Baseline groundwater quality: Contrasting geochemical evolution in selected Celtic and Viking aquifers.

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Abstract

The geology of the Celtic regions and Norway display many similarities being dominated by hard-rock lithologies and a substantial surface water resource. Minor aquifers are also important in these countries and provide an important groundwater resource, particularly for rural communities. Water quality in many of the minor aquifers of both countries is often poorly documented and therefore the baseline conditions are difficult to assess. The effects of anthropogenic pollution may be important because the dominance of fracture flow may allow rapid transport to the water table with little time for pollutant attenuation or degradation. An attempt has been made to assess the baseline water quality in selected British and Norwegian aquifers. There is considerable overlap in water quality between the different aquifers, but several chemical differences are apparent which can be interpreted in terms of aquifer mineralogy and residence time. In addition, there are some significant differences between the UK and Norwegian aquifers studied. Most of the Norwegian groundwaters have relatively high pH compared with those of the UK (including carbonate aquifers), which is surprising considering that they are mainly composed of hard rocks. In addition, Na-HCO\textsubscript{3} type waters are much more prevalent in Norway compared to a dominance of Ca-HCO\textsubscript{3} type waters in the UK. The reasons for some of these differences may relate to subtle differences in mineralogy and exchangeable cations as a consequence of differences in sea-level following the last glaciation. Differences are also noted in several trace elements e.g. high F, U and Rn concentrations in many of the granite and sedimentary groundwaters in Norway and high barium in the UK sedimentary aquifers.

1. Introduction

The Celtic regions contain abundant minor aquifers which provide important local resources, particularly in rural areas. Many of these are classed as hard-rock aquifers with storage largely confined to fracture networks. This is also the case in Norway, where much of the bedrock comprises Pre-Cambrian and Caledonian rocks. Such aquifers are often at risk from pollution because of rapid transport in lithologies dominated by fracture flow. These areas are often overlain by thin acidic soils making the rivers and groundwater prone to the effects of acidic deposition. Many such aquifers are poorly understood in terms of hydrogeology and the quality of the groundwater they contain. The complex and variable mineralogy and structure of many hard-rock aquifers make it difficult to constrain flow-pathways, to determine the natural baseline concentrations and make a reasonable risk assessment.

The only waters which are likely to have escaped the effects of anthropogenic pollution are those which have been isolated from the atmosphere for some time and these generally occur as palaeowaters or those which are present under confined conditions. Such resources are limited and abstraction may be considered as groundwater “mining” and thus unsustainable. However, younger waters may be present for which many individual components are naturally-derived. Conversely, many waters contain concentrations of elements which, although naturally derived, exceed drinking water standards. Such “natural” contamination of groundwater should not be confused with anthropogenic pollution, and should also be considered as representing baseline.
The concept of chemical baseline is useful to discriminate natural inputs from those of anthropogenic origin. In addition, the baseline sets limits on the extent to which remedial measures may be necessary or indeed possible. The variations in bedrock geology, soil type and thickness, residence time of the groundwater, and the presence of drift deposits give rise to a range in the natural baseline concentrations. Therefore, it is necessary to establish criteria for defining precisely the term baseline: a simple average concentration is of little use in establishing a meaningful tool for use by policy makers and end users. However, it is possible to define baseline using simple mathematical tools or the use of simple statistical methods.

2. The Baseline Concept

The term Baseline can be defined in different ways and a clear definition is required. The definition used here for groundwater baseline is “the range in concentration of an element, species or chemical substance present in solution which is derived from natural geological, biological, or atmospheric sources”. Terms such as background or threshold can have a similar meaning, but these terms are not generally used to infer no anthropogenic influence.

There are several approaches to determining background water chemistry relative to pollution from a mining and smelter site which are of use in baseline studies:

1) up-gradient and cross-gradient sampling
2) extrapolation using historical water quality data
3) extrapolation from similar geochemical environments
4) geochemical modelling
5) statistical methods

All of these methods have application in the determination of baseline geochemistry and can be used in conjunction to deduce the baseline chemistry of groundwaters. It is unlikely that there will be sufficient data available for all of these approaches to be successful, and it is recommended that these be used together to determine the natural baseline.

One aspect of baseline geochemistry that has proved difficult to get across to policy makers and stakeholders is the variation that exists in nature; therefore, it is necessary to provide ranges in baseline values and not simply a single concentration. This range can be described in many ways e.g. by mean and standard deviation; the total range in values; or by describing a maximum baseline concentration. The value of traditional statistical parameters such as mean, median or mode are of use when comparing the baseline chemistry of different aquifers, but use of the median value is preferred because it is much more robust and less affected by outlying values.

Many authors have used a limit to define an upper baseline e.g. Edmunds et al., (1997) and Langmuir (1997) chose values of the 95th percentile and 97.7 % respectively. However, there is no a priori reason that anomalous or non-base line data should fit such an arbitrary choice and the problems of representative sampling are paramount. Most of the outcrop areas of UK aquifers, for example, show the effects of enhanced concentrations of nitrate from agricultural practices. A simple cut-off value or threshold concentration would be meaningless as values below the threshold may not represent baseline. In addition, such techniques do not take into account the fact that anomalous and background concentrations often show significant overlap or have natural multimodal distributions.

Traditionally, the use of statistical techniques has assumed that geochemical distributions are either normal, or more generally, lognormal (Ahrens 1954). Such an assumption was heavily criticised because the datasets studied did not generally display normal or lognormal distributions and therefore statistical techniques which assume such distributions are invalid.
for their treatment. In most natural systems geochemical distributions are generally polymodal and are usually skewed (Reimann & Filzmoser, 2000).

Probability plots are useful in highlighting different populations of data. In this context they could be of use in baseline studies to discriminate natural baseline chemistry from that due to pollution. In addition, they display very effectively the range and distribution of data and allow clear comparisons of water quality from different aquifers. However, it needs to be assessed to what degree natural variations produce multi-modal populations. There are several types of geochemical reaction which will alter distributions by removing or limiting concentrations in solution (Box 1). These include redox-processes e.g. in reducing environments nitrate may be completely removed from solution even from polluted waters; adsorption onto solid mineral phases may remove many trace metals or contaminants; and saturation with respect to a mineral phases will limit the solubility of one of more elements e.g. Ca and F through precipitation of fluorite.

**Box 1 Use of cumulative frequency diagrams to indicate baseline characteristics in groundwaters**

<table>
<thead>
<tr>
<th>LOG CONCENTRATION</th>
<th>CUMULATIVE FREQUENCY %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bimodal distribution</td>
<td>Bimodal distribution</td>
</tr>
<tr>
<td>Saline mixing or pollution</td>
<td>Saline mixing or pollution</td>
</tr>
<tr>
<td>Upper limit controlled by mineral solubility</td>
<td>Upper limit controlled by mineral solubility</td>
</tr>
<tr>
<td>Rapid solution of mineral to solubility limit</td>
<td>Rapid solution of mineral to solubility limit</td>
</tr>
<tr>
<td>Removal of trace concentrations</td>
<td>Removal of trace concentrations</td>
</tr>
<tr>
<td>Normal distribution</td>
<td>Normal distribution</td>
</tr>
<tr>
<td>Below analytical detection limit</td>
<td>Below analytical detection limit</td>
</tr>
</tbody>
</table>

i) The median concentration is used as a single reference point for the element baseline which can be compared regionally or in relation to other elements.

ii) Normal to multi-modal distributions are to be expected for many elements reflecting the range in recharge conditions, water-rock interaction and residence times under natural aquifer conditions.

iii) Narrow ranges of concentration may indicate rapid attainment of saturation with minerals (e.g. Si with silica, Ca with calcite).

iv) A strong negative skew may indicate selective removal of an element by some geochemical process (e.g. NO₃ by *in situ* denitrification).

v) A narrow range in concentration at the upper limit may indicate a mineral solubility control (e.g. F by fluorite).

vi) A positive skew most probably indicates a contaminant source for a small number of the groundwaters and this gives one simple way of separating those waters above the baseline. Alternatively the highest concentrations may indicate waters of naturally higher salinity.

Other techniques which have been used to illustrate hydrogeochemical datasets include boxplots which display the median and/or the mean, specified percentiles and outliers; histograms (but these can show different distributions depending on buckets used for concentration); Piper diagrams, X-Y plots and maps of data showing the areal variation in concentration. In this report boxplots and probability plots will be used since these show
unbiased statistical data (although it must be remembered that analytical and sampling errors still exist). One other problem in characterising the groundwater chemistry of an aquifer or groundwater body is that most analyses relate to samples which are collected as discharge by pumping. Such samples may have been collected from a large screened interval and represent a mixture of chemically different groundwaters.

3. Aims of paper

The aims of this paper are to present chemical data from selected aquifers in the UK (Cornish granites, Ordovician-Silurian metasediments of Wales, Devonian Sandstone of Scotland) and Norway (Pre-Cambrian granites, anorthosites and Ordovician-Silurian metasediments); to assess the variations in natural baseline quality, and to compare and contrast groundwater chemistry in these countries.

4. Summary of studied aquifers

The aquifers selected from the UK include shallow groundwaters in the Cornish granites, groundwaters from the Ordovician-Silurian metasediments of Wales and groundwaters from the Devonian Sandstones of Fife in Scotland (Figure 1).

![Figure 1. Map of the UK showing the localities of the selected aquifers.](image)

The aquifers selected from Norway include the Precambrian Iddefjorden granite, the Precambrian Egersund anorthosite and Cambro-Silurian metasediments (Figure 2).
The Lower Palaeozoic metasedimentary rocks of Wales comprise mudstone and siltstones with minor amounts of greywacke and provide local supplies of groundwater, particularly for farms, but the resource is not significantly exploited. The data used here (Figure 1) are for groundwaters sampled in the Teifi Valley of south Wales (Robins et al., 2000) and from the Plynlimon experimental catchment in central Wales (Shand et al., 1996). Groundwater occurs both in deep fractures (generally bedding plane fractures) and in a shallow (< 10 m) weathered and fractured zone. Vertical stratification is apparent in some of these boreholes with acidic oxidising waters in the shallow system and alkaline reducing waters at depth (> 20 m). Groundwater also occurs in fractures and lodes of the Permian Carnmenellis granite in Cornwall. Water yields are generally small and sufficient only for small-scale water supply. Geothermal waters are found in deep fractures within the granite but the data presented here are from the shallow aquifer (Smedley et al., 1989). The Devonian aquifer in Fife represents one of the most important Scottish aquifers and is situated in a graben structure, the Midland Valley. The aquifer supplies 20 MI d⁻¹ during winter periods, increasing to 40 MI d⁻¹ in the summer due to abstraction for irrigation. Unlike the aforementioned aquifers, the Fife aquifer has relatively high porosity varying between 10 and 20% due to varying degrees of cementation by calcite and dolomite.

The Precambrian Iddefjorden granite was formed during the Sveco-Norwegian orogeny in Middle Proterozoic (900 million years BP) and intrudes older metamorphic rocks. Most of the terrain has emerged from the sea during the last 10,000 years due to about 200 m of net isostatic uplift following the last glaciation. The primary porosity of the granite is negligible and practically all water flow takes place in fractures. Some of the most prominent fracture zones are filled with low-permeability clay minerals and thus yield little water. The boreholes have generally low yield and mainly supply single households and farms. The Egersund anorthosite province is part of the Rogaland igneous complex of Middle Proterozoic age. These also provide groundwater to single farms and households. The boreholes have a median normalised yield of 5.1 L h⁻¹ per drilled metre (Morland 1997), one of the lowest normalised yields among the different lithological groups in Norway. The lower Palaeozoic
metasediments of Norway overlap with in terms of age with those in Wales, but show a much larger range in rock types from mudstones, shales to phyllite and mica-schist.

The aquifers chosen show a large range in rock types and mineralogy and it is to be expected that large chemical differences will exist between the groundwaters. The selection of study areas was chosen to maximise similar rock types. However, anorthosites are rare in the UK being confined to a small area of outer Hebrides. Sedimentary aquifers are not very common in Norway which is dominated by hard-rock aquifers of Lower Palaeozoic or older age.

5. Hydrochemical characteristics of the groundwaters

Details on the hydrochemistry have been presented elsewhere (Shand & Frengstad, 2000) and this paper will deal with comparisons between the study aquifers. This section will deal with the main hydrochemical characteristics of groundwater in the aquifers. The Chalk aquifer of England has been included on plots as a comparison of a well characterised major carbonate aquifer.

5.1 Major elements

The relative proportions of major cations are shown on a piper diagram on Figure 3. Although there is a large variation and significant overlap, there are clearly defined groupings.

Figure 3. Piper diagram showing the relative concentrations of major elements.
The major element data are summarised using boxplots on Figure 4. One of the most striking features of the dataset is the variable range in pH of the UK aquifers and the consistently high pH of the Norwegian hard-rock aquifers. The Carnmenellis granite groundwaters and to a lesser degree, the Welsh groundwaters, are relatively acidic, typical of hard rocks with little buffering capacity. The Norwegian granites, in contrast have a much higher pH. The carbonate cemented Fife aquifer and the carbonate chalk aquifer have pH ranges close to that imposed by carbonate buffering but with median pH significantly less than the Norwegian groundwaters. The UK hard rock aquifers show many similarities being of low total dissolved solids (TDS), Na as an important cation and low Ca and HCO₃ concentrations. The Fife sandstone aquifer shows many characteristics of carbonate aquifers e.g. high Ca and HCO₃ (c.f. the Chalk) due to the dominant control of its carbonate cements. One distinctive feature of these groundwaters is the very high Mg concentrations as a consequence of dolomite dissolution. Often, these waters are supersaturated with respect to dolomite.

![Figure 4. Boxplots comparing pH and major elements in groundwater samples from selected British and Norwegian aquifers.](image-url)
The Norwegian groundwaters also have relatively high HCO₃ concentrations but low Ca and the cations are typically dominated by Na giving rise to waters of Na-HCO₃ type. Although Na-HCO₃ type waters are found in the UK, these are normally present in deeper parts of the aquifers where the groundwaters are old and have undergone significant ion-exchange. Recent studies in the Lower Palaeozoic rocks at Plynlimon have found such waters at shallow depth (c. 20 m) which may be due an important input of sea salts from atmospheric deposition.

The distribution of element concentrations is best displayed on cumulative probability plots and two examples are shown on Figures 5 and 6. The plot for Na shows that all of the aquifers display a considerable range in concentrations. The ranges are high in all of the Norwegian aquifers stretching over at least one order of magnitude whilst the three UK study areas show a much smaller range. The Chalk aquifer shows that two distinct populations are present, the higher concentrations coinciding with confined groundwaters which have undergone mixing with an older Formation water.

These ranges are typical of most elements. The high concentrations of Mg in the Fife aquifer derived from dissolution of dolomite are clearly displayed on Figure 6 in comparison with the other study areas. In terms of baseline chemistry it is probable that most of the elements considered above represent baseline concentrations. Samples were collected only from boreholes which did not show any signs, or have a history, of point source pollution. However, it is clear from the nitrate concentrations (Figure 4) that most of the aquifers have been affected by diffuse agricultural pollution.

![Cumulative probability plot showing the range in Na concentrations in the groundwaters. Note that although several groups have similar median concentrations, their ranges can be very different.](image)

**Figure 5.** Cumulative probability plot showing the range in Na concentrations in the groundwaters. Note that although several groups have similar median concentrations, their ranges can be very different.

The use of probability plots to determine a polluted population is difficult because the natural process of denitrification will lead to modification of such distributions as shown in Box 1. There is little historical data available for most of these aquifers, but on-going studies in the UK indicate that baseline concentrations of c. 2-6 mg l⁻¹ are to be expected in oxidising
aquifers prior to agricultural intensification. It is difficult to estimate the degree to which other elements have been affected (e.g. Cl, K) by diffuse pollution because the ranges in the natural baseline are large and the additional inputs are within this range of natural concentrations concentrations of Mg in the Fife aquifer and the bimodal distribution in the Chalk aquifer.

5.2 Minor elements

Boxplots for the minor elements are shown on Figure 7. Each of the aquifers shows distinctive ranges (often over several orders of magnitude). Some of the more obvious differences include the high Ba concentrations in the UK sedimentary aquifers and the very high Sr in the Chalk. The large ranges in Fe and Mn reflect the redox conditions in the aquifer with low concentrations in the unconfined oxidising parts and high concentrations where the waters are reducing. The neutral to alkaline pH in most groundwaters has kept Al concentrations low but the higher concentration in the acidic groundwaters in the Carnmenellis granite is evident. The Precambrian granites of Norway generally have high F concentrations but this is not seen to the same degree in the Cornish groundwaters. The granite groundwaters of both countries also have high U. There is a contrast in the metasedimentary aquifers with regard to U in that the Norwegian groundwaters have high U concentrations but the Welsh ones low concentrations (Figure 8).

![Figure 6. Cumulative probability plot for Mg in the study aquifers.](image)

It is clear from this comparison of similar aquifers in the UK and Norway that rock type is not the only control on trace element species in these groundwaters. In order to understand why this is the case, it is necessary to look in detail at the potential reactions which occur in the aquifer. It is useful to study the changes which take place along flowlines, however, in hard-rock aquifers where flowlines are complex or poorly understood this makes unravelling the hydrochemical evolution very difficult. Nevertheless, a knowledge of the aquifer mineralogy and the geochemical environment provide insights into the geochemical controls and evolution of groundwaters in these aquifers.
Figure 7. Boxplots comparing minor elements in groundwater samples from selected British and Norwegian aquifers.

6. Controls on the baseline major and minor element chemistry

The primary control on geochemical evolution in groundwater systems is the reaction between recharge and the aquifer minerals present along flowpaths. A series of reactions dominate over the time scales involved in groundwater flow including mineral dissolution, ion-exchange, adsorption-desorption and redox reactions. However, it is not always the major mineral phases which dominate the types of reaction involved because different reactions occur at different rates. The dissolution of evaporite and carbonate mineral for example are relatively fast whilst reactions involving silicate minerals are generally very slow.

The dominance of Ca, Mg and HCO₃ in the Fife and Chalk aquifers is related to a dominant control by carbonate (calcite and dolomite) dissolution. Although the Fife aquifer is dominated by quartz, the kinetics of dissolution of quartz is extremely slow. The Fife aquifer does contain some silica but this is derived from the dissolution of other silicate minerals such as feldspar. The Welsh metasedimentary rocks are dominated by illite and chlorite which are relatively unreactive. The buffering capacity of the rocks to acidic rainfall is, therefore, relatively low and this is reflected in the relatively low TDS of the groundwaters. The
groundwaters are of variable type but many are of Ca-HCO₃ type due to the presence of minor amounts of calcite in fractures or present in drift above the bedrock (Robins et al., 2000). The larger range of concentrations found in the Norwegian metasedimentary aquifer groundwaters is partly due to the larger range in rock types and mineralogy. The anorthosites of Norway are basic rock types with mineralogy dominated by plagioclase (Ca-Na) feldspar and orthopyroxene (Mg-Fe silicate) and one would expect that the groundwaters would be of Ca- or Mg-HCO₃ type. The granites on the other hand would be expected to have poor buffering capacity and low pH similar to the Cornish granites. The relatively high pH and dominance of these Na-HCO₃ types in Norway require a different interpretation to the Ca-HCO₃ dominated groundwaters of the UK. The most likely interpretation is ion exchange reactions (Frengstad & Banks, 2000) during aquifer freshening (a process which is still seen in deeper UK groundwaters). Ion exchange reactions occur relatively rapidly in comparison with mineral dissolution. During aquifer freshening, Ca in the groundwater is exchanged for Na which is the dominant cation present on clays where saline or seawater has been present.

![Cumulative probability plot showing the range in U concentrations in the groundwaters.](image)

**Figure 8.** Cumulative probability plot showing the range in U concentrations in the groundwaters.

The Norwegian and UK aquifers studied all have relatively low Cl concentrations indicating that extensive flushing has occurred. The differences between the two sets of aquifers, therefore, must relate to the timing or intensity of flushing. Many of the Norwegian coastal aquifers were below sea level until relatively recently. Although these aquifers have subsequently been well flushed by fresh water, the dominance of Na left behind on the exchange sites of aquifer minerals, due to more recent sea-level decline, and has allowed the waters to evolve to Na-HCO₃ compositions (Figure 3) which occurred relatively recently.

The differences between trace element concentrations in the granite and metasedimentary aquifers also needs to be studied in more detail. The complexity of the metasediments in Norway and their original sources may be largely responsible for the lack of similarity. In the case of the granites, it should be noted that these are of significantly different age and also tectonic history. The differences may therefore relate to differences in minor mineral phases such as fluorite and uranium-bearing minerals. In addition the glacial history may have had a significant effect in that the upper weathered parts of the Norwegian granites have been scoured during glaciation providing access to fresh mineral surfaces, whereas the Cornish
granites are overlain by relatively altered granite where leaching may have depleted the rocks in certain trace elements.

7. Summary and conclusions

The groundwaters in both countries show large ranges in baseline concentration within and between different aquifer rock types. Although similarities exist in the hydrochemistry of groundwaters in these two “regions”, some chemical distinctions are apparent: groundwaters from Norway have relatively high pH compared with those in the UK (including carbonate aquifers). In addition, Na-HCO₃ type waters are much more prevalent in Norway compared to a dominance of Ca-HCO₃ type waters in the UK. This is most likely caused by cation-exchange and freshening of the studied Norwegian aquifers as a consequence of more recent isostatic readjustment following the last ice age.

Many trace elements show variations in concentration ranging over several orders of magnitude within aquifer units. Much of the variation in trace elements is related to the occurrence of accessory or secondary mineral phases and their associated trace constituents e.g. F, Rn, Be, U, and Ba. The concentrations of such elements are generally related to tectonic setting and provenance e.g. in the case of granites, those from convergent margin boundaries are geochemically distinct from within-plate orogenic granites. Therefore, each aquifer needs to be assessed individually and the application of the baseline concept to problems in groundwater quality such as pollution or remediation needs to take into account the natural variation in both lithology and groundwater chemistry. Indeed, the variation of some parameters in natural waters may be as great or greater than that produced by pollution and water quality standards may be breached by entirely natural processes.

References


