# Natural background levels for chemicals in Icelandic aquifers

Maria J. Gunnarsdottir, Sigurdur M. Gardarsson, Gunnar St. Jonsson, Halldor Armannsson and Jamie Bartram

## ABSTRACT

Information about natural background levels (NBLs) of chemicals in source waters allows water utilities to identify trends in drinking water contamination. We estimate NBLs for chemicals in source waters for Icelandic water utilities at both national levels with all data pooled, and according to geological regime. NBLs were derived by collecting samples from 79 aquifers considered largely unimpacted by human activities. The aquifers were categorized into four geological settings that are representative of the geology of Iceland. NBLs were calculated as 90%iles of all aquifers in each setting and in all pooled. There was a statistical difference between the geological settings in 11 parameters of 37 tested. The 90%ile for nitrate for all aquifers pooled was 1.36 mg/l, indicating little anthropogenic influence on water used for public water supply in Iceland. The results were compared to the chemical status of 60 European aquifers, collected for the European Union's Sixth Framework Program Background Criteria for the Identification of Groundwater Thresholds project, revealing lower dissolved solids concentration for Icelandic groundwater than that from other parts of Europe. The explanation is likely due to high permeability of young geology settings and low population density in Iceland whereas there is a long history of agriculture and industry in most European countries.

**Key words** | chemicals, drinking water, groundwater, natural background levels, water safety management

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## INTRODUCTION

Information on the natural background levels (NBLs) of chemicals in aquifers is necessary for effective and early detection of anthropogenic influence and to inform potential remediation. Such information assists water utilities, which are ultimately responsible for delivering safe drinking water, to trace pollution, react to trends in drinking water contamination and manage risk.

The European Union (EU) Water Framework Directive (WFD) requires that pollution trends be identified and reversed (EC 2000). The directive applies to surface water, groundwater, transitional water and coastal water. The WFD and the subsequent EU directive on groundwater (EC 2006) require that the starting point for trend reversals be defined as well as criteria for assessment of good groundwater status. The resulting threshold values (TVs) should be established nationally as quality standards for pollutants in groundwater in order to protect human health and the environment (Hinsby *et al.* 2008). They are intended to reflect good chemical status and take into account knowledge of human toxicology and ecotoxicology. Information on NBLs of chemicals in groundwater informs TV setting. In principle, NBLs can be determined by use of water quality data from aquifers unaffected by human impact. However, where there is a longstanding human impact 'natural' groundwater is hardly present and methodologies have to be developed to distinguish between natural and polluted conditions (BRIDGE D10 2006; Molinari *et al.* 2012).

In the EU's Sixth Framework Program a methodology for the derivation of NBLs and TVs was developed, with the participation of 16 European countries. The methodology was tested on 14 aquifers selected to represent most of the major European aquifer types that were defined in Background Criteria for the Identification of Groundwater Thresholds (BRIDGE) project (Pauwels *et al.* 2007, 2009). The BRIDGE project defined an NBL as 'the concentration of a given element, species or chemical substance present in solution which is derived by natural processes from geological, biological or atmospheric sources'.

European water directives have been incorporated into the Icelandic regulatory environment: the Drinking Water Directive (ECD 1998) through updated Icelandic Drinking Water Regulation (IDWR ME 2001); and the WFD through adoption into Icelandic legislation (Parliament of Iceland 2011). In recent Icelandic legislation incorporating the groundwater directive (ME 2012), TVs for the seven inorganic chemicals (arsenic, cadmium, lead, mercury, ammonium, chloride and sulphate) of the WFD minimum list (ECD 2006 Annex II) are set at 75% of the maximum allowed concentration (MAC) in the IDWR, and the TVs for nitrate are set as 50% of MAC in the IDWR.

The goal of this study is to initiate evaluation of NBLs of naturally occurring substances in Icelandic groundwater to inform early warning of pollution and estimation of threshold values. We compare the values with those from the BRIDGE project. Icelandic geology is different from that of other parts of Europe. These results therefore add to the knowledge of NBLs in areas with a similar geology elsewhere, augment information on NBLs in the European region, and provide specific reference values for areas with a low environmental impact as the impact of human activity on groundwater quality is minimal in Iceland.

## GEOGRAPHICAL AND GEOLOGICAL SETTING

Iceland is situated on the Atlantic Ridge on a basalt plateau that is thought to have begun to be formed 24 million years ago with its oldest rocks on land 14–16 million years old (Thordarson & Larsen 2007). The principal elements of the geology of the country are the Postglacial active volcanic zone (Postglacial zone), adjacent Pleistocene belts and an older Tertiary part. Infiltration is high and surface runoff limited in the active volcanic zone; whereas infiltration is much less extensive and surface runoff is greater in the older Tertiary part (Sigurdsson & Einarsson 1988).

The natural chemical composition of groundwater is largely determined by the composition of the rock it is abstracted from and varies with depth and residence time. Rock formations in Iceland are 80–85% basaltic and almost totally volcanic (Saemundsson 1979; Sigurdsson 1993). Groundwater from basaltic rock has lower chemical concentrations of major elements compared to many other rock types (Reimann *et al.* 1996); however, there are higher concentrations of chemicals in younger geological settings, especially within the active volcanic rift zone (Oskarsdottir *et al.* 2011). Basaltic glass is much more abundant in the younger rock and chemical denudation is greater in glassy rock than crystalline basalt, explaining to some degree the higher concentrations (Gislason *et al.* 1996).

Precipitation, with marine components, influences the chemical composition of groundwater in Iceland (Sigurdsson & Einarsson 1988; Sigurdsson 1990). In populated areas, which are mostly situated along the coast, precipitation was between 500 and 4,000 mm/year on annual average in the period 1971–2000 (Crochet *et al.* 2007). The precipitation percolates into the ground more easily where soil cover is thin and the bedrock is open and porous, as in the Postglacial zone. Most of the water sources for municipal water supplies in Iceland are less than 30 km from the sea. Rock formations in the Postglacial zone are usually very permeable and are frequently present close to the sea and thus amenable to sea water infiltration.

Geothermal areas are common in volcanic areas and geothermal water can mix with cold groundwater and increase the level of certain chemicals including many of the major elements (silica, fluoride, sodium and sulphate) and trace elements (boron, arsenic, mercury, cadmium and lead) while there is a reduction of magnesium as temperature and salinity-dependent silicate mineral equilibria control a very low $Mg^{+2}$ concentration in geothermal water (Sigurdsson & Sigbjarnarson 1989; Kristmannsdottir & Armannsson 2004; Baba & Tayfur 2011). During volcanic eruptions large quantities of ash have the potential to increase turbidity, acidity and fluoride in drinking water

and can also elevate the concentrations of various heavy metals (Gudmundsson *et al.* 1992; Stewart *et al.* 2006).

In the BRIDGE project, aquifer typology was classified into 10 basic units based primarily on the hydro-geochemical characteristics of groundwater and secondarily on processes such as redox conditions and geological age (Pauwels *et al.* 2009). The 10 basic units are merged into four groups: carbonated, unconsolidated, sandstones and hard-rock. Icelandic aquifers fall into two of these groups: unconsolidated and hard-rock. The unconsolidated group is divided into two subgroups: sand and gravel and marls and clays. Icelandic aquifers belong to the first of these. The hard-rock group is mainly divided into three subgroups: crystalline basement, schists and volcanic rocks. Icelandic aquifers are classified as volcanic. The BRIDGE methodology recommends establishing NBLs for chemicals by pre-selection of sample results used and the 90%ile calculated for the remaining samples.

About 95% of Iceland's drinking water supply is extracted from springs, wells or boreholes and is classified as groundwater. Surface water used for drinking amounts to less than 5% (EEA 2010). Groundwater is not treated unless there is a danger of surface water intrusion when treatment with filtration and UV is applied. Residual disinfection is not practised (Gunnarsdottir *et al.* 2013) and application of precautionary principles in water supply is therefore critical (Hasler *et al.* 2007; Smeets *et al.* 2009; Gunnarsdottir *et al.* 2012b). The water utilities in Iceland have adopted the principle of a water safety plan, whereby systematic risk management to prevent contamination of drinking water is a major focus (Gunnarsdottir & Gissurarson 2008; Gunnarsdottir *et al.* 2012a). This has proven to be effective in protecting water quality and human health (Gunnarsdottir *et al.* 2012b). In the associated risk assessment it is important to identify contamination at an early stage and therefore information on NBLs supports effective water safety management.

## METHODS

### Design of study

Data on drinking water quality were obtained from routine surveillance activities overseen by IDWR to verify the chemical safety of drinking water for the period 2002 to 2012 from 79 water resources supplying 65 separate water supply systems managed by 42 water utilities. Of the 79 resources, four are surface water from rivers with bank filtration and UV treatment whereas the rest is from untreated groundwater aquifers from springs or boreholes (Figure 1).

The data were analysed with respect to four classes: three hard-rock formations of basaltic volcanic distinguished by their age and one unconsolidated gravel deposit:

1. Difference in chemical content between geological settings. Water resources were classified into four classes: Postglacial (<10,000 years), Pleistocene (10,000 years to 3.3 million years), Tertiary formation (>3.3 million years) and unconsolidated gravel deposits (rock slides, glacial or fluvial deposits).
2. The NBLs of groundwater using the BRIDGE methodology, both classified according to geological settings and combined for all aquifers.
3. Evaluation of the natural groundwater status in Iceland and comparison with European groundwater.

The main characteristics of the water source locations are shown in Table 1. The water resources are relatively equally distributed except that only few are in the Tertiary formation.

### Data collection

Samples were collected by the health inspectors at the Local Competent Authorities (LCAs) who also measured pH at the sampling site. Conductivity was analysed by accredited local laboratories. For chemical analyses samples were sent to Matis Ltd – Icelandic Food and Biotech R&D, which forwarded them to the accredited laboratory ALS Scandinavia AB in Sweden (www.alsglobal.se). The LCAs deliver the results to the water utilities and follow up on non-compliance. Analytical results were made available to the authors by the water utilities or the LCAs. The results included analysis of indicator parameters, which indicate pollution in drinking water as conductivity, and pH, all major chemicals (except bicarbonate which was not determined), and most trace elements and heavy metals. All parameters used in the study are shown in Table 2. The
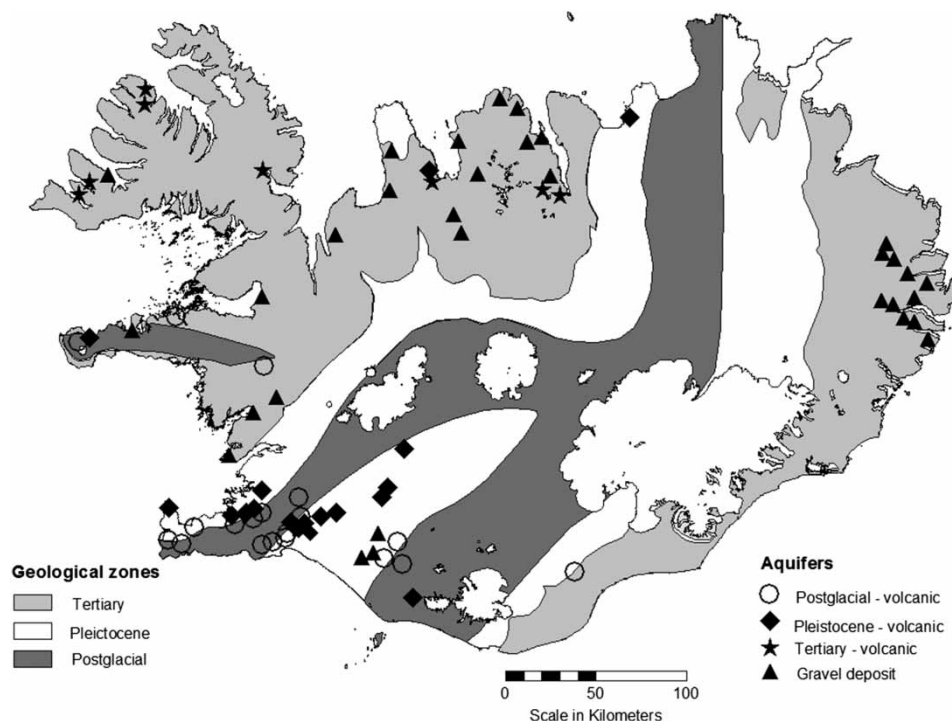
**Figure 1** │ Map of water sources locations categorized by geological settings. Note that smaller variations in the geological zones are not shown.

**Table 1** │ Characteristics of the aquifer locations

|  |  | Number of water resources |
| --- | --- | --- |
| Total |  | 79 |
| Geological setting | Postglacial | 21 |
|  | Pleistocene | 18 |
|  | Tertiary | 8 |
|  | Gravel deposit | 32 |
| Geographical area | W – West | 15 |
|  | N – North | 17 |
|  | E – East | 11 |
|  | S – South | 23 |
|  | SV – South-west | 12 |

total dissolved solids (TDS) concentration was estimated by calculating the bicarbonate concentration from the ionic balance and then adding the concentrations of all major chemicals. Analysis for pH and conductivity were performed in Iceland soon after sample collection. Bicarbonate and total dissolved solid concentrations, and total hardness were calculated from analyses and ionic balances. The samples were sent to ALS, Luleå, Sweden from where they were allocated to the appropriate laboratories

according to components analysed. An overview of the methods used and the laboratories that carried out the analysis is presented in Table 3.

Most often there was only one sample available from each aquifer but if two or more were available the results of the most recent analysis was used as these tend to have a lower detection limit indicating better analytical quality, yielding 79 data points: 53 direct from resource, 14 from service reservoirs and 12 from distribution networks. The service reservoirs are most often situated in the system upstream of the distribution network.

### Statistical analysis

As stipulated in the BRIDGE methodology, the 10th, 50th and 90th percentiles (%iles) were calculated for the 37 parameters analysed by ALS Scandinavia AB. Cumulative frequency plots were produced for all the chemicals (except nitrite as it was always below detection limits), in all 30 chemicals. Results with values below detection limits (DLs) were included in the percentile statistics but not displayed in the plots, as explained in the BRIDGE

**Table 2** | Chemical composition of Icelandic aquifers in four geological settings

| Parameters | | Postglacial | | | | Pleistocene | | | | Tertiary | | | | Unconsolidated | | | | Total | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | N | 10%ile | 50%ile | 90%ile | N | 10%ile | 50%ile | 90%ile | N | 10%ile | 50%ile | 90%ile[a] | N | 10%ile | 50%ile | 90%ile | N | 10%ile | 50%ile | 90%ile |
| TDS[b] | mg/l | 21 | 46 | 86[U] | 258 | 18 | 47 | 76 | 115 | 7 | 49 | 59 | | 32 | 37 | 58 | 146 | 78 | 41 | 75 | 139 |
| Hardn[b] | °H | 21 | 0.7 | 1.5 | 3.7 | 18 | 0.5 | 1.1 | 2.1 | 8 | 0.5 | 1.0 | | 32 | 0.6 | 1.1 | 3.1 | 79 | 0.5 | 1.2 | 2.8 |
| HCO$_3$[b] | mg/l | 21 | 14 | 38 | 79 | 18 | 23 | 36 | 56 | 8 | 14 | 25 | | 32 | 8 | 27 | 78 | 79 | 14 | 35 | 73 |
| Na | mg/l | 21 | 6.19 | 10.7[U] | 51.84 | 18 | 6.29 | 10.1 | 17.19 | 8 | 4.03 | 8.38 | | 32 | 3.04 | 6.51 | 12.27 | 79 | 4.03 | 9.31 | 15.5 |
| K | mg/l | 21 | 0.46 | 0.78[U] | 1.95 | 18 | DL | 0.42 | 1.53 | 8 | DL | DL | | 32 | DL | DL | 1.04 | 79 | DL | 0.61 | 1.33 |
| Si | mg/l | 21 | 4.74 | 8.11 | 12.36 | 18 | 6.27 | 8.1 | 12.82 | 8 | 4.29 | 6.6 | | 32 | 3.36 | 7.53 | 11.64 | 79 | 4.57 | 7.86 | 12 |
| Ca | mg/l | 21 | 2.45 | 5.66 | 10.04 | 18 | 2.64 | 5.6 | 10.66 | 8 | 2.8 | 4.03 | | 32 | 2.59 | 5.42 | 15.01 | 79 | 2.7 | 5.5 | 11.2 |
| Mg | mg/l | 21 | 0.99 | 2.69[Pl,T] | 9.93 | 18 | 0.15 | 0.87 | 3.57 | 8 | 0.47 | 0.99 | | 32 | 0.8 | 1.63 | 6.15 | 79 | 0.63 | 1.69 | 6.21 |
| S | mg/l | 14 | 0.66 | 1.1[U] | 8.61 | 13 | 0.42 | 0.73 | 1.52 | 7 | 0.21 | 0.67 | | 22 | DL | 0.62 | 1.33 | 56 | 0.32 | 0.74 | 2.73 |
| Fe | mg/l | 21 | DL | 0.002 | 0.174 | 18 | DL | 0.003 | 0.034 | 8 | DL | 0.007 | | 32 | 0.001 | 0.003 | 0.018 | 79 | DL | 0.004 | 0.031 |
| SO$_4$ | mg/l | 21 | 1.56 | 3.2[U] | 15.44 | 18 | 1.52 | 2.22 | 5.63 | 7 | 0.75 | 2.03 | | 32 | 0.93 | 1.87 | 4.75 | 78 | 1.18 | 2.3 | 6.8 |
| Cl | mg/l | 21 | 5.06 | 9.9 | 108.88 | 18 | 4.45 | 8.76 | 16.96 | 7 | 2.3 | 11.1 | | 32 | 3.66 | 7.15 | 18.53 | 78 | 3.88 | 8.92 | 22.65 |
| NH$_4$ | mg/l | 21 | DL | DL | DL | 18 | DL | DL | DL | 7 | DL | DL | | 32 | DL | DL | DL | 78 | DL | DL | DL |
| NO$_2$ | mg/l | 21 | DL | DL | DL | 18 | DL | DL | DL | 7 | DL | DL | | 32 | DL | DL | DL | 78 | DL | DL | DL |
| NO$_3$ | mg/l | 19 | DL | 0.19 | 0.62 | 18 | DL | 0.19 | 1.62 | 7 | DL | 0.14 | | 29 | DL | 0.21 | 2.0 | 73 | DL | 0.18 | 1.36 |
| P | mg/l | 21 | 0.007 | 0.026 | 0.064 | 18 | 0.016 | 0.029 | 0.058 | 8 | 0.002 | 0.024 | | 32 | 0.003 | 0.019 | 0.049 | 79 | 0.004 | 0.024 | 0.051 |
| F | mg/l | 21 | DL | DL | 0.28 | 18 | DL | DL | 0.20 | 7 | DL | DL | | 32 | DL | DL | 0.15 | 78 | DL | DL | 0.14 |
| TOC | mg/l | 19 | DL | DL | 1.9 | 17 | DL | DL | 3.1 | 7 | DL | DL | | 31 | DL | DL | 1.1 | 74 | DL | DL | 1.6 |
| Colour | | 15 | DL | DL | 7,0 | 16 | DL | Dl | 6,5 | 6 | DL | Dl | | 28 | DL | DL | 5,2 | 65 | DL | Dl | 5,8 |
| Cond | µS/cm | 11 | 56 | 121 | 270 | 13 | 66 | 104 | 289 | 3 | 48 | 57 | | 14 | 47 | 84 | 170 | 41 | 52.4 | 91.4 | 190 |
| pH | | 12 | 7.12 | 8.4[U] | 8.86 | 13 | 7.18 | 8.85[T,U] | 9.61 | 6 | 7.36 | 7.79 | | 14 | 6.7 | 7.1 | 7.8 | 45 | 6.88 | 7.7 | 8.95 |
| Al | µg/l | 21 | 1.58 | 5.79 | 18.88 | 18 | 3.09 | 12.55[Po,T,U] | 42.87 | 8 | 2.79 | 4.18 | | 32 | 0.29 | 2.12 | 8.15 | 79 | 0.63 | 5.09 | 18.7 |
| As | µg/l | 21 | DL | DL[U] | 0.19 | 18 | DL | DL | 0.17 | 8 | DL | DL | | 32 | DL | DL | 0.09 | 79 | DL | DL | 0.11 |
| B | µg/l | 21 | DL | DL[Pl,U] | 32.24 | 18 | DL | DL | 4.01 | 8 | DL | DL | | 32 | DL | DL | DL | 79 | DL | DL | 12.1 |
| Ba | µg/l | 21 | 0.08 | 0.34[Pl,T,U] | 0.95 | 18 | DL | 0.05 | 0.25 | 8 | DL | 0.08 | | 32 | DL | 0.06 | 0.34 | 79 | DL | 0.1 | 0.51 |
| Cd | µg/l | 21 | DL | DL | 0.002 | 18 | DL | DL | 0.005 | 8 | DL | DL | | 32 | DL | DL | 0.009 | 79 | DL | DL | 0.005 |
| Co | µg/l | 21 | DL | DL | 0.27 | 18 | DL | 0.01 | 2.07 | 8 | DL | 0.006 | | 32 | DL | 0.008 | 0.02 | 79 | DL | 0.008 | 0.024 |
| Cr | µg/l | 21 | 0.045 | 0.23 | 0.78 | 18 | 0.09 | 0.85[Po,T,U] | 3.33 | 8 | 0.03 | 0.20 | | 32 | 0.04 | 0.18 | 0.46 | 79 | 0.05 | 0.23 | 0.96 |
| Cu | µg/l | 21 | 0.15 | 0.48 | 1.57 | 18 | DL | 0.17 | 0.48 | 8 | 0.15 | 0.48 | | 32 | DL | 0.38 | 2.09 | 79 | DL | 0.34 | 1.53 |
| Hg | µg/l | 21 | DL | DL | 0.008 | 18 | DL | DL | DL | 8 | DL | DL | | 32 | DL | DL | DL | 79 | DL | DL | DL |
| Mn | µg/l | 21 | DL | 0.19 | 1.82 | 18 | DL | 0.23 | 1.56 | 8 | DL | 0.07 | | 32 | DL | 0.14 | 1.14 | 79 | DL | 0.15 | 1.46 |
| Mo | µg/l | 21 | DL | 0.11 | 1.12 | 18 | 0.07 | 0.11 | 0.46 | 8 | DL | 0.06 | | 32 | DL | 0.06 | 0.2 | 79 | DL | 0.1 | 0.45 |

(*continued*)

**Table 2** │ continued

| Parameters | | Postglacial | | | | Pleistocene | | | | Tertiary | | | | Unconsolidated | | | | Total | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | N | 10%ile | 50%ile | 90%ile | N | 10%ile | 50%ile | 90%ile | N | 10%ile | 50%ile | 90%ile[a] | N | 10%ile | 50%ile | 90%ile | N | 10%ile | 50%ile | 90%ile |
| Ni | µg/l | 21 | DL | 0.07 | 0.37 | 18 | DL | DL | 0.24 | 8 | DL | 0.24 | | 32 | DL | 0.07 | 0.67 | 79 | DL | 0.07 | 0.46 |
| Pb | µg/l | 21 | DL | 0.019 | 0.18 | 18 | DL | 0.011 | 0.086 | 8 | DL | 0.067 | | 32 | DL | 0.023 | 0.125 | 79 | DL | 0.02 | 0.13 |
| Sb | µg/l | 21 | DL | 0.011 | 0.02 | 18 | DL | DL | 0.02 | 8 | DL | DL | | 32 | DL | DL | 0.02 | 79 | DL | DL | 0.02 |
| Se | µg/l | 21 | 0.08 | 0.19$^U$ | 0.35 | 18 | 0.05 | 0.14 | 0.36 | 7 | 0.04 | 0.08 | | 32 | 0.04 | 0.1 | 0.17 | 78 | 0.05 | 0.12 | 0.28 |
| Sr | µg/l | 21 | 3.38 | 13 | 45.8 | 18 | DL | 2.98 | 21.96 | 8 | DL | 5.5 | | 32 | 0.81 | 6.18 | 33.76 | 79 | 0.64 | 6.2 | 27 |
| Zn | µg/l | 21 | DL | 1.52 | 24.88 | 18 | DL | 0.36 | 5.41 | 8 | DL | 1.95 | | 32 | DL | 5.44 | 40.94 | 79 | DL | 1.68 | 30.5 |

aToo few samples to calculate 90%ile.

bCalculated value.

NBLs of parameters are reported as 90%ile. A statistically significant difference is marked (Po = Postglacial, Pl = Pleistocene, T = Tertiary and U = unconsolidated) in superscript at the median of the aquifer type whose level was statistically significantly higher (underlined). N is number of aquifers.

methodology (Pauwels *et al.* 2007, 2009). Therefore the probability can start at a value greater than zero, depending on the number of observations below DLs. For purely anthropogenic substances, such as synthetic organic pollutants, the NBLs were set to zero and samples containing these pollutants were excluded, consistent with the BRIDGE methodology (Müller *et al.* 2006; Wendland *et al.* 2008a). In all, two samples from aquifers had to be excluded because of synthetic organic pollutants: one because of tetrachloroethane and trichloroethene content, and one because of benzene. Due to the lack of analytical data on bicarbonate it was not possible to exclude samples with an incorrect ionic balance exceeding 10% as required by BRIDGE.

Percentiles were calculated using an SPSS algorithm and it is noted that for aquifer typology with relatively few samples the uncertainty is relatively large. One-way analysis of variance (ANOVA) with a Bonferroni post-hoc test (alpha = 0.05) was used to identify statistically significant differences in concentrations of chemicals and indicators between geological settings. All statistical calculations were carried out with SPSS 20.

## RESULTS AND DISCUSSION

### Natural background levels

Table 2 shows the 10%ile, 50%ile and 90%ile of 37 parameters for the four types of aquifers: Postglacial, Pleistocene, Tertiary and unconsolidated gravel deposits, as well as for all 79 aquifers combined. The 90%ile was interpreted as the NBL, the 50%ile as the central tendency and the difference between the 10 and 90%ile as the range. The 90%ile for Tertiary aquifers was not calculated as there were too few data points. Table 2 shows that nitrate and ammonium contents are low, which indicates low anthropogenic influence on the aquifers. Ammonium in groundwater may originate from the mineralization of organic matter but observations suggest that this is uncommon in Iceland. In 10 chemicals and one indicator parameter, out of 37 (K, Mg, Ba, Al, B, Na, SO₄, As, Cr, Se and pH), there was a statistically significant difference between aquifer types. Most often the concentration of these constituents is higher in the Postglacial than in the

**Table 3** | Analytical methods and laboratories

| Component | Method | Laboratory |
|---|---|---|
| pH, conductivity | Electrometric | Matís, Reykjavík, Iceland |
| $HCO_3$, TDS, hardness | Calculated. $HCO_3$ difference from ionic balance using all other major ions; TDS sum of all components. Hardness from carbonates | |
| Na, K, Si, Ca, Mg, S, Fe, B, Sr, Zn | Inductively coupled plasma/Atomic emission spectrometry | ALS Scandinavia, AB, Luleå, Sweden |
| P, Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb | Inductively coupled plasma/Sector field mass spectrometry | ALS Scandinavia, AB, Luleå, Sweden |
| Hg, Se | Atomic fluorescence spectrometry | ALS Scandinavia, AB, Luleå, Sweden |
| Cl, $SO_4$, F | Ion chromatography | ALS Laboratory Group, Na Harfé, Prague, Czech Republic |
| $NO_3$ | Ion chromatography | AK Lab AB, Borås, Sweden |
| $NH_4$ | Flow injection Analysis/Spectrophotometry (CSN ISO 11732) | ALS Laboratory Group, Na Harfé, Prague, Czech Republic |
| $NO_2$ | Flow injection Analysis/Spectrophotometry (SS-EN ISO 13395-1) | ALS, Scandinavia AB, Taby, Sweden |
| Total organic carbon | CSN EN 1484 | ALS Laboratory Group, Na Harfé, Prague, Czech Republic |
| Colour | SS-EN ISO 7887:1988-4 | ALS, Scandinavia AB, Taby, Sweden |

unconsolidated gravel aquifers. Some chemicals are principally of marine origin, such as Cl, Na, K, Mg, Sr and $SO_4$ (Gislason *et al.* 1996). Cl is considered to be derived mostly from marine aerosol in precipitation and has been shown to be highest close to the coast (Sigurdsson & Einarsson 1988). When oceanic ratios for these elements with respect to chloride were calculated from the 50%ile (median) in Table 2, for all samples they revealed that the marine contribution was approximately 100% for $SO_4$, about 50% for Na, Mg and Sr, but much less for K and Ca. Other chemicals in unpolluted groundwater have their origin mostly from rocks.

Acidity was statistically significantly higher in the gravel deposit than in both the Postglacial and Pleistocene aquifers, and also higher in the Tertiary than in the Pleistocene aquifers, indicating a short residence time in the ground. Tertiary aquifers tend to have fissure permeability while Pleistocene aquifers have porous permeability explaining a shorter residence time in the Tertiary aquifers. Other indicators were not statistically significantly different, although values for hardness and temperature were highest in the Postglacial areas, total

organic carbon (TOC) values were highest in gravel, and colour in the Tertiary aquifers. The average temperature of the water at the time of collection was 4.6 °C, the range being from 2 to 10 °C.

For the major chemicals K, Mg, Na and $SO_4$, there was a statistically significant difference between their concentrations in the Postglacial aquifer settings than either those in the Tertiary aquifers or gravel deposits or both. Their concentrations were always highest in the Postglacial aquifers. This difference can partly be explained by the high permeability of the neo volcanic zone where precipitation percolated easily into the rock, introducing a possible marine influence and partly dissolution from glassy rock.

The trace elements, Al, As, B, Ba, Cr and Se, showed statistically significant differences between aquifer types. The As, B, Ba and Se concentrations were highest in the Postglacial setting and most often lowest either in Tertiary or gravel deposit, with a significant difference most often between Postglacial and gravel deposits. Al and Cr concentrations were highest in the Pleistocene aquifers, much higher than in all other settings. The calculated TDS concentration was highest in the Postglacial areas

and significantly higher than in the gravel deposits. Chemical denudation is much greater in glassy rock and crystalline basalt, and basaltic glass is more abundant in the younger volcanic areas, explaining also the higher concentration of chemicals in the younger geological settings (Gislason *et al.* 1996).

Figures 2–4 show the concentrations of 30 chemicals that were tested. The data were organized according to
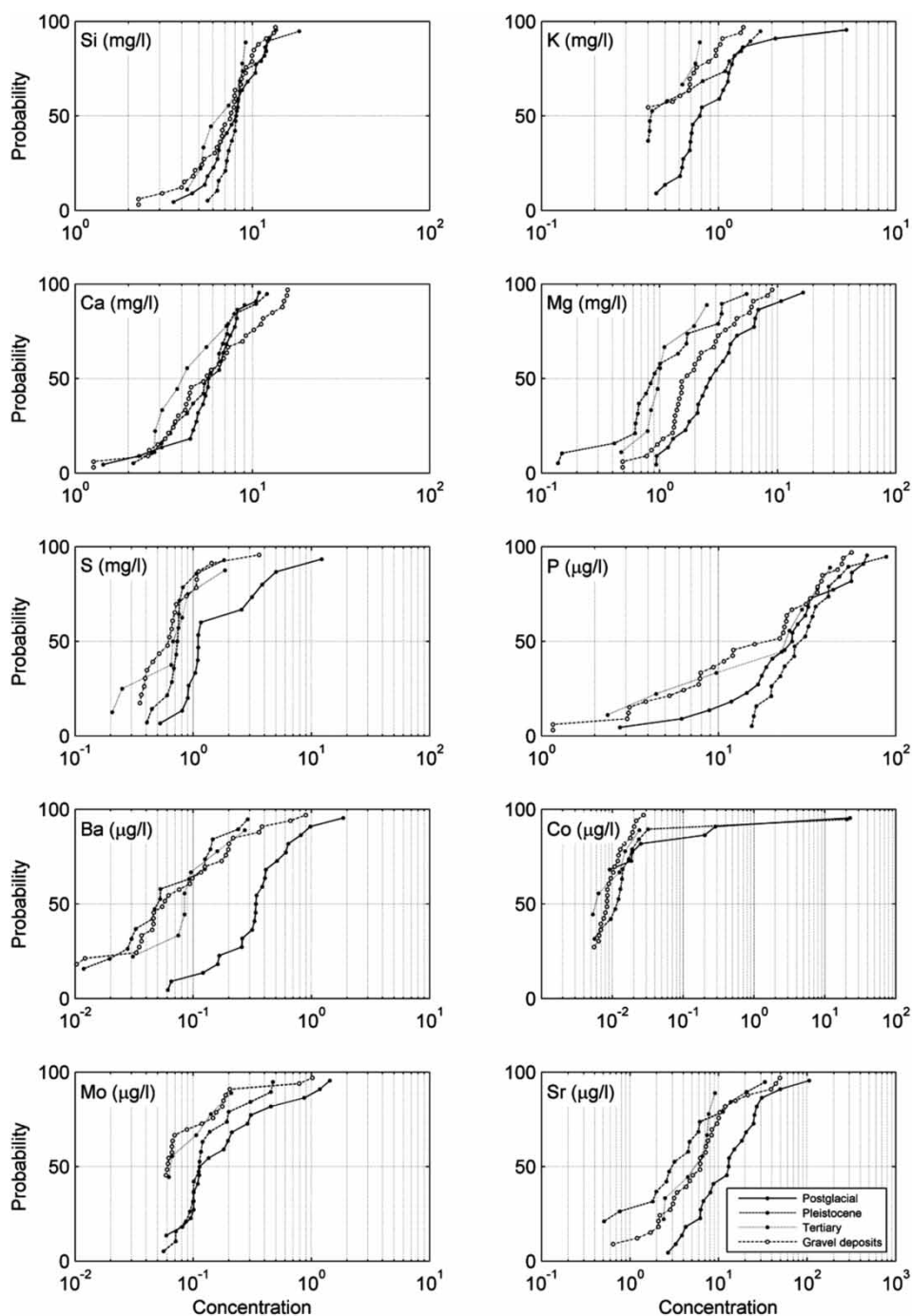


**Figure 2** │ Cumulative frequency plot for 10 parameters: Si, K, Ca, Mg, S, P, Ba, Co, Mo and Sr.
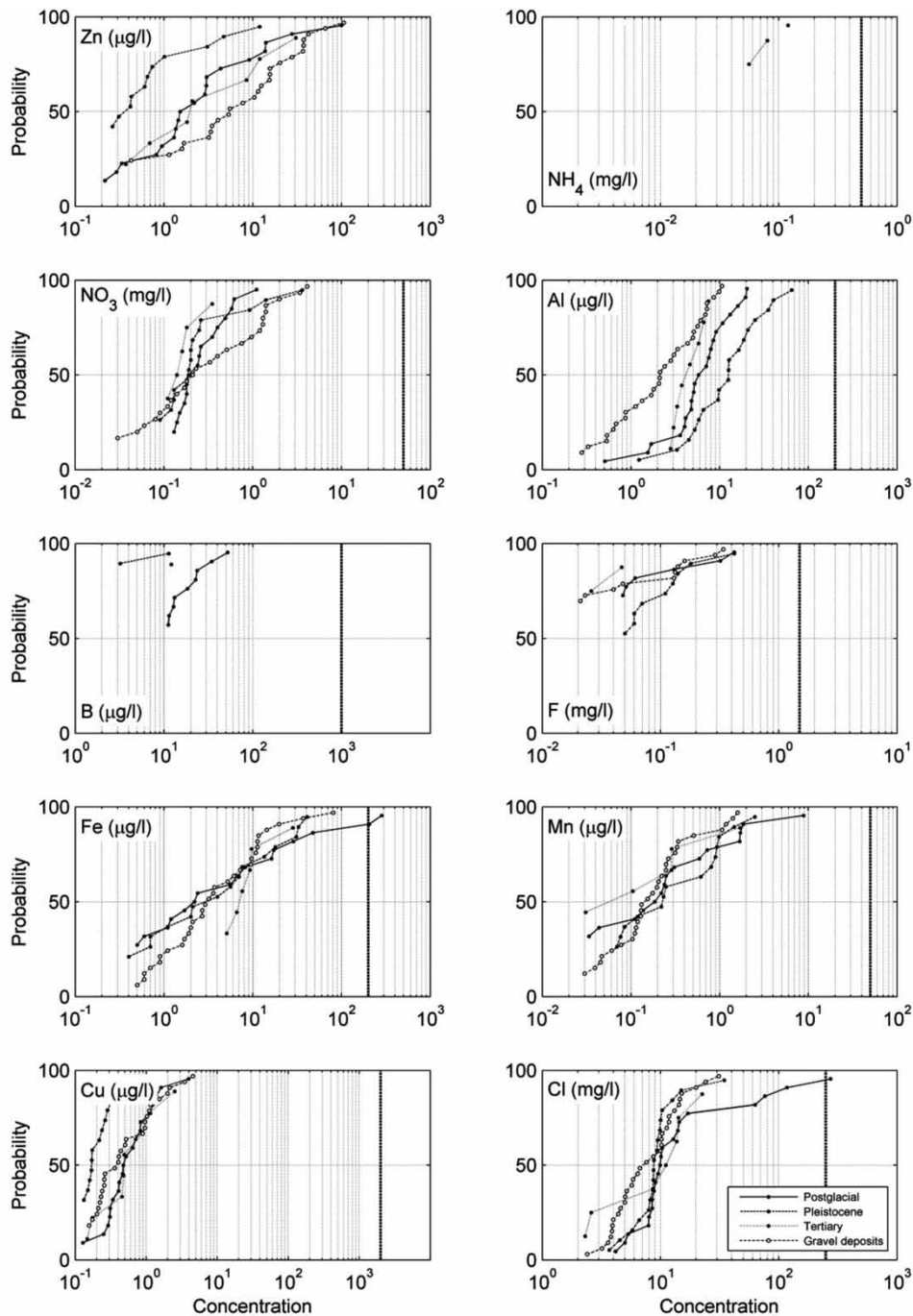
**Figure 3** │ Cumulative frequency plot for 10 parameters: Zn, NH$_4$, NO$_3$, Al, B, F, Fe, Mn, Cu and Cl. The vertical line to the the right is the MAC for drinking water.

the four main geological types of aquifers and plotted as cumulative frequency diagrams. The figures also show the MAC according to the drinking water regulation, demonstrating that the concentrations of these 30

chemicals were much lower than MAC in drinking water. The values for many parameters were highest either in the Postglacial or the Pleistocene areas except for the heavy metals Zn, Pb, Cd and Ni, which were
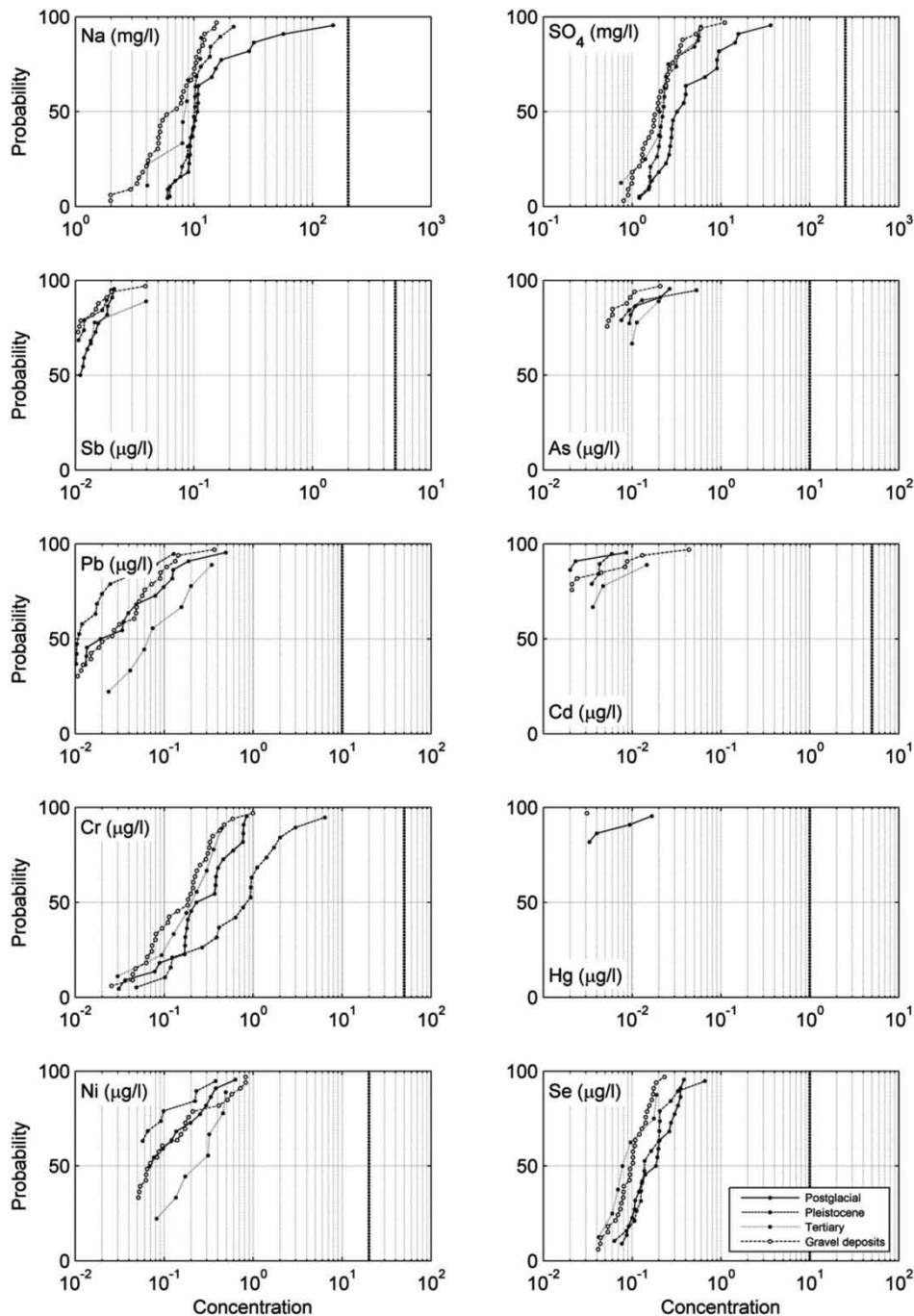
**Figure 4** | Cumulative frequency plot for 10 parameters: Na, SO₄, Sr, As, Pb, Cd, Cr, Hg, Ni and Se. The vertical line to the right is the MAC for drinking water.

highest in the Tertiary or the gravel deposit. Nitrate concentrations were also highest in the gravel deposit aquifers, showing the influence of surface water infiltration on this type of aquifer.

The figures also show the portion of the concentrations that were found below their detection limits. Sb, As, Cd and Hg concentrations were in 50 to 90% of the cases below the DLs, while Pb and Ni were below the DL in 20 to 50% of

the cases. Hg was rarely detected; only five times out of the 79 samples were concentrations above its DL and these were, with one exception, in the Postglacial zone and near high temperature geothermal areas indicating geothermal influence. The ammonium concentration was found to be above the DL only three times out of the 79 samples with concentrations of 0.056, 0.08 and 0.12 mg/l, all well below MAC in IDWR. The boron concentration was only

12 times out of the 79 samples found to be above the DL, which is usually $<10\,\mu g/l$, which is too high a detection limit to reveal the natural level of boron in groundwater. The boron concentration in sea water is very low, the Cl/B ratio being 4350/1 so boron origination from sea water is extremely unlikely. The DL for arsenic is also often too high to enable estimation of natural concentration levels.

Table 4 shows that the 90%iles are much lower than the new Icelandic TVs set in the WFD minimum list (ME 2012). The results show that in order to ensure the appropriate protection of the aquifers against anthropogenic influence TVs have to be chosen carefully.

**Table 4** | WFD minimum list of chemicals

| WFD minimum list | Unit | 90%ile Icelandic aquifers | 90%ile European aquifers | MAC in IDWR | Icelandic TVs 2012 |
|---|---|---|---|---|---|
| Arsenic As | μg/l | 0.11 | 6.95 | 10 | 7.5 |
| Cadmium Cd | μg/l | 0.005 | 0.27 | 5 | 3.75 |
| Lead Pb | μg/l | 0.13 | 2.0 | 10 | 7.5 |
| Mercury Hg | μg/l | < 0.002 | 0.07 | 1 | 0.75 |
| Ammonium NH₄ | mg/l | < 0.06 | 1.2 | 0,5 | 0.4 |
| Nitrate NO₃ | mg/l | 1.36 | 59 | 50 | 25 |
| Chloride Cl | mg/l | 23 | 213 | 250 | 187.5 |
| Sulphate SO₄ | mg/l | 6.8 | 163 | 250 | 187.5 |

The NBLs are from the current study, the European aquifers are from GQDB, MAC allowed from the IDWR, and the TVs are from the new Icelandic Environmental Quality Standard (ME 2001, 2012; Griffioen *et al.* 2006).

## Comparison with continental Europe

Table 4 and Figures 5 and 6 reveal that values are low in Icelandic aquifers compared to aquifers in Europe. The 90%ile values for chemicals for the European aquifers tested in the BRIDGE test group were 10 to 60 times higher than for the Icelandic aquifers. The ammonium and nitrate load on groundwater was much lower in Iceland than in other parts of Europe, probably due to the low population density. The ammonium concentration was nearly always below DL in Icelandic groundwater aquifers. The mercury
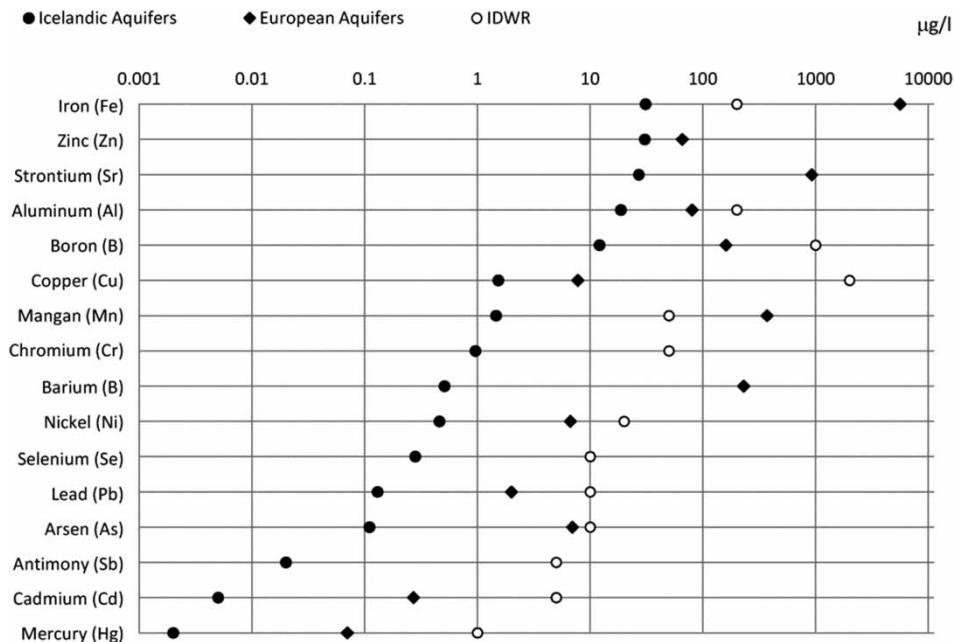


**Figure 5** | Comparison of 90%ile of trace elements between the values from the current study and European aquifers (GQDB), with IDWR values as reference.
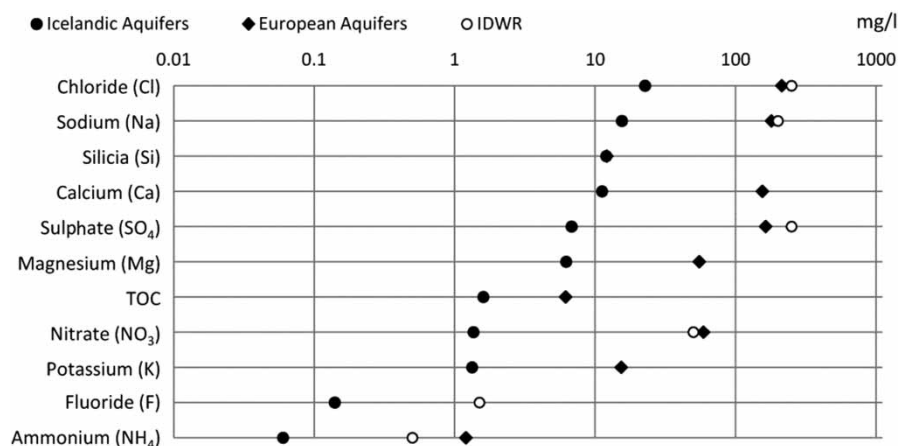
**Figure 6** | Comparison of 90%ile of major elements between the values from the current study and European aquifers (GQDB), with IDWR values as reference.

concentration rarely exceeded the detection limit ($<0.002\,\mu g/l$) whereas it was $0.07\,\mu g/l$ in the 90%ile for the 60 European aquifers. For heavy metals not on the WFD minimum list, such as copper and nickel, NBLs were lower in Iceland, the exception being zinc whose concentration was similar in Iceland and Europe, especially when comparing the median in the Tertiary and unconsolidated groups in Europe with the Tertiary and gravel deposit group in Iceland. Comparison between glacial sand and gravel deposits in Germany, Denmark and the Netherlands versus Iceland also shows that the concentrations of most major chemicals are three to ten times higher (Wendland *et al.* 2008b) there than in Iceland.

### Management of pristine aquifers

The results show little anthropogenic influence in groundwater used for public water supply in Iceland. Furthermore, the differences in chemical concentrations indicate that when assessing the NBLs of many chemicals in groundwater it is necessary to take the geological settings of the aquifer into account. The setting of TVs should therefore account for the preservation of pristine aquifer conditions, as has been suggested by some of the participants in BRIDGE (Coetsiers *et al.* 2009) and not aim for the highest permissible values as is practised in some European countries because of elevated levels due to a long history of human occupation, agriculture and industry (Reimann & Garrett 2005; Griffioen *et al.* 2006). It is also

important to have sufficient differences between threshold values and reference values if they are to be used for early warning management. For example, one of the three methods described by BRIDGE (Wendland *et al.* 2008a) recommends that the TV be twice the NBL and this is the method most suited for pristine aquifers (Pauwels *et al.* 2007; Coetsiers *et al.* 2009) and aims at preserving the low external environmental pressure and preventing anthropogenic influence on the water bodies. Exceptions may include TVs for chloride and sulphate that have a marine origin in Icelandic aquifers.

### CONCLUSIONS

The results of this research revealed that Icelandic aquifers used for water supply in Iceland are mostly devoid of anthropogenic influence. The NBLs are low compared to most aquifers in Europe, which should be taken into account when threshold values are determined, allowing for effective management of the pristine aquifers. The explanation is likely due to high permeability of young geology settings as well as low population density in Iceland. The aquifers are divided between four geological settings that represent the geology of Iceland and NBLs were calculated as the 90% iles of all aquifers in each setting and in all pooled. There was a statistical difference between the geological settings in 11 of the 37 parameters tested. This should be considered when threshold values are determined. Further research is

needed to strengthen the database for NBLs, especially with regard to numbers of aquifers of each type. The data provided here are useful to water utilities and regulators in evaluating whether anomalies or extreme values occur naturally or are due to local anthropogenic influence in order to identify, plan and execute early reaction for trend reversal.

## ACKNOWLEDGEMENTS

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