelly and Fitzsimons, 2002, Burdon, 1983).

## Aquifer mineralogy

The Calp Limestone typically has a calcareous matrix, parts of which may be micriitic with argillaceous grains and chert also present. The limestone may be dolomitised in places, especially along faults (Buckley and Fitzsimons, 2002).

Drift deposits, overlying the Calp Limestone in places, are of a glacial origin containing mainly limestone phenoclasts in a clayey matrix (Warren, 1991).

## Rainfall and recharge

The rainfall chemistry monitoring station at Kinnitty is the closest to most of the Calp Limestone outcrop. However, this monitoring station lies further inland than the majority of the monitoring points within the Calp Limestone so values from Cork monitoring station will also be used and averages taken. Average rainfall statistics for the two stations for the period 1992 to 1994 are presented in Table D1.1 (Jordan, 1997).

Buckley and Fitzsimons (2002a) estimated the recharge rate in County Kilkenny as 440 mm/a. This is used in Table D1.1 to estimate solute concentrations in infiltration, assuming that that is a reasonable estimate of effective precipitation and that the solutes are conservative through the soil zone.

**Table D4.2. Rainfall statistics and quality**

| Station | Rain (mm/a) | $SO_4$ (mg/l S) | Cl (mg/l) | $NO_3$ (mg/l N) | $NH_4$ (mg/l N) |
|---|---|---|---|---|---|
| Kinnitty | 904 | 0.78 | 6.68 | 0.12 | 0.07 |
| Cork Airport | 1266 | 0.88 | 6.82 | 0.27 | 0.29 |
| Mean rainfall/conc. | 1085 | 0.83 | 6.75 | 0.195 | 0.18 |
| Recharge depth/conc. | 440 | 2.05 | 16.6 | 0.48 | 0.44 |

### Hydrochemistry

Sample locations

Within the Calp Limestone of the SERBD, 13 monitoring points have been used to obtain 126 analyses (Table D4.3); the locations of the monitoring points are shown on Figure D4.1. All boreholes have been used to sample for a range of determinands over a six to ten year period. An exception is the monitoring point at Cordangan, which was sampled only in May 1993. The sampling locations within are quite well spatially distributed across the outcrop providing an adequate coverage to identify regional variations. It is not possible to identify whether points are in recharge or discharge zones without detailed local hydrogeology.

All groundwater chemistry data recorded in the EPA database for the Calp Limestone has been in the last 13 years so no historic data prior to the intensification of agriculture around 1973 are available. Ionic balances are in general, good, however, several of the recent samples from the EPA database have ionic balance errors greater than ± 10%.

**Table D4.3. Sample point locations and dates**

| Sample Point | Source | Samples | Period |
|---|---|---|---|
| Bausheenmore | EPA | 8 | Jun 1993 – Feb 2003 |
| Clara GWS | EPA | 10 | Nov 1993 – Feb 2003 |
| Cordangan | EPA | 1 | May 1993 |
| Fermoyle | EPA | 13 | Aug 1996 – Jan 2003 |
| Galmoy GWS | EPA | 10 | Jun 1993 – Feb 2003 |
| Holycross | EPA | 5 | Sep 1993 – Jan 2001 |
| Littleton WS | EPA | 9 | Sep 1993 – Feb 2003 |
| Moycarkey | EPA | 8 | Sep 1993 – Feb 2003 |
| Paulstown Castle | EPA | 16 | Apr 1992 – Sep 2000 |
| Rhode | EPA | 15 | Dec 1995 – Feb 2003 |
| Springmount House | EPA | 10 | Mar 1991 – Oct 2000 |
| Toberdorah | EPA | 9 | May 1993 – Feb 2003 |
| Urlingford Johnstown | EPA | 12 | Jun 1993 – Feb 2003 |

Major ion chemistry

Within the Calp Limestone groundwater is of calcium bicarbonate type with very little variation in chemistry, reflecting the carbonate nature of the rocks. The results shown in Figure D4.2 show clearly that there are magnesium rich waters within the limestone reflecting dolomitised regions of the aquifer. The median Ca:Mg ratio of the groundwater at each sampling point has been plotted on Figure D4.3; smaller circles denote a more dolomitic signature. There appears to be no particular regional pattern to the dolomitisation.

The statistical distribution of all major ion species within the Calp Limestone is shown in the box and whisker plot in Figure D4.4 which also shows rainfall composition normalised to the median groundwater chloride concentration. The high calcium and bicarbonate are expected due to the carbonate nature of the aquifer but it shows that potassium, sulphate and nitrate are all derived from sources other than rainfall.

### Regional variation

Sulphate concentrations tend to increase in a north easterly direction through County Tipperary and Kilkenny. The maximum concentration occurs at Galmoy GWS, located in the north of County Kilkenny. The maximum nitrate concentration also occurs at Galmoy GWS and follows a similar spatial distribution to that of sulphate.

Additionally, the largest magnesium concentration occurs at the Galmoy GWS monitoring point and potassium concentrations are generally higher in County Kilkenny than the surrounding counties. Comparisons of selected median concentrations at Galmoy and in the rest of the aquifer are shown in Table D4.4 and represent a regional variation within the Calp Limestone. Both magnesium and nitrate show a significant increase between the median concentration in the whole aquifer and that at Galmoy GWS.

**Table D4.4. Selected median concentrations at Galmoy**

| | Sulphate (mg/l as S) | Nitrate (mg/l as N) | Magnesium (mg/l) |
|---|---|---|---|
| Galmoy | 17.1 | 11.0 | 25.9 |
| Rest of aquifer | 16.0 | 6.2 | 19.3 |

### Depth variation

There is currently no information relating to depth variation of water chemistry within the Calp Limestone aquifer.

### Temporal variation

No seasonal variations are apparent within the dataset for the Calp Limestone aquifer. Some sampling points do not have sufficient data to make this observation, but for those that do, no trend was evident.

At Galmoy GWS over the period from 1993 to 2003 there are insufficient time series data to accurately identify any significant trends apart from in the nitrate data. There are 19 nitrate data and they show a marginally increasing trend with time (Figure D4.5). The seven highest concentrations from the entire limestone aquifer were recorded at this locality and the maximum nitrate concentration was detected in August 1997.

There is also a distinctive nitrate concentration peak detected in three monitoring locations, Moycarkey, Littleton WS and Holycross in September 2000 (Figure D4.5).

Fermoyle, to the north east of Galmoy GWS, has significantly elevated calcium in 2002, with concentrations being over 100 mg/l greater than mean concentrations for all the years (Table D4.5). Although calcium concentrations measured over the entire aquifer are approximately 20% greater in 2002 than for the period 1995 to 2003, at Fermoyle there is an 80% increase in measured calcium values between the 1995 to 2003 data and 2002 data (Figure D4.6).

**Table D4.5. Calcium concentration distributions (mean and SD) for different periods**

| | Ca (mg/l) 1995 – 2003 | Ca (mg/l) 2002 |
|---|---|---|
| Total aquifer | 121 ± 38 | 145 ± 55 |
| Fermoyle | 152 ± 67 | 274 ± 7 |

In Rhode, in the north of the Calp Limestone study area, all major ions show fairly steady concentrations with time and no elevated results have been recorded.

Exclusions

There are no monitoring localities exhibiting particularly anomalous data that need to be omitted from further analysis.

### Indicator chemistry

Redox indicators

No data regarding dissolved oxygen concentrations within the Calp Limestone aquifer are available. The main limestone aquifer is predominantly unconfined (Flynn, 2001) implying dissolved oxygen concentrations maybe reasonably high due to the presence of fresh recharge waters within the aquifer.

Sulphate has been detected at all boreholes within the aquifer, except Cordangan but manganese and iron concentrations have been recorded at all sampling locations. Median concentrations of iron, manganese and sulphate within the Calp Limestone in the SERBD are shown in Table D4.6.

**Table D4.6. Median concentrations of redox indicators for all samples**

| | Mn (µg/l) | Fe (µg/l) | $SO_4$ (mg/l as S) |
|---|---|---|---|
| Total aquifer | <2 | <50 | 16 |

Sulphate concentrations are generally low throughout the entire limestone aquifer. These concentrations, however, do not correlate with elevated iron and manganese concentrations, indicating that the low sulphate concentrations are not caused by reducing conditions within the aquifer. This is consistent with the lack of confining Drift cover.

Median manganese concentrations are highest in the boreholes with the fewest data. Ten of the sampling locations have a median manganese concentration of < 2 mg/l and all of the sampling locations have a median iron concentration of < 50 mg/l. The spatial distributions of iron and manganese closely coincide indicating that they are a good indicator for more reducing conditions within the aquifer where concentrations are elevated.

There are sufficient data for the Calp Limestone aquifer to determine natural background concentration limits (Table D4.7) for manganese, iron and sulphate from cumulative probability plots (Figure D4.7). The sulphate plot clearly shows a log-normal distribution so the lower limit was chosen at the 5th percentile concentration.

Both the iron and manganese plots show that there are many samples below the detection limit indicating the groundwater within the aquifer is generally oxidised. Concentrations recorded above the limit of detection are spatially well distributed throughout the aquifer, indicating the cause is more likely to be natural variation rather than point source pollution. However, within the datasets there are five concentrations (two in the manganese data and three in the iron data) that seem anomalously high. These were omitted from the analysis for the purposes of limit determination.

Because of the high number of non-detects in the iron and manganese data sets, the ratio AM0/AM100 was computed. The AM0/AM100 ratios for iron and manganese have values of 0.57 and 0.84 respectively, implying that some statistics for iron may be biased by the choice of limit of detection multiplier. However, since the natural background limit is obtained from the cumulative frequency plot, this is not an issue.

Since the Calp Limestone is unconfined over the majority of the study area, dissolved oxygen concentrations should be relatively high except in regions where overlying Drift deposits are present. The dissolved oxygen limit is based on a groundwater with 95% saturation at 15ºC.

**Table D4.7. Natural background concentration limits for redox indicators**

| | Observed Range* | Limit | |
|---|---|---|---|
| Dissolved oxygen (mg/l) | n/a | Upper | 9.4 |
| Manganese (µg/l) | < 1 – 344 | Upper | 20 |
| Iron (µg/l) | 10.3 – 926 | Upper | 186 |
| Sulphate (mg/l as S) | 8.5 – 37.6 | Lower | 9.7 |

* for the whole groundwater body

Chloride

The majority of chloride concentrations from the Calp Limestone typically lie in the range from 10 to 30 mg/l. The maximum chloride concentration was detected at Bausheenmore but eight of the 12 highest concentrations were detected at the Paulstown Castle monitoring point. The highest median concentration also occurs at Paulstown Castle, while the lowest is calculated from Rhode.

Given the absence of evaporite deposits within the aquifer, the only natural source of chloride is from precipitation containing sea spray. Bausheenmore and Paulstown Castle are the two monitoring points within the limestone aquifer located nearest to the south coast, therefore it may not be surprising that they have the highest chloride concentrations. Based on this hypothesis it would be expected that the most inland points would have the lowest chloride concentrations. This appears to be true as concentrations at Rhode borehole are significantly lower than those recorded at the other monitoring points within the Calp Limestone.

Chloride concentrations within individual boreholes are quite variable but there are no apparent trends in the dataset.

Table D1.1 suggests that, assuming chloride is conservative through the soil zone, its concentration in recharge water will be approximately 16.6 mg/l, a little less than the median groundwater concentration of 22 mg/l.

A natural background concentration limit for chloride will therefore be calculated from a cumulative probability plot (Figure D4.7). The plot shows a reasonable log-normal distribution and an upper limit of 32 mg/l is determined.

**Table D4.8. Natural background concentration limit for chloride**

| | Observed Range | Limit | |
|---|---|---|---|
| Chloride (mg/l) | 8.81 – 41 | Upper | 32 |

Nitrogen species

Nitrate concentrations within the study area are fairly high with a median value shown of 6.2 mg/l as N and a maximum of 16.4 mg/l as N. The largest values generally occur in the centre of the study area, decreasing in a south westerly direction into Co. Tipperary (Figure D4.8). There is an increasing temporal trend within the nitrate dataset at Galmoy GWS, and a nitrate concentration peak in September 2000 reflected in Moycarkey, Littleton WS and Holycross boreholes, as described above and shown on Figure D4.5. Low nitrate concentrations are typically seen at Moycarkey and Rhode.

Ammonium concentrations range between <0.001 and 0.636 mg/l as N with a median of <0.01 mg/l as N. The maximum value was detected at Urlingford Johnstown and is 0.4 mg/l as N greater than the next largest concentration. The highest median concentration occurs at Holycross and has a value of 0.025 mg/l as N. The AM0/AM100 ratio for ammonium has a value of 0.505, indicating that the calculated mean concentrations are biased by the choice of detection limit multiplier and only tentative conclusions may be drawn.

From Table D1.1 it can be seen that nitrate and ammonium in rainfall collectively contribute 0.92 mg/l as N to the aquifer. This accounts for only a minor proportion of the total measured nitrogen species, indicating that the groundwater concentrations are influenced by anthropogenic activities, probably associated with agriculture.

Natural background concentrations for nitrogen species cannot therefore be determined for the limestone aquifer based on measured concentrations. The best estimate for the natural background limit of nitrate is based on the infiltration contribution of 0.48 mg/l as N, scaled by the ratio between the 95th percentile and estimated infiltration concentrations of chloride.

It is unlikely that the aquifer is still in its natural state with regards to ammonium concentrations, since it has been shown to be subject to anthropogenic nitrogen inputs. However, concentrations are too low to use for meaningful analysis. The best estimate is that the natural background limit should currently be the detection limit.

**Table D4.9. Natural background concentration limits for nitrogen species**

| | Observed Range | Limit | |
|---|---|---|---|
| Nitrate (mg/l as N) | 1.9 – 16.4 | Upper | 0.93 |
| Ammonium (mg/l as N) | < 0.001 – 0.636 | Upper | 0.001 |

<u>Electrical conductivity</u>

Groundwater conductivity ranges from 484 to 832 µS/cm with the highest values detected at Fermoyle. The Calp Limestone is not at risk from saline intrusion so it is assumed that variations in conductivity are caused by variations in the hardness of the groundwater, which varies from 269 to 768 mg/l as $CaCO_3$. These groundwaters are classified as hard to very hard (EPA, 2002).

Saline intrusion is not a risk at the Curragh so derivation of a natural background limit is meaningless in that context. Since the background concentrations are high due to the hardness of the water, impacts from pollution will not be observed against the natural variation.

An upper limit has been set at the mean concentration plus two standard deviations of the log concentrations.

**Table D4.10. Natural background limit for electrical conductivity**

| | Observed Range | Limit | |
|---|---|---|---|
| Electrical conductivity (µS/cm) | 484 – 832 | Upper | 896 |

### pH and alkalinity

In the Calp Limestone pH measurements vary between 6.88 and 7.8 and alkalinity varies from 231 to 411 mg/l as $HCO_3$. These high values are indicative of alkaline conditions within a carbonate aquifer. There may be a small chance of acidification to the aquifer as it is unconfined across the majority of the study area, but this is insignificant due to the well-buffered nature of the Calp Limestone. Therefore, in this case, the derivation of natural background limits for pH and alkalinity are not required.

**Table D4.11. Natural background limits for pH and alkalinity**

| | Observed Range | Limit | |
|---|---|---|---|
| pH | 6.88 – 7.8 | Lower | 7.06 |
| Alkalinity (mg/l as $CaCO_3$) | 231 – 411 | Lower | 307 |

### Sulphate

The median of the total sulphate dataset is 16 mg/l as S. A significant number of elevated sulphate concentrations, greater than 20 mg/l as S, were detected at Fermoyle. There was a large peak in sulphate concentrations in February 2001 seen in Clara GWS, Galmoy GWS and Urlingford Johnstown (Figure D4.9), followed by a rapid decline and minima in February 2002. It is not believed that the sulphate has been derived from fertiliser use, as elevated sulphate concentrations would be expected to correlate with elevated potassium concentrations. However, this is not observed. The three elevated concentrations in February 2002 are most likely caused by an undetermined anthropogenic influence so will be removed from the dataset prior to statistical analysis.

Table D1.1 suggests that, assuming sulphate in rainfall is conservative through the soil zone, its concentration in recharge water will be approximately 2.05 mg/l as S, which is only a small proportion of the measured groundwater concentrations.

The cumulative frequency plot for sulphate shows a log-normal distribution up to approximately the 75th percentile and then a positive skew at high concentrations. It is possible that the lower concentrations represent the natural sulphate and the elevated concentrations the anthropogenic influence.

The upper limit of background concentrations has been calculated by extrapolating the natural concentrations up to the 95th percentile, 25.3 mg/l as S (Figure D4.7). The natural background concentration limit is calculated by subtracting the anthropogenic atmospheric input from the above value (Table D1.11).

**Table D4.12. Natural background concentration limit for sulphate**

| | Observed Range | Limit | |
|---|---|---|---|
| Sulphate (mg/l as S) | 8.5 – 37.6 | Upper | 23.3 |

### Phosphate

No hydrochemical data relating to phosphate are available for the Calp Limestone aquifer. However, concentrations are expected to be low as phosphorous binds strongly to soils and other compounds and readily forms insoluble salts in alkaline groundwater conditions.

As concentrations are expected to be low within this aquifer the natural background concentration limit has been set at the limit of detection.

**Table D4.13. Natural background concentration limits for phosphate**

| | Observed Range | Limit | |
|---|---|---|---|
| Phosphate (mg/l as P) | n/a | Upper | 0.001 |

Metals

Data for heavy metals, including zinc, lead, cadmium, arsenic and mercury, have not been made available for the Calp Limestone aquifer. Therefore, the natural background concentration limits have been set at the respective detection limits (Table D4.12).

It has been noted by Buckley and Fitzsimons (2002) that the underlying limestone formation is associated with lead and zinc ore deposition but it is considered unlikely that this will affect concentrations within the overlying Calp Limestone.

When data become available the spatial distribution of the concentrations should be analysed, as groundwater concentrations are expected to depend upon the degree of mineralisation and diagenesis that has occurred locally.

**Table D4.14. Natural background concentration limits for heavy metals.**

| | Observed Range | Limit | |
|---|---|---|---|
| Cadmium (µg/l) | n/a | Upper | 0.1 |
| Lead (µg/l) | n/a | Upper | 1 |
| Arsenic (µg/l) | n/a | Upper | 1 |
| Zinc (µg/l) | n/a | Upper | 1 |
| Mercury (µg/l) | n/a | Upper | 0.1 |

Natural background quality

The fairly limited temporal distribution of data available for the Calp Limestone means only tentative decisions can be made at this stage. There is an absence of data in the majority of boreholes prior to 1993, although Springmount House has data as far back as 1991. Therefore, the impact on groundwater of agricultural intensification in 1973 cannot be assessed.

**Table D4.15. Natural background concentration limits for indicator species**

| | Observed Range | Limits | |
|---|---|---|---|
| Dissolved oxygen (mg/l) | n/a | Upper | 9.4 |
| Manganese (µg/l) | < 1 – 344 | Upper | 20 |
| Iron (µg/l) | 10.3 – 926 | Upper | 186 |
| Chloride (mg/l) | 8.81 – 41 | Upper | 32 |
| Nitrate (mg/l as N) | 1.9 – 16.4 | Upper | 0.93 |
| Ammonium (mg/l as N) | < 0.001 – 0.636 | Upper | 0.001 |
| Electrical conductivity (µS/cm) | 484 – 832 | Upper | 896 |
| pH | 6.88 – 7.8 | Lower | 7.06 |
| Alkalinity (mg/l as $HCO_3$) | 231 – 411 | Lower | 307 |
| Sulphate (mg/l as S) | 8.5 – 37.6 | Upper | 23.3 |
| Sulphate (mg/l as S) | 8.5 – 37.6 | Lower | 9.7 |
| Phosphate (mg/l as P) | n/a | Upper | 0.001 |
| Cadmium (µg/l) | n/a | Upper | 0.1 |
| Lead (µg/l) | n/a | Upper | 1 |
| Arsenic (µg/l) | n/a | Upper | 1 |
| Zinc (µg/l) | n/a | Upper | 1 |
| Mercury (µg/l) | n/a | Upper | 0.1 |

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**Buckley, R. and Fitzsimons, V. 2002.** County Kilkenny Groundwater Protection Scheme. Volume 1: Main Report.

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**Environmental Protection Agency, 2000.** The hardness of Irish drinking waters, a simple guide based on conductivity data. EPA, Johnstown Castle Estate, Wexford.

**Flynn, E., Daly, D., Keegan, M. and Wright, G. 2001.** County Tipperary (South Riding) Groundwater Protection Scheme Main Report. 2nd Revised Version.

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## Figures

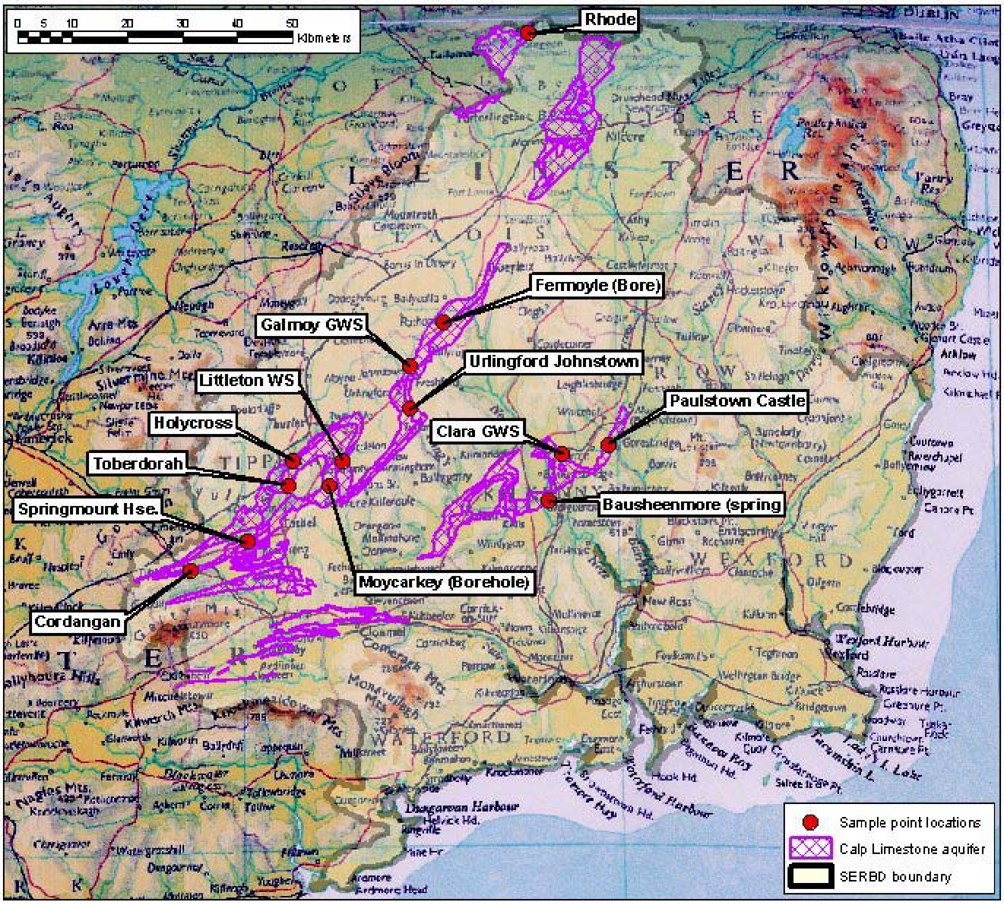

Figure D4.1. Location of Calp Limestone and monitoring points in the SERBD

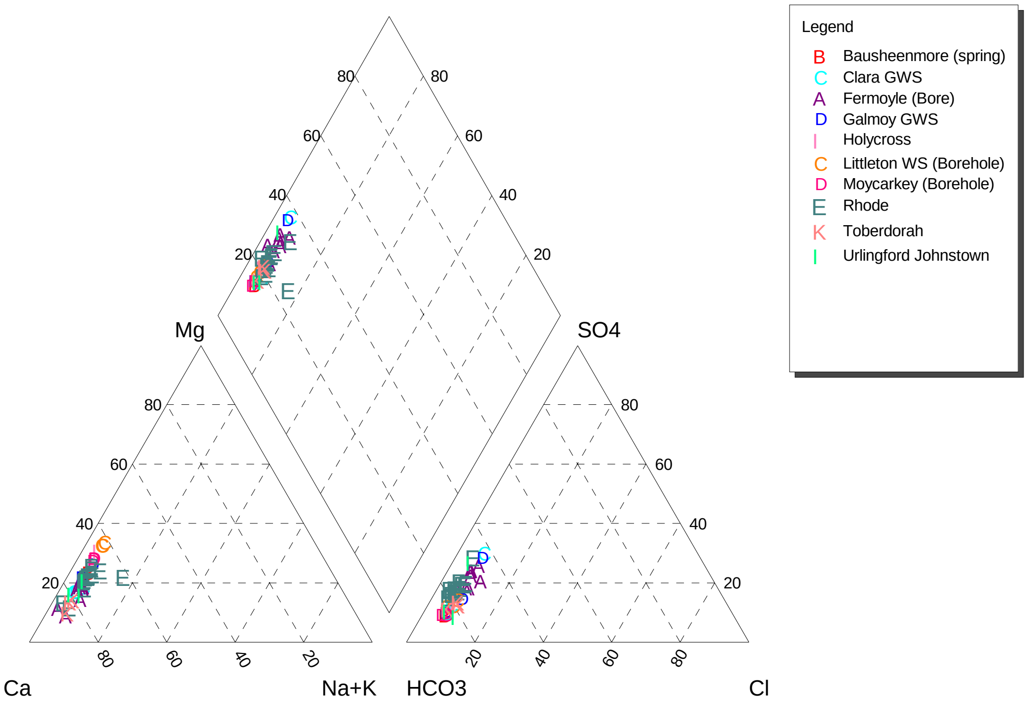

Figure D4.2. Piper plot for Calp Limestone

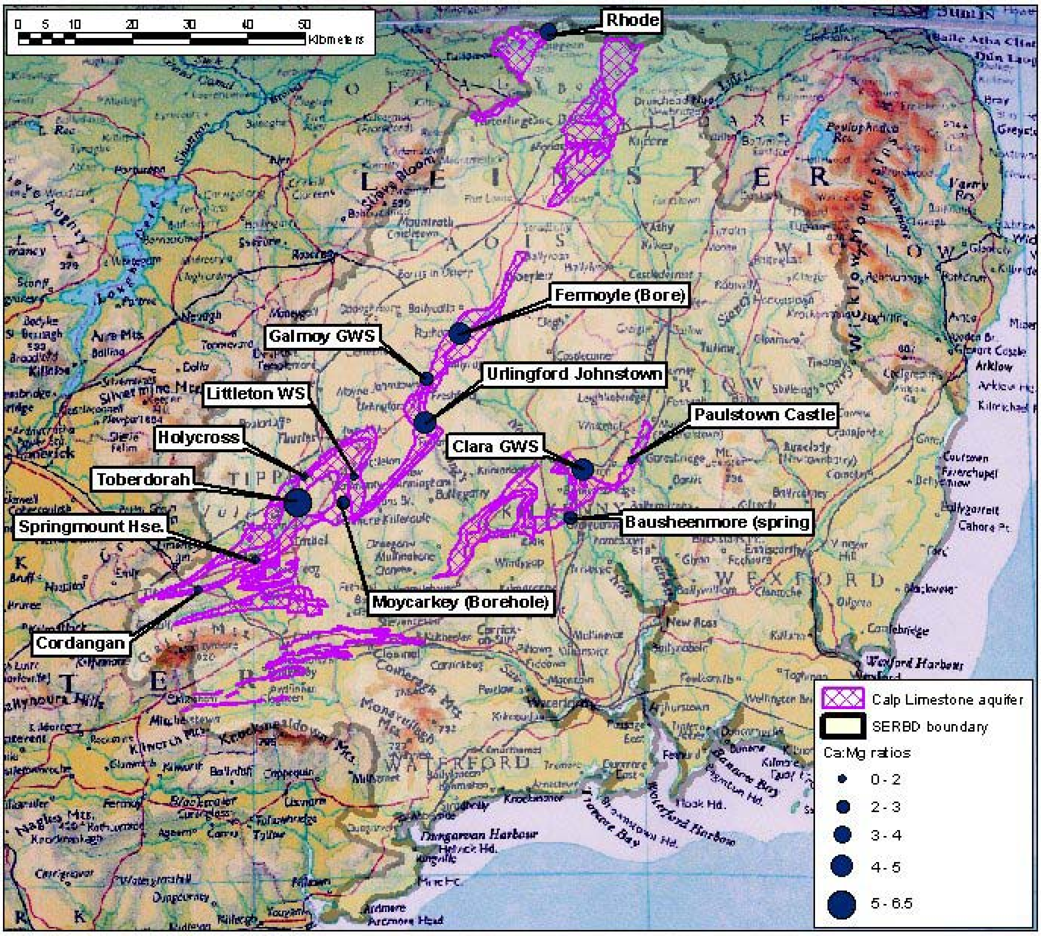

**Figure D4.3. Median Ca:Mg ratios at each sampling location**

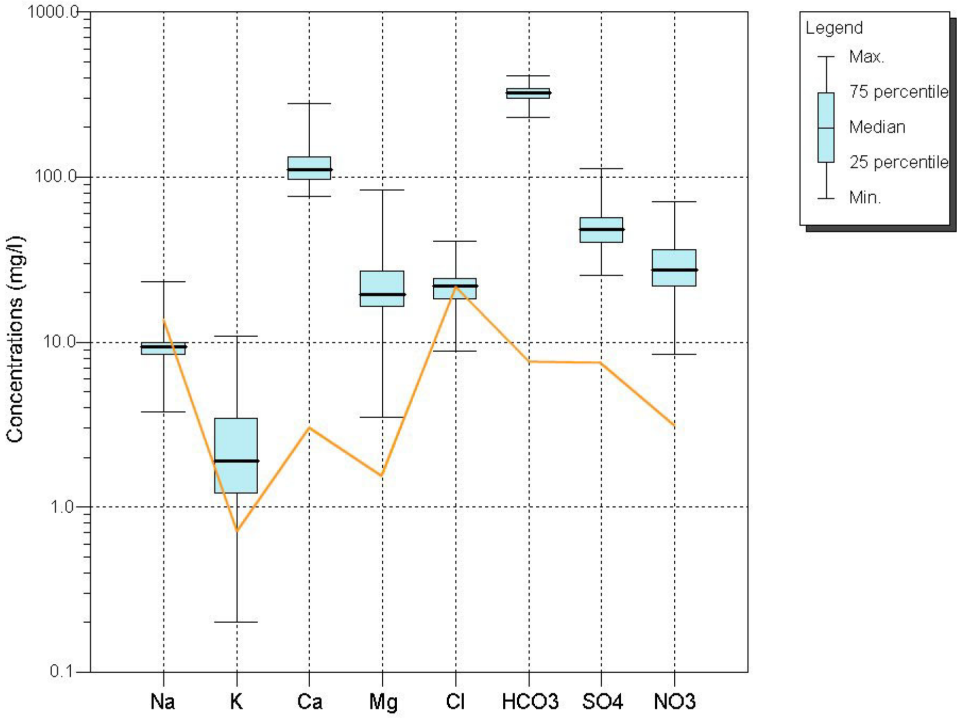

**Figure D4.4. Box and whisker plot for total major ion concentrations within the Calp Limestone aquifer. Orange line shows rainfall composition normalised to median groundwater chloride concentration.**

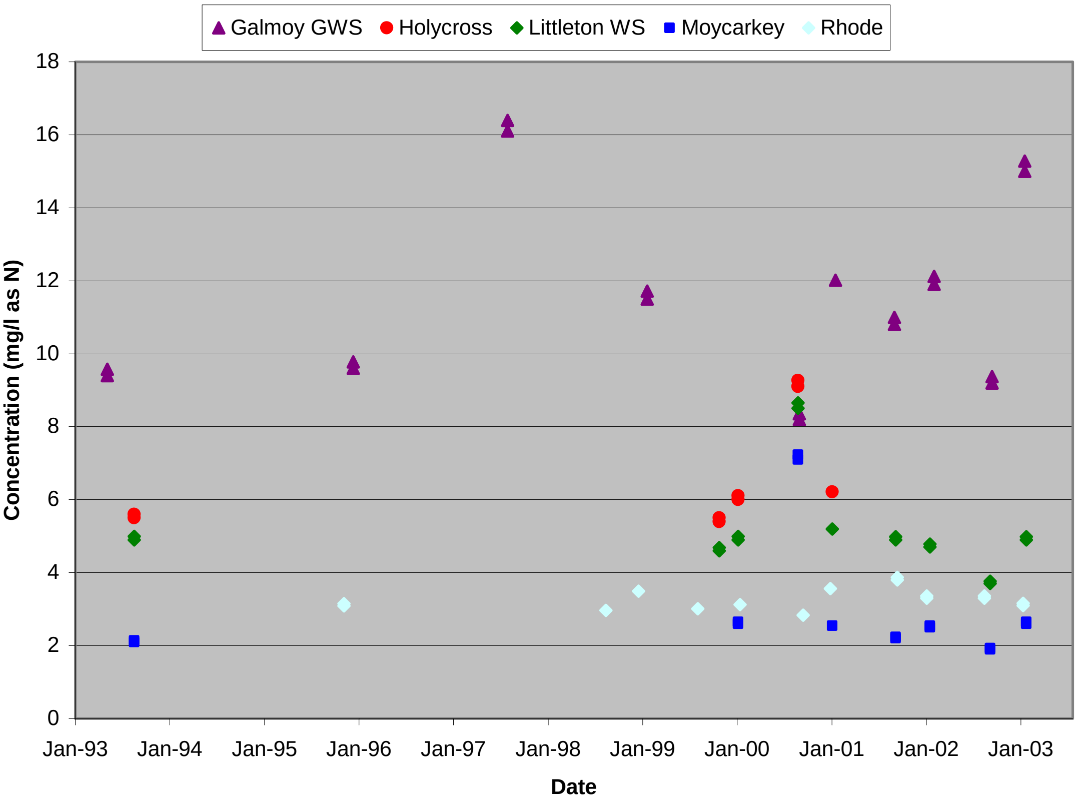

**Figure D4.5. Nitrate variation with time at selected sampling locations within the Calp Limestone**

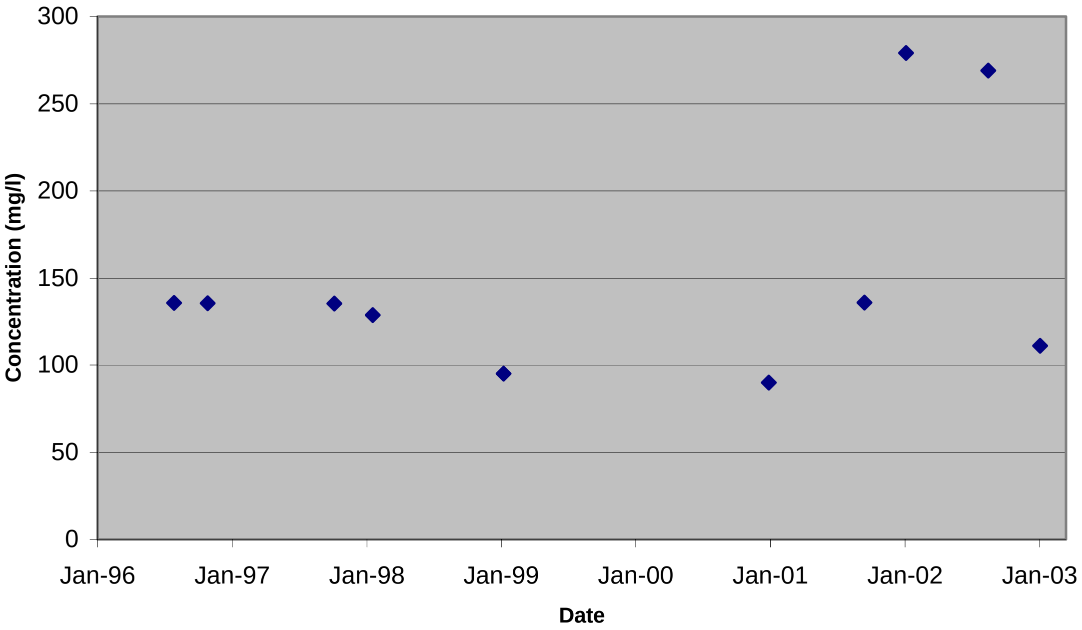

**Figure D4.6. Calcium variation with time at Fermoyle borehole**

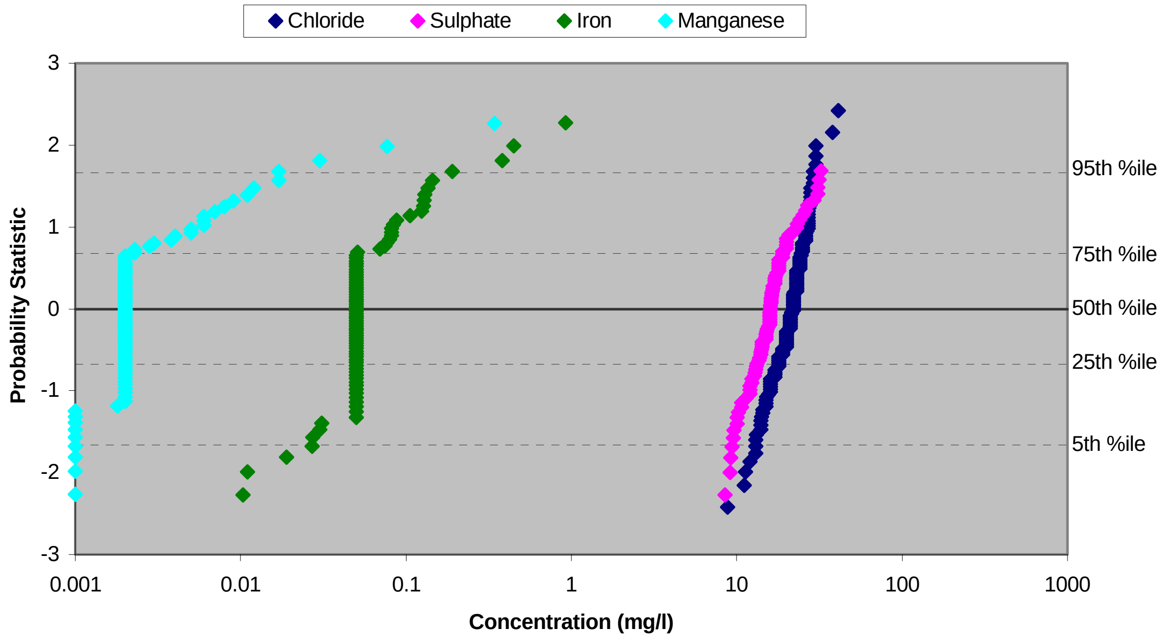

**Figure D4.7. Cumulative frequency plots for chloride, sulphate, iron and manganese**

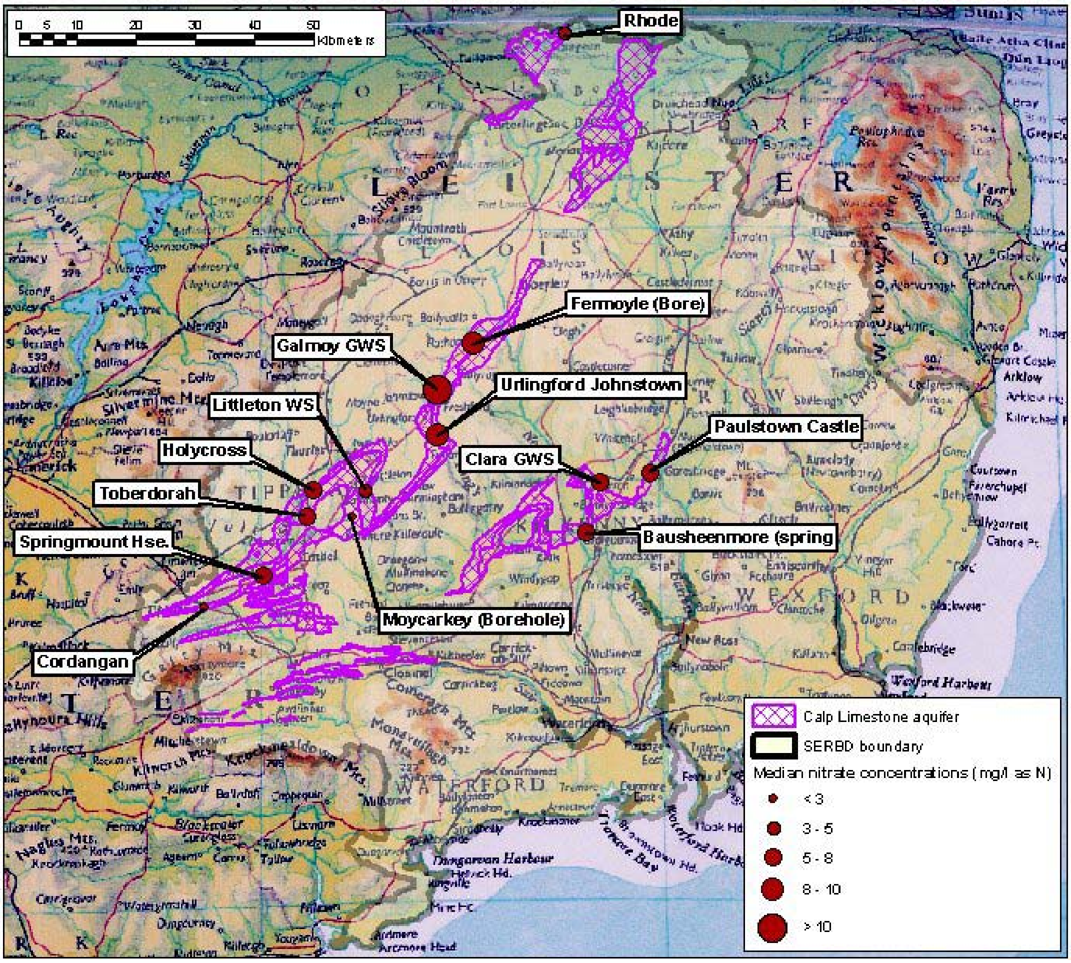

**Figure D4.8. Median nitrate concentrations**

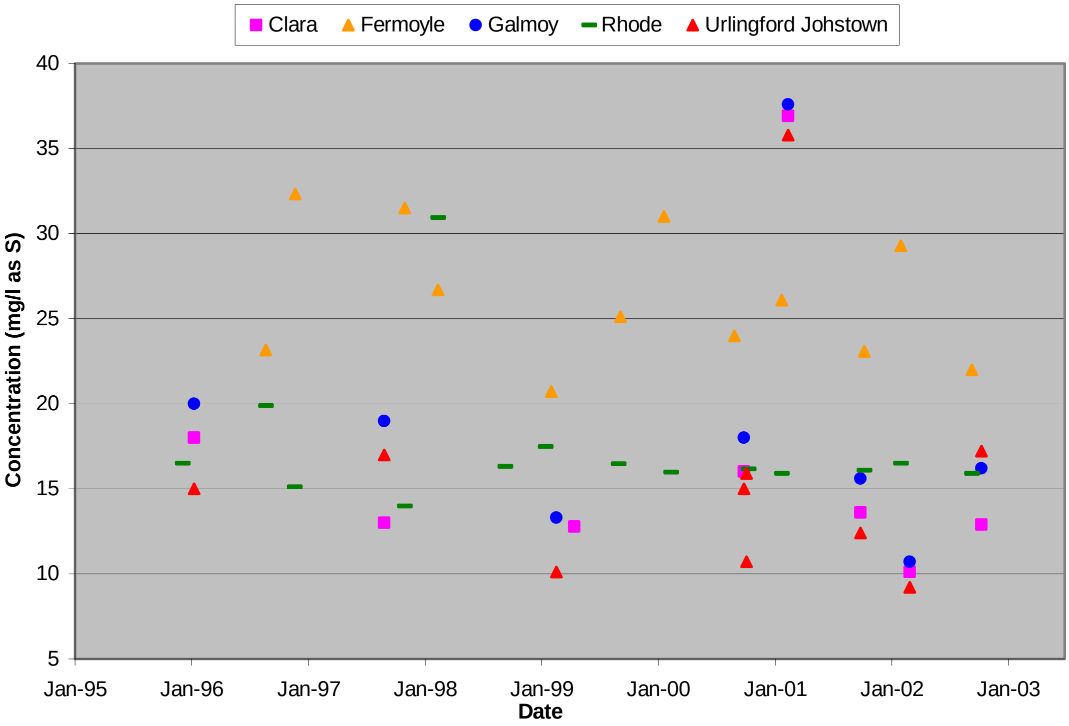

**Figure D4.9. Sulphate concentrations with time in selected boreholes**