

Environmental RTDI Programme 2000–2006

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

Synthesis Report

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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 determining which groundwater bodies are of good status, and which are not 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 concentrations of indicator 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 are preferred. However, more recent data may be used with due allowance for anthropogenic impacts. Regardless of when or where the data were collected, they must be professionally assessed for their reliability before being used for characterisation of natural background quality of groundwater bodies.

1 Introduction

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 waterbody. 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 the potential pollutant sources. These results can be used to classify these bodies and prioritise them for treatment to mitigate the risks. However, the defined natural background quality will not necessarily form part of any definition of 'good status'.

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.

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.

2 Relevant Aspects of the Water Framework Directive

2.1 Background

The 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. Dependent surface water ecosystems and terrestrial ecosystems should also be identified. In Ireland, these activities will be undertaken by consultants in consultation with the RBDs, the EPA and the 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 waterbody, and to establish the presence of any significant and sustained upward trend in concentration of any pollutant.

2.2 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 the 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, the GSI is 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-Eastern 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, personal communication).

2.3 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 dependent 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), the Drinking Water 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 Keegan (2003). In assessing status, the results of individual monitoring points within a groundwater body should be aggregated for the body as a whole.

2.4 The Groundwater Directive

Article 17 of the WFD 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 to be implemented in the new Groundwater Directive, which, at the time of writing this report, is still in proposal form [2003/0210 (COD)].

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 early drafts, it is recognised that the natural variability of groundwater chemical composition and the present general lack of systematic monitoring data make 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 to 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 waters and dependent ecosystems.

2.5 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 concentrations of 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 body. 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 the 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 the 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 body 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 body of natural background quality need not necessarily be pristine¹ 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.

A groundwater body in which some concentrations exceed the natural background concentrations is,

1. A pristine groundwater body 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.

therefore, not necessarily polluted: it is merely impacted by human activity. The WFD 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 body 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 Irish 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.

3 Principles Governing the Chemical Composition of Groundwater Bodies

3.1 Sources

The natural chemistry of groundwater is initially determined by the chemistry of rainfall falling on the recharge area of a groundwater body. On an island, sea spray can be a significant component of rainfall and all over Ireland it contains ions derived from sea spray (Jordan, 1997). Concentrations derived from seawater are highest on south- and west-facing coasts, while the lowest influence is seen in the centre of the island.

During movement over land, air masses and clouds pick up aerosols and gases from natural and industrial origin. Combustion from power generation and transport emits large quantities of chlorine, sulphur and nitrogen into the atmosphere, which, when oxidised and precipitated, contribute to acid rain. In rural areas, intensive agriculture releases ammonia into the atmosphere.

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).

Advancement in agricultural techniques, such as deep ploughing and the use of artificial fertiliser, have been a major contributor to a sustained upward trend in nitrate and phosphate concentrations in European groundwaters since the middle of the 20th Century (Heathwaite *et al.*, 1996). 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 widespread adoption of these techniques.

Rural dwellings in Ireland are mostly unsewered and rely on on-site facilities for the treatment and disposal of domestic wastewater, primarily via septic tank and percolation areas. In cases where the site is unsuitable

and/or there is poor installation and maintenance, on-site disposal of wastewater may cause local contamination of groundwater by pathogens; these discharges also contribute sodium, chloride, nitrogen and dissolved organic carbon to groundwater. Recent research by the EPA shows that on-site wastewater facilities work when properly sited, constructed and maintained (Rodgers *et al.*, 1998).

Landfills (especially the old 'dilute and attenuate' sites) and contaminated land are concentrated around main population centres and 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.

3.2 Processes

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.

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. Where there are thin soil zones (e.g. on karstic limestone terrains), the nutrients in rainwater may move through relatively unimpeded.

Carbon dioxide in the atmosphere is dissolved by rainfall to form a weak solution of carbonic acid, and the respiration of plants and bacteria in the soil zone strengthen the acidity. In soils and subsoils containing carbonate minerals, this percolating acidic water rapidly dissolves the minerals, releasing calcium and magnesium into solution along with impurities in the minerals. 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.

Reduction and oxidation processes involve the transfer of electrons between chemical species 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 and is replaced by equilibration with gases in the unsaturated

zone. However, in confined aquifers the oxygen cannot be replaced and the microbes start to reduce other compounds. Key redox reactions in natural groundwaters are: reduction of nitrate to nitrogen, reduction of iron and manganese oxides (this releases other metals from the oxides into solution, typically arsenic at very low concentrations), oxidation of ammonium to nitrate in the soil zone and unconfined aquifers, and oxidation of iron pyrites (Stumm and Morgan, 1996).

4 Review of International Approaches

Concise reviews, outline methodologies and key results for the international approaches reviewed are presented in Appendix B of the Main Report. 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.

4.1 European Union (Position Paper) (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.

4.2 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 are given in Shand and Frengstad (2001). The baseline conditions will be used to determine the thresholds that will be used to define 'good status'.

4.3 Germany

The German approach to defining natural concentrations is statistical, and relies on the availability of large amounts of data (Wendland *et al.*, 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.

4.4 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.

5 Characterisation

5.1 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. A number of Member States (including the UK and Germany) have also adopted this approach for reporting environmental trends in groundwater. 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 5.1 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 always be derived for each of these 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 5.1, 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 5.1 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 5.1, 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 5.1, sufficient analyses be made to enable an ionic balance to be obtained 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 draft 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

Table 5.1. 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 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: faecal coliforms, 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 the Biocides Directive (98/9/EEC)
Phosphate	From artificial fertilisers, sewage and farm wastes. Phosphate is not normally considered a risk to groundwater but can lead to eutrophication of surface waters at low concentrations
Radon	From natural sources, but a nationwide survey should be made
Uranium	From natural sources, but a nationwide survey should be made
Zinc	Present on galvanised steel and in acid mine drainage, it is liberated at low pH. Can be an indicator of elevated cadmium concentrations. Harmful to aquatic organisms at low concentrations

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. leaking sewers or septic tanks) or from high stock densities. In both cases, elevated 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.

5.2 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 (Fig. 5.1):

1. **Data collation and handling procedures and protocols.** Collation of the data for all groundwater bodies 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 also be required to ensure that the groups have constant lithologies. In addition, some groundwater bodies might be subdivided (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 5.3), it is essential that the following steps be undertaken:

3. **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 a 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.
4. **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.

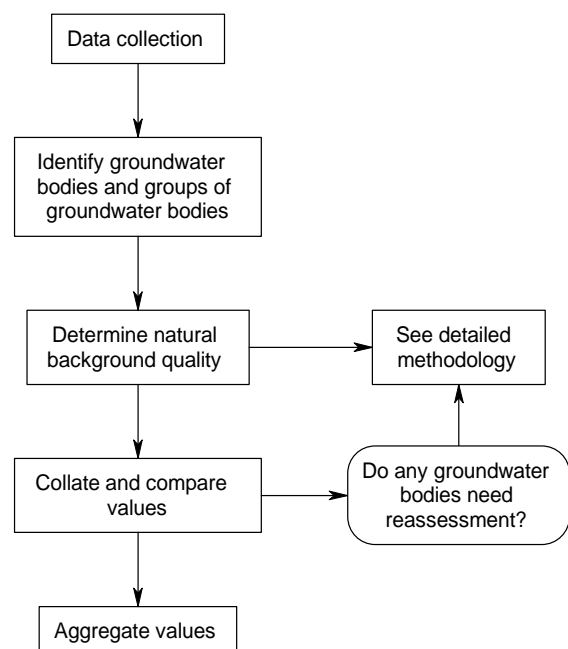


Figure 5.1. Recommended overall strategy for characterisation.

5.3 Recommended Methodology

The following is a summary of the methodology in approximate order of execution for each groundwater body or group of groundwater bodies (Fig. 5.2).

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 still 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,

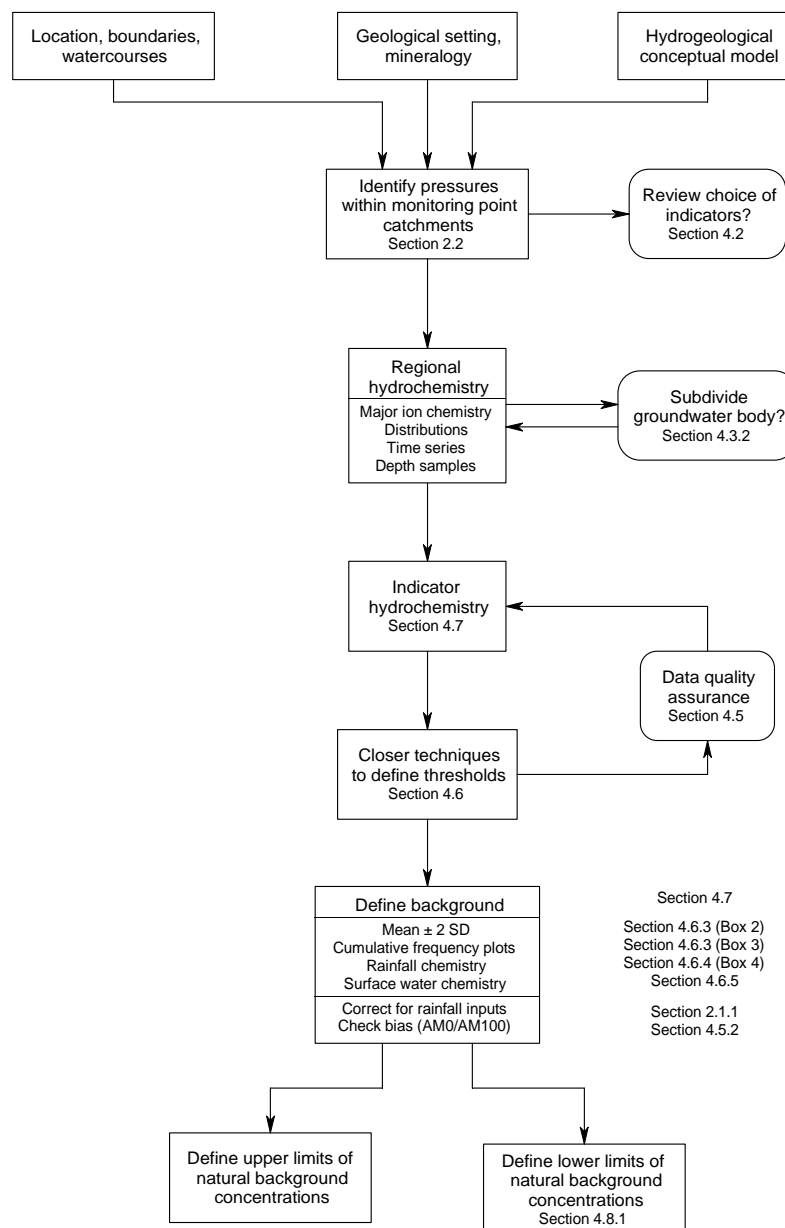


Figure 5.2. Recommended detailed methodology for characterisation. Section numbers refer to detailed guidance in the Main Report.

and is critical for the selection of 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 some 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 dependent on the chemistry of the indicator species, the amount of data available, and whether anthropogenic impacts have been identified.

5.4 Techniques

5.4.1 Hierarchy of preferred techniques

Table 5.2 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 the amount of data required are provided.

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 likely that, even if sufficient historical data for one contaminant are available, there may be insufficient data for another contaminant, so other techniques should be applied in that case.

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

5.4.2 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 the introduction of the Common Agricultural Policy prompted many farmers to invest in modern, intensive agricultural practices. 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 ¹⁴C 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, are of good quality.

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 value of the concentrations.

5.4.3 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

Table 5.2. 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, rainwater chemistry
= 3	Surface waters	Surface water chemistry at medium flows

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, they 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 polluted samples. The preferred techniques are graphical methods (cumulative frequency plots and time series) by which statistics can be obtained manually.

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 (Fig. 5.3). 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.

Upper and lower concentration 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 pollutant impact through time and may allow natural background or background concentrations to be hindcasted given sufficient independent data.

5.4.4 Atmospheric inputs

Determination of natural background concentrations from atmospheric inputs is simple for conservative species such as chloride by performing a mass balance. For species such as sulphate, which have both natural and anthropogenic atmospheric sources, and when background concentrations have been obtained from groundwater chemistry data (such as by using a cumulative frequency plot), they should be corrected for anthropogenic atmospheric inputs

The results of aquifer trialling suggest that chloride is conservative through the soil zone, but nitrate, ammonium and sulphate are not. To determine upper concentration limits of non-conservative species, it is necessary to scale the average concentrations in infiltration to obtain an estimate of the 95th percentile concentration. Evapotranspiration in the soil zone enriches all chemical species equally, so if an estimate of the 95th percentile

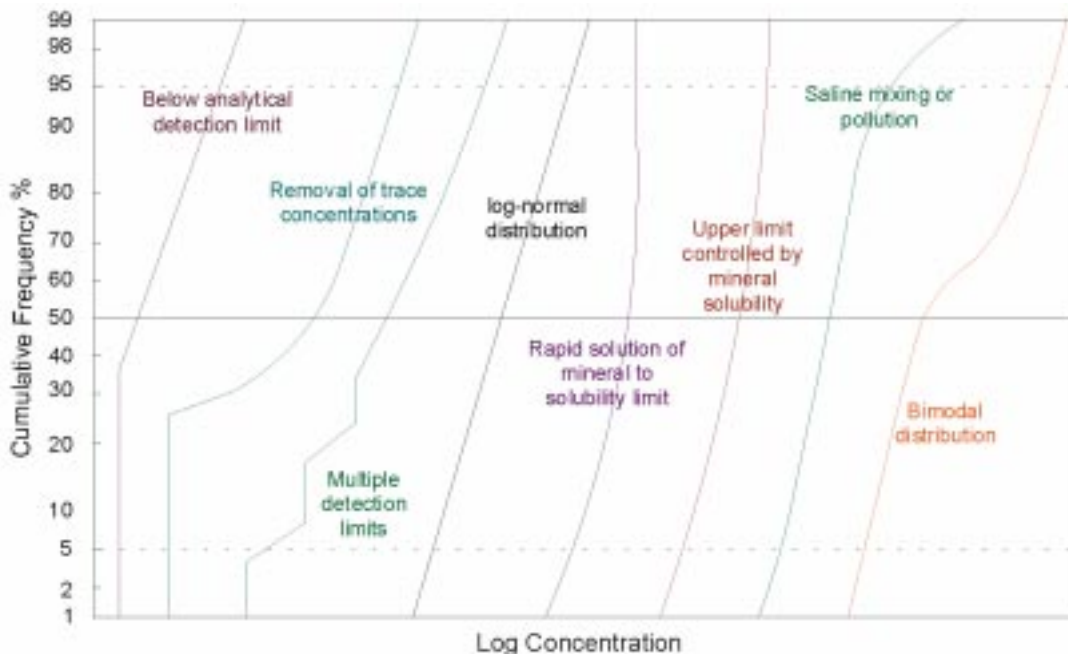


Figure 5.3. Examples of concentration profiles on cumulative frequency plots.

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).

5.4.5 Analysis of surface water data

Systematic surface water monitoring in Ireland has taken place since 1971. 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 dependent 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.

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.

5.5 Definition of Limiting Concentrations

The definition of upper limit concentrations will be quite straightforward using the techniques presented in Section 5.4; however, the definition of lower limit concentrations may be complicated due to issues with limits of detection (LOD) in the data series.

Lower natural background limits are required when describing the concentrations of species that are depleted by pollution (e.g. dissolved oxygen or sulphate). 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.

5.6 Grouping or Subdivision of Groundwater Bodies

5.6.1 Grouping

The definition of a groundwater body is made on the basis of hydrogeological continuity and flow patterns (Section 2.2) 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.

The following points describe the factors that should be taken into account when considering the grouping of groundwater bodies for this purpose:

- **Bedrock lithology**
Basic grouping of groundwater bodies by bedrock lithology could be accomplished by comparison within the 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 Till 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 (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.

5.6.2 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 can be removed from groundwater in naturally 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 are not likely to be available to support it. Subdivision will only be possible where there are adequate data for both sets of conditions.

6 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 5. The purpose of undertaking the trials was two-fold:

1. to demonstrate the applicability of the selected methodology in a relevant and representative range of hydrogeological conditions; and
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 of the Main Report. 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 hydrogeologists with experience in data handling and interpretation of regional hydrochemistry, under the supervision of the principal author of this report.

6.1 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 the GSI as described below (Fig. 6.1). 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.

6.1.1 The Curragh Gravel groundwater body

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.

6.1.2 The Wexford Limestone groundwater body

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.

6.1.3 Old Red Sandstone (ORS) in the SERBD

A continuous but multiple-catchment group of groundwater bodies, primarily inland, mostly in Co. Waterford. The ORS 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.

6.1.4 Calp Limestone outcrop in the SERBD

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.

6.2 Lessons Learned

6.2.1 Data availability

The confidence in the results of the Curragh Gravels and the 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.

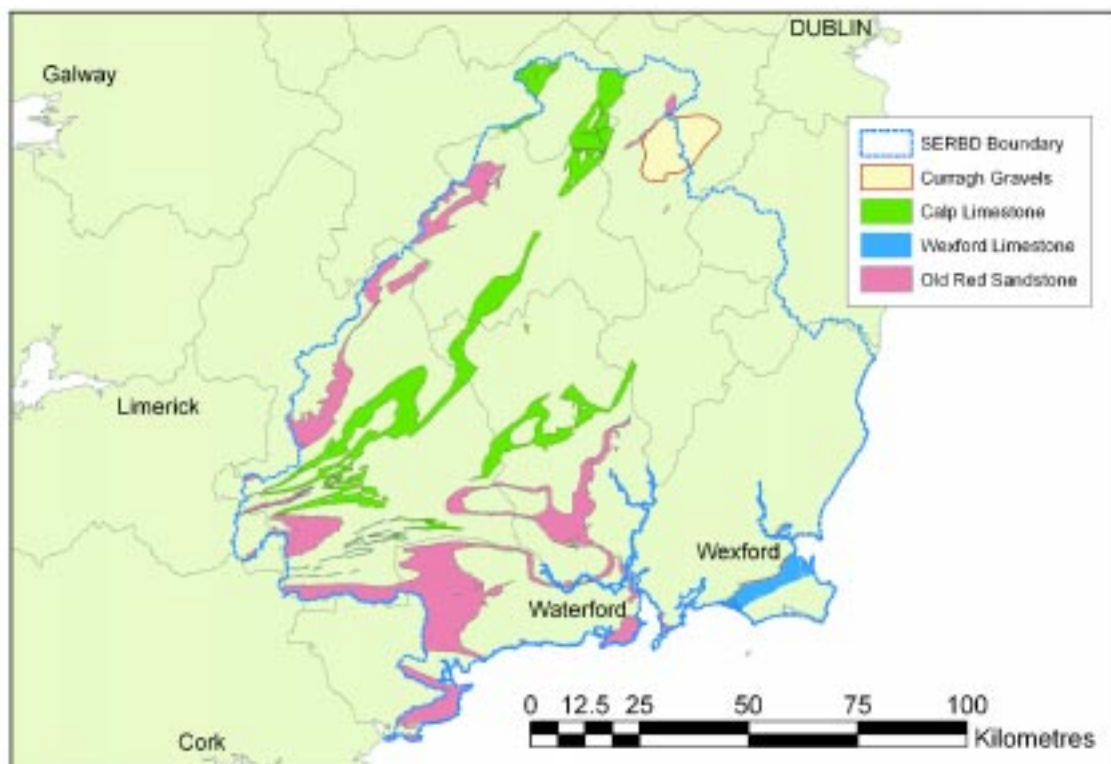


Figure 6.1. Location of trial groundwater bodies and groups of groundwater bodies.

6.2.2 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 $\pm 10\%$ 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 were measured and entered as mg/l but, as the database was expecting values in $\mu\text{g/l}$, values were therefore output (as $\mu\text{g/l}$) 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).

6.2.3 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.

6.2.4 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.

In unconfined, well-oxygenated groundwater bodies with naturally very low iron and manganese, there were so few positive results for those two species that 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.

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

6.2.5 Key issues for professional judgement

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

1 Which sample results have been impacted upon by anthropogenic activity?

Because sources of pollution are potentially widespread within any particular groundwater body, this question 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.

2 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 40, 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. Results from the trials show 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 5.6.2), 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.

6.3 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 Keegan (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 and uranium be consistently monitored for as a core parameter.

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.

7 Summary

The Water Framework Directive requires an assessment of the qualitative (chemical) status of groundwater bodies. This is to be accomplished by comparison of the existing groundwater quality with the natural background quality of the groundwater body. This project has interpreted the phrase 'natural background' as:

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.

A set of chemical species or parameters ('indicator species') has been chosen that indicate the nature and extent of diffuse pollution to a groundwater body. The choice of appropriate indicator species reflects the pressures acting on a particular groundwater body.

This project has identified a number of techniques that can be used to derive the ranges of concentrations of indicator species in groundwater at its natural background quality. In order of preference, these are:

1. **Historical data analysis.** Using concentrations of indicator species from several representative locations for reliable pre-1973 data.
2. **Recent data analysis.** Using recent measurements for which correction can be reliably made to exclude those impacted by human influences.
3. **Atmospheric inputs.** Using the quality of rainfall to predict the quality of infiltrating waters.
4. **Surface waters.** Using surface water chemistry at medium flows to predict the quality of infiltrating waters.

These techniques have been trialled using a number of groundwater bodies, and groups of groundwater bodies, in Ireland, and have been shown to be generally applicable. However, the trialling has demonstrated the need for expert judgement in deriving appropriate ranges of concentrations.

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