A survey of the inorganic chemistry of bottled mineral waters from the British Isles

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Abstract

The inorganic chemistry of 85 samples of bottled natural mineral waters and spring waters has been investigated from 67 sources across the British Isles (England, Wales, Scotland, Northern Ireland, Republic of Ireland). Sources include boreholes, springs and wells. Waters are from a diverse range of aquifer lithologies and are disproportionately derived from comparatively minor aquifers, the most represented being Lower Palaeozoic (10 sources), Devonian Sandstone (10 sources) and Carboniferous Limestone (9 sources). The waters show correspondingly variable major-ion compositions, ranging from Ca-HCO_3, through mixed-cation-mixed-anion to Na-HCO_3 types. Concentrations of total dissolved solids are mostly low to very low (range 58–800 mg/L). All samples analysed in the study had concentrations of inorganic constituents well within the limits for compliance with European and national standards for bottled waters. Concentrations of NO_3-N reached up to half the limit of 11.3 mg/L, although 62% of samples had concentrations <1 mg/L. Concentrations of Ba were high (up to 1010 µg/L) in two spring water samples. Such concentrations would have been non-compliant had they been classed as natural mineral waters, although no limit exists for Ba in European bottled spring water. In addition, though no European limit exists for U in bottled water, should a limit commensurate with the current WHO provisional guideline value for U in drinking water (15 µg/L) be introduced in the future, a small number of groundwater sources would have concentrations approaching or in excess of this value. Two sources had groundwater U concentrations >10 µg/L, both being from the Welsh Devonian Sandstone. The highest observed U concentration was 13.6 µg/L.

Solute concentrations in waters contained in glass bottles compared with waters in PET showed slightly though significantly higher concentrations of Al, Ce, Cu, La, Nd, Mn, Sn, W, Zn and Zr (rank-sum testing, $p < 0.05$). By contrast, Sb concentrations were significantly higher ($p < 0.001$) in samples contained in PET bottles. This accords with other studies that have recognised Sb contamination in water from PET bottles. However, in no cases did the concentration of Sb exceed or approach the national and European limit for Sb in natural mineral water/spring water (5 µg/L), the highest observation being 1.35 µg/L.

Bottled water compositions were mostly similar in their major-ion characteristics to raw groundwaters from the equivalent aquifers in Britain, although concentrations of several trace elements (Al, Cd, Cu, Fe, Mn, Pb, and Zn) were appreciably lower, in some cases by one or two orders of magnitude. The most likely mechanism for the reduction is use of aeration,

settling and filtration to remove unstable constituents before bottling. The comparatively low concentrations of Cd, Cu, Pb and Zn are likely to be due to co-precipitation with/adsorption to precipitated metal oxides, although choice of resilient pipework (e.g. stainless steel) in bottling plants may also be a factor. Although for the most part the major ions in the bottled waters appear representative of the groundwater in their host aquifers, the results suggest that many of the trace elements have been modified significantly from natural compositions in situ.

1 Introduction

The bottled water industry in the UK is worth around £1.5 billion per annum. Sales of UK bottled water nationally have risen from some 500 million litres per annum in the early 1990s to 1.6 billion litres in 2009 (BSDA, 2010), although the last couple of years have seen a decline in response to both the economic downturn and growing environmental awareness. In the early 1990s, there were around 37 recognised UK natural mineral waters (Robins and Ferry, 1992). This compares with around 80 today. Spring waters and bottled drinking waters increase the list of available options further. Around 78% of the bottled water on sale in the UK is from UK sources, the remainder largely being from other European countries, particularly France (e.g. BSDA, 2010). Around 72% of that sold is still water (non-carbonated).

In the UK, the natural mineral water, spring water and bottled drinking water industry is regulated by a number of statutory instruments that implement existing EC legislation. EC Directive 2009/54/EC repeals former Directive 80/777/EEC and amendments in 96/70/EC relating to the marketing and exploitation of natural mineral water; Directive 98/83/EC applies to water for human consumption other than natural mineral water and Directive 2003/40/EC establishes the list, concentration limits and labelling requirements for the constituents of natural mineral waters. These collectively have produced a complex system of legislation. The Natural Mineral Water, Spring Water and Bottled Drinking Water Regulations 2007 consolidated these existing requirements and simplified the overall legislative framework, although four separate but parallel statutory instruments apply for England (OPSI, 2007), Wales, Scotland and Northern Ireland and two further amendments to these requirements have been issued in the four devolved regions/countries subsequently (OPSI, 2009; OPSI, 2010). Ireland also implements EC regulations on bottled waters via national legislation (SI No. 225 of 2007).

Labelling as a natural mineral water requires that the water has been abstracted from a recognised groundwater source protected from known risks of pollution, is bottled at source, fulfils the requirements for physical, chemical and microbiological quality, has a consistent composition and has not been subject to treatment other than for limited purposes by recognised methods. These methods are oxidation by ozone-enriched air with filtration and decanting for removal of unstable elements such as Fe, Mn, S and As, physical addition or removal of CO_2, and removal where necessary of fluoride by activated alumina. Waters subjected to such treatments should be labelled as such (OPSI, 2007).

Waters labelled as spring water must also be from a groundwater source (although a formal recognition process is not required) and must be bottled at source. There is no formal requirement for source protection from known pollutants. Spring waters may undergo treatments (disinfection by e.g. UV or microfiltration; softening or desalination) in addition to the treatment options allowed for natural mineral waters. They must also comply with regulations on physical, chemical and microbiological quality of water intended for human consumption but do not require demonstration of a consistent composition. Softened or desalinated waters must comply with a requirement for hardness not to reduce below 60 mg/L Ca, in recognition of the health benefits of hard water (OPSI, 2007). This presumably allows for some remineralisation of treated water in order to maintain compliance.

Bottled drinking water (sometimes labelled as ‘table water’) can be from a variety of sources, including public mains supply, but may not be labelled as spring or natural mineral water. There are no restrictions on treatment, provided such treatments do not make the water unsafe for consumption and do not lead to a contravention of the relevant prescribed limits.

One of the consequences of the complex legislative framework outlined above is that different limits exist for chemical constituents in natural mineral water compared to spring water and other bottled water. These are outlined in Table 1.

The bottling companies are required to label natural mineral waters with their characteristic chemical composition and most bottled waters are labelled with major-ion and basic physical characteristics. However, the concentrations of trace elements are rarely provided. This contrasts with the information for many public-supply sources which is often available in summary form for a comprehensive suite of determinands e.g. on the web. This study provides a summary of the major- and trace-element compositions of a selection of bottled waters (natural mineral waters and spring waters) which are currently or have been recently available on sale in the British Isles. The chemical compositions are also compared with those of other groundwaters in Britain abstracted from the corresponding aquifers in order to identify systematic similarities and differences. The database represented in this study is distinct from that for UK waters reported by Reimann and Birke (2010) in their parallel study of bottled waters in Europe, but the studies contain some complementary observations.

2 Bottled waters in the British Isles

Bottled waters in the British Isles are abstracted from a diverse range of aquifers (Figure 1), many of them considered minor in terms of groundwater storage. In England, the most significant water-supply aquifer is the Cretaceous Chalk (Figure 1), followed by the Permo-Triassic Sandstone. Yet comparatively few bottled water plants in England abstract from these aquifers, and comparatively few are located in southern England. This is probably related in large part to the perceived greater marketability of sites located in rural and upland settings (e.g. Highland Spring water from the Scottish Midland Valley has the largest share of the UK sales market despite relatively large distances involved in transportation to markets in England).

Many of the bottling plants abstract water from springs, which typically discharge young, oxic groundwater from shallow depths of circulation. Others abstract from borehole sources, or from mixtures of sources. Where specified on bottle labels or websites, depths of boreholes used for abstraction are in the range 27–250 m depth, the shallowest being within superficial Quaternary aquifers (Aqua Pura (2), Church Stretton) and the deepest from boreholes penetrating the Permo-Triassic Sandstone (Chase Spring water, Lichfield, Staffordshire). Many abstract groundwater from boreholes more than 50 m deep, in various aquifer lithologies.

A few bottled waters have been identified, by radiometric dating and other techniques, as pre-industrial waters, in some cases palaeowaters. Abbey Well water in Morpeth, Northumberland is abstracted from a borehole with a depth of 117 m in the Carboniferous Millstone Grit aquifer. Radiocarbon and tritium dating of the groundwater has established a model age of around 3000–4500 years (W.G. Darling, pers. comm., 2010). Radiocarbon and tritium dating has also been carried out of thermal groundwater (27.5ºC) from St Ann's Well, the source for Buxton Spring water in Derbyshire. This has established that the water has a mixed origin with a proportion containing low though detectable concentrations of tritium (Edmunds, 1971; Evans et al., 1979) and an old tritium-free component with non-radiogenic carbon, together yielding a bulk age of some 5000 years (Barker et al., 2000; Evans et al., 1979). The water discharges from fractures in the karstic Carboniferous Limestone aquifer and circulation depths as great as 1 km have been postulated for this spring source (Brassington, 2007). The groundwater discharging from St Ann's Well appears to be sub-oxic in composition (dissolved oxygen 1.6 mg/L at source; BGS unpublished data), though this may represent a mixture between anoxic old water and a younger more oxic fraction.

3 Sample collection and analysis

Bottles of water were collected from various retail outlets in Britain and Ireland during the period 2007–2010. All were non-carbonated forms. Bottles were opened in the laboratory, and aliquots decanted immediately into factory-new LDPE bottles, pre-rinsed with sample water. Three aliquots were collected. One was acidified with 1% (v/v) Aristar® HNO_3 for the analysis of major cations, SO_4 and trace elements by ICP-OES and ICP-MS. One was acidified with 1% (v/v) Aristar® HCl for the analysis of As by HG-AFS. A third was left unacidified for the analysis of anions (Cl, NO_3, Br and F) by ion chromatography. All aliquots were unfiltered, with the exception of a subset of 20 samples from which additional filtered (0.2 µm) aliquots were separated in order to compare analyses with unfiltered aliquots prepared at the same time. The filtered aliquots were analysed by ICP-MS only. Arsenic analyses for samples collected in 2010 were analysed by collision-cell ICP-MS (Agilent 7500CX) rather than HG-AFS and SO_4 was determined on the unacidified aliquot by ion chromatography. Additional analysis of I by ICP-MS was carried out for the 2010 samples.

Immediately after opening the bottles, waters were analysed for pH and alkalinity using a laboratory titrator. Quality-control standards and blanks were run regularly throughout the course of the analysis. Acid blanks were also run periodically to confirm the purity of the acid used to preserve the samples. No blank correction to the sample data was considered necessary. Analytical charge imbalances were <5% for all samples. For data cited in the Supplementary Tables (S1–S3), lower limits of quantification were taken as long-term laboratory values: approximately 6s (standard deviations) on long-term blank concentrations. However, for statistical handling, detection limits were taken as 3s on the in-run blank concentrations. Analyses were carried out in the BGS laboratories in Keyworth and Wallingford, UK.

A total of 85 bottled water samples were analysed. These were from 67 separate groundwater sources (boreholes/springs/wells) from approximately 38 locations across the British Isles (England, Wales, Scotland, Northern Ireland and Republic of Ireland; Figure 1). Of the 85 analyses, 18 were replicates using separate bottles bought at different times and places.

Sources were from a range of aquifer lithologies (Table 2). Of those sources sampled, 43 (64%) were of natural mineral waters and 23 (34%) were spring waters. These roughly represent the proportions of waters sold in these categories in the UK (61% and 27% respectively) (BSDA, 2010).

4 Results

4.1 Chemical compositions

Comparison of chemical analyses from the 20 paired filtered and unfiltered aliquots revealed that concentrations of major and minor ions in most cases differed by less than 5% (larger differences for trace elements were due to larger absolute errors at low concentrations; the concentrations were not systematically higher in unfiltered aliquots). As a result of the similarities, concentrations of analysed parameters in the unfiltered aliquots are taken to be representative of dissolved concentrations without a significant colloidal or particulate fraction. Hereafter, discussions relate to the compositions of the unfiltered aliquots. A list of samples investigated with background details is given in Table 3 and summary statistical data are given in Table 4. In addition, a full list of chemical compositions for the unfiltered aliquots of the bottled waters is given in Supplementary Tables S1–S3.

Results for most major ions showed a broad agreement with the values quoted on bottle labels, though correlations were comparatively poor where the number of significant figures quoted on labels was small (e.g. for K). The highest alkalinity values quoted on labels (>400 mg/L HCO_3) were generally not reproduced in laboratory measurements, the latter results being some 40% lower. Alkalinity values for Shepley and Ice Valley water, both from the Carboniferous Millstone Grit of Shepley, Yorkshire, were quoted as 412 mg/L, but the measured laboratory analyses were in the range 240–270 mg/L. Calcium concentrations were also lower in the laboratory analyses (11.6–14.8 mg/L) compared to the labelled concentrations (32 mg/L). These observations suggest some degassing of CO_2 and precipitation of calcite since abstraction. Shepley water (as bottled) is saturated with respect to calcite (and dolomite). Loss of alkalinity through precipitation of iron oxide is also a possibility. Measured laboratory pH values were also higher for these samples, giving a range 8.1–8.4 compared to “pH at source” values of 7.8. Again, this presumably relates to degassing of CO_2 since abstraction. Comparisons of at-source and laboratory pH values were in general worst at the high-pH end of the range (>7.8).

Rank-sum testing showed no significant difference (95% confidence) in the concentrations of most parameters between the natural mineral waters and spring waters investigated in the study. Exceptions were for Br, Ca, Cl, Fe, HCO_3, P and Se. In each case, these were higher ($p < 0.05$) in the spring water samples, although the magnitude of the differences was small.

4.2 Compliance in inorganic water quality

Distributions of the major ions and selected trace elements in the bottled waters are shown as box plots in Figures 2 and 3. Boxes indicate the interquartile ranges, whiskers (no more than 1.5 times the interquartile range, Tukey, 1977) and outliers. Distributions for elements that include non-detect data are derived using the robust regression-on-order-statistics (ROS) method within the NADA package in R (Helsel, 2005; Lee and Helsel, 2005). Where relevant, national/European limits for parameters in bottled waters are also given and in cases where limits differ between natural mineral waters and spring waters/bottled drinking waters (Table 1), the lowest limit is shown. The results indicate, unsurprisingly, that all measured water samples have inorganic compositions which comply with the relevant legal limits. In most cases, concentrations are much below the respective limits, sometimes by an order of magnitude or more.

The two parameters with highest concentrations relative to prescribed limits are NO_3 and Ba. The highest observed concentration for NO_3-N is 6.3 mg/L (Table 3) compared to national and EC limits of 11.3 mg/L. The limit for Ba in natural mineral waters is 1000 µg/L although there is no limit for Ba in spring/bottled drinking waters. Concentrations of Ba in two of the bottled water samples were close to or above the natural mineral water limit, though in each case they were spring waters (1010 µg/L in one sample of Drench water; 971 µg/L in a sample of Purezza; Table 4).

Concentrations of B reach up to 483 µg/L, just under half the limit for B in spring water/bottled drinking water (Figure 3). However, the highest concentration was from a natural mineral water (Montgomery Spring). The highest value in a water classed as spring water was 123 µg/L.

No limit exists currently for U in European drinking water or natural mineral water (exception Germany). However, the WHO provisional guideline value for U in drinking water, promulgated in 2004, is 15 µg/L. Most bottled waters have concentrations much below this value, although two sources, both abstracting from Devonian (Old Red Sandstone) strata and from the same location (Heartease, Powys, Wales), had concentrations close to the guideline value. Three analyses of Love One spring water gave values of 13.4, 13.6 and 13.2 µg/L and one analysis of Radnor Hills natural mineral water gave a concentration of 10.2 µg/L. FSA (2004) also reported high U concentrations in Radnor Hills natural mineral water: two separate analyses gave concentrations of 11 and 7.8 µg/L U. Love One water and Radnor Hills water are bottled by the same company.

Likewise, no European/national limits exist for Mo in bottled water although the WHO guideline value for Mo in drinking water is 70 µg/L. The highest observed Mo value in the samples was an order of magnitude lower at 2.8 µg/L.

Concentrations of As in the bottled waters lie in the range <0.2–4.2 µg/L and 88% are ≤2 µg/L. All are less than half the European and national drinking water limit of 10 µg/L. Samples with >1 µg/L were all from either the Devonian (Old Red Sandstone), Carboniferous Limestone, Permo-Triassic Sandstone or Lower Palaeozoic aquifers (one sample was from an unspecified aquifer source in Ireland).

Concentrations of F were well below the limit of 1.5 mg/L for spring water/bottled drinking water and at least an order of magnitude below the limit for F in natural mineral water (5 mg/L; Table 1). The highest observed F concentration was 0.58 mg/L.

To the best of my knowledge, none of the spring waters tested has been softened or desalinated before bottling. Interestingly, most of the waters tested (spring waters and natural mineral waters) would contain insufficient Ca had they been subject to such treatment: 72% have concentrations <60 mg/L, the minimum set for softened or desalinated waters.

4.3 Compositions in relation to bottle type

In the UK, around 93% of bottled water is marketed in PET bottles, the remaining 7% mainly in glass (BSDA, 2010). Comparisons were made between the compositions of waters analysed from glass bottles (14 samples) and those from PET bottles (71 samples) to investigate whether the storage medium has any significant influence on the inorganic chemical composition of the waters. Rank-sum testing of samples divided into glass and PET groups showed slightly though significantly higher concentrations in glass samples of Al, Ce, Cu, La, Nd, Mn, Sn, W, Zn and Zr ($p < 0.05$). Results also showed significantly higher Sb ($p<0.001$) in samples from PET bottles. As noted in Section 3.1 however, in no cases do the concentrations of these elements exceed or even approach the respective statutory limits, maximum observed concentrations of Al, Cu, and Sb mostly remaining around an order of magnitude lower (highest observed concentrations being 14.6, 32.2 and 1.35 µg/L respectively).

It was generally not possible to compare results for a single identifiable water source contained in separate glass and PET bottles as the two options appear to be rarely provided by the bottling companies (or at least they were not readily available). Highland Spring is an exception: analyses of two samples of Highland Spring water taken from bottles purchased in 2010 (one each from glass and PET) also gave slightly higher concentrations of Al, Ce, La, Nd, Mn and Zr and lower Sb in the sample from the glass bottle (Cu measurements were within 3%, Sn and W measurements were identical and Zn concentration was lower in the glass sample; Tables S1–3). Further analysis would be required to assess whether the differences observed between the bottle types for this site are statistically significant.

Ranges of concentrations for the elements identified as differing significantly are shown as box plots in Figure 4. The groups did not reveal significant differences in major-ion concentrations or pH that could have explained the dissimilarities in terms of real geochemical variation. Differences are therefore likely to be related to leaching of solutes from and/or adsorption to bottle materials. For a few elements (e.g. W, LREE), a substantial number of the observations were below the highest detection limit and some caution in attributing significance to the data is therefore required.

Increased concentrations of Sb in water collected in PET bottles compared with those in glass have been reported in previous studies by Shotyk et al. (2006) and Shotyk and Krachler (2007a) and recently by Reimann et al.(2010a; 2010b). Relatively high Pb concentrations in water contained in glass bottles were reported by Misund et al. (1999), Shotyk and Krachler (2007b) and Reimann et al. (2010a), although significant differences for Pb between bottle types were not apparent in this study. Of the elements identified as being significantly higher in glass than PET in this study, many were similarly identified in the Reimann et al. (2010a) investigation. Correspondingly high concentrations were reported by these authors for Al, Ce, Cu, La, Nd, Sn, Zn and Zr, although concentrations were also noted to be higher in glass for Bi, Cr, Fe, Nb, Th, Ti, Y, many of the other REE and (as mentioned above) Pb, which did not show significant differences in this study. Although the Reimann et al. (2010a) investigation found a significant increase in Cr in water stored in green glass compared to that in clear glass, this could not be investigated in the British bottled waters as few of the glass bottles collected were coloured.

4.4 Compositions related to regional geological control

The most frequently represented lithologies in aquifer sources of the bottled waters are Lower Palaeozoic (10 sources), Devonian Sandstone (10 sources) and Carboniferous Limestone (9 sources) (Table 2). This suggests a preference by the bottled water industry for relatively minor aquifers as bottling sources.

One of the key conclusions to be drawn from a Piper plot of the bottled waters of the British Isles (Figure 5) is the large variability in their chemical compositions. This is borne out of the wide variation in the nature of the aquifers from which the groundwaters have been abstracted (Table 2). Concentrations of dissolved solids are in general low, with TDS values in the range 58–800 mg/L. Water types vary from Ca-HCO_3 through mixed-anion-mixed-cation compositions to Na-HCO_3 types. Total hardness varies from 19–460 mg/L (median 161 mg/L) as $CaCO_3$, the range encompassing very soft to very hard water.

Despite the large variation, some consistency is apparent in the bottled waters from individual aquifer types (Figure 5). The few Chalk sources represented have Ca-HCO_3 compositions, as expected for fresh groundwater in equilibrium with a pure calcium carbonate matrix. Groundwaters from Carboniferous Limestone are also Ca-HCO_3 dominated but with a higher proportion of Mg, reflecting the higher Mg content of the carbonate minerals in this aquifer (e.g. Schofield and Adams, 1985). Relatively high Mg contents in the Permo-Triassic Sandstone samples are also a reflection of the presence and dissolution of dolomite in that aquifer (Edmunds and Smedley, 2000; Smedley and Edmunds, 2002). Groundwaters from the Carboniferous Millstone Grit have a larger range of major-ion compositions, trending towards Na-HCO_3. This likely reflects the influence of ion-exchange reactions in the Millstone Grit, the occurrence of which has been noted in earlier studies (e.g. Banks, 1997). Ion exchange is also a major factor affecting groundwaters of Na-HCO_3 composition from Jurassic Limestone (Edmunds and Smedley, 2005; Edmunds and Walton, 1983). Samples from granite have comparatively high Na/Ca ratios reflecting the influence of interaction with Na-rich, Ca-poor minerals in this rock type. Quaternary sand and gravel appears to have waters with mixed-ion compositions, probably in response to the mixed compositions of their host lithologies.

4.5 Compositions compared to British groundwater chemistry

Figures 6 and 7 indicate the variations in major- and trace-element compositions respectively, for the bottled waters in comparison with British groundwaters, distinguished by aquifer. For the British groundwaters, data have been collated from numerous BGS datasets, including some datasets from studies on the baseline chemistry of groundwaters in England and Wales (Shand et al., 2007) and Scotland (e.g. O'Dochartaigh et al., 2006). Efforts were made to screen the data as well as possible to include only groundwater sources used for public and private supply. While it cannot be guaranteed that such sources only include those used for drinking water (such information is often not recorded specifically on sample collection), the screening has served to exclude obvious sources used for e.g. industry, irrigation and river augmentation. All groundwaters in the dataset are raw (untreated) waters, filtered (0.2–0.45 µm depending on sampling purpose and vintage) and preserved at source. Box plots for the British groundwaters have been constructed, again, using the ROS method for non-detect data.

For the groundwaters, large ranges are seen for some parameters because they are an amalgamation of samples taken from various parts of Britain with varying regional controls. Major-ion content (e.g. Na, Cl, SO_4) is particularly variable in groundwaters from the Permo-Triassic Sandstone, Chalk and Jurassic Limestone. Nitrate concentration also shows a large range in British groundwaters because of the effects of agricultural and domestic pollution at the high end (the significance of which varies from region to region and aquifer to aquifer) and because of denitrification at the low end (Figure 6). The range of nitrate concentrations in bottled waters is smaller for most aquifers. The lower maximum observed for natural mineral waters and spring waters possibly reflects the fact that the sources require the implementation of pollution protection measures (e.g. restricted agricultural practices within catchments). Such protection measures are also applied to sources used for public water supply (some of which are included in the British groundwater dataset), though not necessarily to private groundwater sources.

For most major ions, the concentrations in bottled waters appear close to the interquartile ranges for the British groundwaters from the corresponding aquifers (Figure 6). Bottled waters from Lower Palaeozoic aquifers appear to have relatively high major-ion concentrations, however.

For most trace elements (Figure 7), the compositions of bottled waters are also broadly comparable with the groundwaters from the corresponding aquifers. However, concentrations of Al, Cd, Cu, Fe, Mn, Pb, and Zn are often notably lower in bottled waters. By contrast, Sb is consistently at the high end of the range in bottled waters (Figure 7), most likely reflecting the influence of the PET bottles.

Figure 8 shows cumulative-probability distributions for most of the major ions in the bottled waters considered as a single group. These are compared to British groundwaters, distinguished by aquifer. The probability distributions for Ca and Mg in bottled waters lie close to the mid-range of concentrations observed in British groundwaters, with distributions and median values similar to those for groundwaters from the Carboniferous Millstone Grit. Concentrations of Na and Cl cross the spectrum of British groundwater compositions, with lowest concentrations being at the low end of, or in the case of Cl, below the British groundwater range, and highest concentrations in the mid range for British groundwaters (Figure 8).

Alkalinity values vary comparatively little for most groundwater types, probably reflecting a solubility control by calcite. The high end of the alkalinity range for the bottled waters is comparable to that of most British groundwaters. The lowest values are below those in most British groundwaters, with the exception of those from the granites and the Lower Palaeozoic aquifers. As with other major ions, the cumulative-probability trend for alkalinity in bottled waters follows most closely the trend in Millstone Grit groundwaters.

Concentrations of NO_3-N also lie within the range of British groundwaters, although at the lower end of the range. For the groundwater dataset, highest concentrations are seen in groundwater from the Chalk, Jurassic Limestone and Quaternary sand and gravel aquifers, reflecting the particular vulnerability of these aquifers to pollution from agricultural and urban sources, in the case of the Chalk and Jurassic Limestone, at least under unconfined conditions. The clear inflexion in the NO_3-N curve for Jurassic Limestone and Chalk groundwaters at around 3–4 mg/L most likely marks the juncture between groundwaters affected by anthropogenic inputs and natural baseline concentrations, with groundwaters having undergone denitrification at the lowest end of the range. Nitrate concentrations in the bottled waters are also relatively high in samples from the Chalk and Quaternary sand and gravel (the maximum observed value being 6.3 mg/L). For NO_3-N, the distribution and median values in bottled waters are most similar to those of groundwaters from the Palaeozoic aquifers (Figure 8).

Cumulative-probability plots are shown for selected trace elements (Ba, F, U, Cu, Zn, Sb) in Figure 9. Concentrations of Ba also lie within the range of British groundwaters, albeit with a larger variation than observed in individual British aquifers. The closest similarities in distributions are with groundwaters from the Carboniferous Limestone and Quaternary sand and gravel aquifers. The highest observed concentrations in the bottled waters and groundwaters are comparable (ca. 1000 µg/L) although such concentrations are attained only rarely in the British groundwaters. The highest observed Ba values in the bottled waters are from the Millstone Grit (Drench) and the Carboniferous Limestone (Purezza) aquifers.

Fluoride concentrations in bottled waters lie within the envelope of British groundwater compositions, closest to the cumulative-probability curves for the Chalk and Lower Palaeozoic aquifers. Highest groundwater concentrations are mainly found in the Carboniferous Limestone and Jurassic Limestone aquifers although, with a few exceptions in the Jurassic Limestone, these are rarely above the national and European drinking-water limit for F (1.5 mg/L). The high-F Jurassic Limestone groundwaters are old waters from a confined aquifer. As noted above (Section 4.4), these are dominantly of Na-HCO_3 composition, having undergone a process of ion exchange (Edmunds and Smedley, 2005; Edmunds and Walton, 1983).

For U, the cumulative-probability distributions indicate that the upper end of the range for bottled waters is high relative to groundwater from British aquifers. Those British groundwaters with the highest U concentrations are derived from the Permo-Triassic Sandstone and Devonian Sandstone (Old Red Sandstone) aquifers (Figure 9). These aquifers are both continental red-bed sequences with notable lithological and mineralogical similarities. The main mineral associations of U are likely to be with metal oxides (goethite, haematite) on grain coatings and cements, phosphate minerals (Michie, 1970) and organic-rich horizons (Metcalfe et al., 1999). Minor refractory minerals such as zircon and sphene also contain U but are unlikely to contribute significantly to the groundwater U concentrations. Concentrations of U in UK Permo-Triassic Sandstone sediments have been found in the range 0.5–5.1 mg/kg (Andrews and Lee, 1979; Haslam and Sandon, 1991), but with extremes up to 14 mg/kg (BGS, unpublished data). High concentrations of U in groundwater from

Permo-Triassic and Devonian red-bed sediments have also been noted in other studies (Reimann and Birke, 2010).

The distributions for Cu and Zn indicate the much lower concentrations in bottled waters compared to British groundwaters, as outlined above. However, a marked inflexion in the bottled waters at a Cu concentration around 2 µg/L (and possibly also 5 µg/L Zn) suggests that these are distinct from the other samples. The high concentrations are in all cases from waters in Deeside, Scotland (Deeside and Royal Deeside water). These are waters from granite with relatively low pH values (labelling for Deeside water lists the pH at source as 6.1). Samples in both glass and PET bottles from these sources were correspondingly high (Cu: 4.61 and 4.64 µg/L in glass and PET respectively; Zn: 7.6 and 8.0 µg/L in glass and PET respectively). The groundwaters from granite shown in Figure 9 also have some of the highest Cu concentrations among the British groundwaters.

The cumulative-probability distribution for Sb in bottled waters (Figure 9) shows the increased concentrations relative to British groundwaters. The marked inflexion at around 0.1 µg/L Sb distinguishes those samples stored in glass from those in PET bottles. Nonetheless, some British groundwaters also have relatively high Sb concentrations, notably some of the Permo-Triassic Sandstone and Chalk groundwaters.

5 Discussion and conclusions

The survey results indicate that bottled waters from the British Isles have generally low dissolved solids concentrations (TDS 800 mg/L or less, and often much lower). This contrasts with many bottled waters from other parts of Europe, including France, where consumers appear to have a taste for more mineralised compositions (Reimann and Birke, 2010; Robins and Ferry, 1992). The bottled waters are abstracted from a large number of aquifers, but comparatively few are derived from what are considered the main aquifers in the UK: the Chalk and Permo-Triassic Sandstone. In that sense therefore, they are not representative of UK groundwater abstracted for drinking water.

Of the inorganic constituents investigated in the bottled waters, the elements showing concentrations most closely approaching bottled-water limits or guideline values were NO_3, Ba and U. Concentrations of Ba in the sources studied would only achieve non-compliance if a limit for spring waters were to be introduced in line with that for natural mineral waters (1000 µg/L). Likewise, no limits currently exist for U in bottled waters in the UK or Ireland, although the highest observed concentrations in the waters investigated approach the WHO provisional guideline value for U in drinking water of 15 μg/L. As there are numerous precedents for WHO guideline values being translated into national legislation some years down the line, it would not be unusual to expect a limit commensurate with the provisional guideline value for U in drinking water to be introduced in Europe for the bottled water industry in the coming years. The impact of such a move for most bottled water sources would be negligible, although some waters from the Devonian (Old Red Sandstone) aquifer could become non-compliant at a threshold of 15 μg/L. The bottled water samples from the Permo-Triassic Sandstone were also relatively high, but much below the WHO guideline value (maximum observed concentrations 4.1 μg/L) and hence less likely to be affected.

The most recent European legislation regarding bottled waters to be introduced has concerned the treatment of waters for removal of excessive concentrations of F (>1.5 mg/L in spring waters/bottled waters). The highest observed F concentration in the bottled waters investigated in this study (0.58 mg/L), together with the observed concentrations in the British groundwaters generally, suggests that F concentrations in groundwaters from the British Isles rarely exceed this concentration (the only notable exception being deep, confined Na-HCO_3 in the Jurassic Limestone of eastern England). For the most part, concentrations of F are unlikely to be so high that treatment to reduce F concentrations is necessary. Certainly, unlike in some other areas of Europe (Reimann and Birke, 2010), concentrations are highly unlikely to approach the limit of 5 mg/L imposed for natural mineral waters. High-F groundwaters that do exist in British aquifers are likely to be of otherwise limited potability through high salinity and/or Na concentrations.

The major-ion compositions of bottled waters from the British Isles are highly variable depending on aquifer lithology. However, for most major ions, consistencies are apparent with the compositions of other groundwaters from the same aquifers, as represented by the British groundwater dataset used in this study.

European legislation often cites distinctive chemical and microbial quality as a defining feature of bottled mineral water (e.g. “Natural mineral water is characterised by its chemical and microbiological composition, which distinguishes it from drinking water”; FSA, 2007). This may well be true if the water sources are different, but not necessarily in cases where both are derived from groundwater, indeed from the same aquifer. The inorganic chemical comparisons outlined in this study suggest, not too surprisingly, that if drinking water supplied to the tap does constitute groundwater derived from the same aquifer as the bottled water, the two are likely to be similar, at least in their major-ion chemical characteristics.

Some of the trace elements do however differ markedly. One area of difference between bottled waters and British raw groundwaters was in the distributions of dissolved Sb. The anomalous concentrations in many bottled waters, seen most clearly in the cumulative-probability distributions (Figure 9), are most likely to reflect contamination from the PET bottles. Antimony (as Sb_2O_3) is used as a catalyst in the bottle manufacturing process (Reimann et al., 2010b). Nonetheless, the concentrations observed in the bottled waters investigated are less than the bottled-water limit for Sb (5 µg/L) and no increased health risks at such concentrations are known or implied.

Some notable differences were also seen between the bottled waters and the raw British groundwaters from the corresponding aquifers in the elements Fe, Mn, Al, Cd, Cu, Pb and Zn. For Fe, Al and Mn the relatively low concentrations in bottled water can be explained most readily by removal processes involving aeration, settling and filtration before bottling. Such processes are rarely labelled on bottles but would be necessary at least in some cases, particularly iron-reducing groundwaters, to avoid precipitation and settling of iron oxides in the bottles. Such a treatment process could also explain the low concentrations of dissolved trace-metal cations (Cd, Cu, Pb, Zn) which would be reduced by co-precipitation with or adsorption to neoformed metal oxides. Lower concentrations of the trace-metal cations may also be due to choices of plumbing materials used in bottling plants, boreholes and pipework (e.g. stainless steel and plastic as opposed to more commonly used plain steel and copper). It should be stressed however, that these differences highlighted are between bottled waters and raw groundwater taken as representative of aquifer conditions, rather than groundwater supplied to consumers' taps in a public-supply network. Public-supply waters are also typically treated where necessary by aeration, settling and filtration, in order to remove excess concentrations of Fe, Al and Mn and any other non-compliant trace elements. A detailed study comparing the concentrations of trace metals in bottled waters with treated groundwaters used for public supply from the same aquifers would be needed to ascertain whether major differences in concentrations of these trace metals exist between the two.

The OPSI (2007) interpretation of a natural mineral water is that it can be "clearly distinguished from ordinary drinking water on account of the following characteristics having been preserved intact because of the underground origin of the water…its mineral content, trace elements or other constituents…”. Despite this legislative definition, the study results suggest that the major-ion compositions of bottled waters (both natural mineral waters and spring waters) may or may not be distinct from ordinary drinking water depending on the source of the latter, and that while many trace elements are indeed likely to be preserved intact, several have been modified from their natural in-situ compositions. Some (e.g. Fe, Mn, Al and potentially Cd, Cu, Pb, Zn) look to have diminished by water-treatment processes, others (most notably Sb) increased as an artefact of the bottling process.

One feature which may well distinguish the bottled waters from tapwater taken from corresponding groundwater sources is their microbiological quality. In public-supply drinking water, water treatments including disinfection are designed to minimise microbial contamination. For European bottled waters, disinfection in such a way as to remove the natural microbial flora is prohibited and the presence of certain microbial groups in bottled waters is expected and has long been recognised. Concentrations and species vary depending on local conditions (e.g. water/aquifer composition, bottle storage temperature, DOC content, bottle volume), but organisms of the genus *Pseudomonas* appear to dominate in many cases (Leclerc and Da Costa, 2005), including those in bottled waters sold in the UK (Armas and Sutherland, 1999). Studies have shown that microbiological populations increase with storage time, particularly during the first few days following bottling (Leclerc and Da Costa, 2005). Nonetheless, bottled waters in the British Isles are generally not marketed on their microbiological quality and results for microbial populations are not stated on bottle labels.

The typical image of a bottled water is one of pure water abstracted from an aquifer without modification. The comparisons between bottled water compositions and groundwaters from the corresponding aquifers suggest that the major ions are for the most part similar and representative of the compositions of in-situ groundwaters. However for many of the trace elements, some major differences from natural in-situ conditions are apparent and there is strong evidence for modification. These arise from processes such as aeration and settling before bottling, coprecipitation/adsorption, and contamination from bottle materials.

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Figure Captions

Figure 1. Simplified geological map showing the locations of bottled mineral water sources (natural mineral waters and spring waters) in the British Isles sampled in this study (geological map of Ireland source: McConnell and Gatley, 2006, with permission).

Figure 2. Box plots for major ions in the sampled mineral waters (n=85 sources). Boxes represent the inter-quartile range of the distribution, whiskers represent no more than 1.5 times the inter-quartile range and outliers are shown as open circles. Where national (and EC) limits for parameters in bottled waters apply (i.e. Na, SO_4, NO_3-N, see Table 1), these are shown as horizontal red lines.

Figure 3. Box plots for trace elements in sampled mineral waters (n=85 sources). Box plot construction is as in Figure 2. Where national (and EC) limits for parameters in natural mineral waters or spring/bottled waters apply, these are shown as horizontal red lines (lowest concentrations given in the event of more than one limit being prescribed); WHO guideline values are given for Mo and U since no European limits are prescribed for these elements.

Figure 4. Box plots showing the concentrations of trace elements in bottled waters sold in glass compared with PET bottles. Parameters shown have small though significant differences ($p<0.05$) between the bottle types. Horizontal lines indicate highest detection limits.

Figure 5. Piper plot of bottled mineral waters of the British Isles.

Figure 6. Box plots for major ions in groundwaters from British aquifers (blue), compared with compositions of bottled waters in equivalent aquifers (red).

Figure 7. Box plots for trace elements in groundwaters from British aquifers (blue), compared with compositions of bottled waters in equivalent aquifers (red).

Figure 8. Cumulative-probability plots for selected major ions in bottled waters compared to British raw groundwaters. Horizontal lines indicate the position of the median values.

Figure 9. Cumulative-probability plots for selected trace elements in bottled waters compared to British raw groundwaters. Horizontal lines indicate the position of the median values. Distributions for non-detect data are calculated for both bottled waters and British

groundwaters using either the Kaplan-Meier method (where <60% of the observations are non-detects) or ROS method (where >60% are non-detects). The methodology follows that described by Helsel (2005).

Table 1. UK (2007) limits for inorganic constituents in natural mineral waters, spring waters and bottled drinking waters (OPSI, 2007).

Parameter	Units	NMW	SW/BDW	Parameter	Units	NMW	SW/BDW
Na	mg/L		200	As	µg/L	10	10
SO_4	mg/L		250	Cd	µg/L	3	5
NO_3	mg/L	50~	50~	CN	µg/L	70	50
NO_2	mg/L	0.1	0.5	Cr	µg/L	50	50
Ca	mg/L		≥60*	Hg	µg/L	1	1
pH			4.5–9.5#	Ni	µg/L	20	20
Al	µg/L		200	Se	µg/L	10	10
Cu	µg/L	1000	2000	Sb	µg/L	5	5
F	µg/L	5000	1500	Pb	µg/L	10	10
Mn	µg/L	500$	50	Ba	µg/L	1000	
B	µg/L		1000	BrO_3	µg/L		10

NMW: natural mineral water; SW: spring water; BDW: bottled drinking water

~11.3 mg/L as N

*For desalinated or softened waters

#Acceptable range

$Set on public health grounds; the limit for SW/BDW is on aesthetic grounds

Table 2. Summary of aquifers represented in the bottled water suite together with numbers of sources.

Aquifer	No. sources analysed	Aquifer details
Quaternary sand and gravel	6	Superficial deposits dominant in valleys; high potential for groundwater throughflow (hence vulnerable to pollution), storage capacity may be low due to limited extent and thickness
Chalk	2	Cretaceous pure limestone with some interbedded marls; dual-porosity aquifer, large storage capacity; the most significant aquifer in England in terms of water supply
Jurassic Limestone	2	Commonly oolitic limestone, purity of carbonate varies; dominated by fracture flow, some karst development, important aquifer in England
Jurassic Sandstone	1	Fluvial/estuarine sandstone, mudstone, siltstone intercalated with thin marine calcareous sandstone, mudstone and limestone; restricted flow due to intercalated mudstone; minor aquifer
Permo-Triassic Sandstone	7	Red-bed sandstones, conglomerates, and marls; intergranular flow important, large storage capacity; the second most significant aquifer in England and the most important in Scotland; large storage though less used in Northern Ireland
Millstone Grit	7	Namurian (Carboniferous) hard cemented coarse sandstone and gritstone; dominated by fracture flow; minor aquifer
Carboniferous Basalt (Scotland)	7	Basaltic rocks with some interbedded sandstone; flow dependent on secondary permeability (e.g. lava flow margins); minor aquifer
Carboniferous Limestone	9	Dinantian impure limestone; fracture flow, sometimes karstic; an important aquifer in Wales and Ireland
Devonian	10	Red-bed sandstones, conglomerates, siltstones, marls and calcrete; some primary permeability but dominated by fracture flow; locally important aquifer in Wales and eastern Scotland
Lower Palaeozoic	10	Mixed marine sandstone, mudstone (‘greywacke’); dominated by secondary permeability; limited storage; minor aquifer
Granite	3	Mixed age (Caledonian, Hercynian) igneous intrusive rock, sometimes associated with mineralisation (Pb, Zn, Cu); dominated by fracture flow; minor aquifer
Precambrian	2	Mixed metamorphic sequences; fracture flow, minor aquifer

N.B. One bottled water did not specify source aquifer

Table 3. Sample sources and details of the sampled bottled waters.

Source name	Location	Country	Water category	Sample No.	Easting	Northing	Purchase date	Bottle type	Aquifer type
Abbey Well	Morpeth, Northumberland	England	NMW	S07-00701	421100	585400	31/03/2007	PET	Millstone Grit
Abbey Well	Morpeth, Northumberland	England	NMW	S08-01387	421100	585400	18/07/2008	PET	Millstone Grit
Abbey Well	Morpeth, Northumberland	England	NMW	12349-004	421100	585400	01/01/2010	PET	Millstone Grit
Aqua Pura (1)	Armathwaite, Cumbria	England	NMW	S07-00664	350400	541800	28/01/2007	PET	PT Sandstone
Aqua Pura (2)	Church Stretton, Shropshire	England	NMW	S07-00671	364600	292500	07/02/2007	PET	Sand and gravel
Ashbeck Mountain Spring	Armathwaite, Cumbria	England	NMW	S07-00672	350500	546000	07/02/2007	PET	PT Sandstone
Ashbeck Mountain Spring	Armathwaite, Cumbria	England	NMW	12349-007	350500	546000	01/01/2010	PET	PT Sandstone
Ashbrook Mountain Spring	Church Stretton, Shropshire	England	NMW	S07-00695	364600	292500	27/02/2007	PET	Sand and gravel
Ballygowan	Newcastle West, County Limerick	Ireland	SW	S07-00690			20/02/2007	glass	Carb Limestone
Belu (A)	Belu spring source, Wenlock Edge, Shropshire	England	NMW	S07-00667	346800	287800	05/02/2007	glass	Wenlock Limestone
Belu (B)	Source B, Trapp, Llandeilo, Carmarthenshire	Wales	NMW	S07-00680	266000	217900	12/02/2007	PET	Carb Limestone
Blenheim	Blenheim Park, Woodstock, Oxon	England	NMW	S07-00685	444100	216000	15/02/2007	glass	Jurassic Limestone
Blue Keld	Blue Keld spring, Cranswick, Yorkshire	England	NMW	S07-00697	505100	449900	13/03/2007	glass	Chalk
Brecon Carreg	Brecon Carreg, Trapp, Brecon Beacons	Wales	NMW	S07-00686	266000	217900	16/02/2007	PET	Carb Limestone
Buxton	St Ann’s Spring, Buxton, Derbyshire	England	NMW	S07-00662	405400	374500	28/01/2007	PET	Carb Limestone
Buxton	St Ann’s Spring, Buxton, Derbyshire	England	NMW	12349-005	405400	374500	01/01/2010	PET	Carb Limestone
Caledonian	Campsie Fells, Lennoxtown	Scotland	NMW	S07-00676	262800	692500	07/02/2007	PET	Carb Basalt
Caledonian	Campsie Fells, Lennoxtown	Scotland	NMW	12349-003	262800	692500	01/01/2010	PET	
Carding Mill	Church Stretton, Shropshire	England	NMW	S08-01388	345800	294500	24/09/2008	PET	Sand and gravel
Celtic Spring	Churchstoke, Montgomery, Powys	Wales	NMW	S07-00706	327300	294000	31/05/2007	PET	Ordovician/Silurian
Chase	Chase Spring, Elmhurst, Staffs	England	SW	12349-010	410500	313600	01/02/2010	PET	PT Sandstone

Source name	Location	Country	Water category	Sample No.	Easting	Northing	Purchase date	Bottle type	Aquifer type
Clearview Spring	Armathwaite, Cumbria	England	SW	12349-009	350400	541800	01/02/2010	PET	PT Sandstone
Cotswold Spring	Dodington Ash, Chipping Sodbury, Gloucestershire	England	SW	S07-00703	374600	178000	21/04/2007	PET	Jurassic Limestone
Deep River Rock	The Green, Lambeg, Lisburn, County Antrim	Northern Ireland	SW	S07-00691	140000	522400	20/02/2007	PET	PT Sandstone
Deeside	Lower Spring, Pannanich Wells, Ballater, Deeside	Scotland	NMW	S07-00663	338000	796800	28/01/2007	PET	Granite
Deveron Valley	Macduff, Banff	Scotland	SW	S07-00681	371400	864300	14/02/2007	PET	Dalradian
Drench	Huddersfield	England	SW	S07-00688	414280	417860	16/02/2007	PET	Millstone Grit
Drench	Huddersfield	England	SW	12349-012	414280	417860	01/02/2010	PET	Millstone Grit
Eden Falls	Armathwaite, Cumbria	England	NMW	S08-01389	350400	541800	01/10/2008	PET	PT Sandstone
Fairbourne Springs	Churchstoke, Montgomery, Powys	Wales	NMW	S07-00677	327300	294000	09/02/2007	PET	Ordovician/Silurian
Fairbourne Springs	Churchstoke, Montgomery, Powys	Wales	NMW	S07-00709	327300	294000	12/04/2007	PET	Ordovician/Silurian
Glenburn Spring	Campsie Fells, Lennoxtown	Scotland	NMW	S07-00683	262800	692500	14/02/2007	PET	Carb Basalt
Glencairn Spring	Glencairn Spring, Lennoxtown	Scotland	NMW	S08-01392	262800	692500	01/10/2008	PET	Carb Basalt
Gleneagles	Blackford, Perthshire	Scotland	NMW	S08-01391	289600	708900	01/10/2008	PET	Devonian Sandstone
Glenpatrick	Glenpatrick Spring, Powerstown, Clonmel, County Tipperary	Ireland	NMW	S07-00694			21/02/2007	PET	Carb Limestone
Good To Go	Ireland	Ireland	Pure natural water	S07-01021			05/08/2007	PET	
Hadrian Spring	Southwick, Northumberland	England	SW	S07-00713	437300	558500	15/06/2007	PET	Carb Limestone
Hadrian Spring	Southwick, Northumberland	England	SW	S08-01386	437300	558500	06/09/2008	PET	Carb Limestone
Harrogate Spa	Harlow Hill, Harrogate, Yorkshire	England	SW	S07-00665	428700	454600	05/02/2007	PET	Millstone Grit
Harrogate Spa	Harlow Hill, Harrogate, Yorkshire	England	SW	12349-001	428700	454600	01/09/2009	glass	Millstone Grit
Highland Spring	HS1, Blackford, Perthshire	Scotland	NMW	S07-00673	289630	708930	07/02/2007	PET	Devonian Sandstone
Highland Spring	HS2, Blackford, Perthshire	Scotland	NMW	S07-00702	289630	708930	13/04/2007	PET	Devonian Sandstone
Highland Spring	Blackford, Perthshire	Scotland	SW	12349-006	289630	708930	01/01/2010	PET	Devonian Sandstone

Source name	Location	Country	Water category	Sample No.	Easting	Northing	Purchase date	Bottle type	Aquifer type
Highland Spring	Blackford, Perthshire	Scotland	SW	12349-008	289630	708930	01/01/2010	glass	Devonian Sandstone
Ice Valley	Shepley, Huddersfield	England	NMW	S07-01019	420100	409800	19/07/2007	PET	Millstone Grit
Kerry spring water	Ballyferriter, Dingle Peninsula, County Kerry	Ireland	NMW	S07-00692			21/02/2007	PET	Devonian Sandstone
Kilty	Ballymena, County Antrim, Northern Ireland (100 Railway Street)	Northern Ireland	SW	S07-01022	125300	560000	05/08/2007	PET	Sand and gravel
Lakeland Willow	Flookburgh, Grange-Over-Sands, Cumbria	England	SW	S07-00666	336800	474900	05/02/2007	PET	Sand and gravel
Lakeland Willow	Flookburgh, Grange-Over-Sands, Cumbria	England	SW	S07-00679	336800	474900	12/02/2007	PET	Sand and gravel
Love One	Love One Spring, Heartsease, Knighton, Powys (Radnor Hills)	Wales	SW	S07-00699	334560	272530	18/03/2007	PET	Devonian Sandstone
Love One	Love One Spring, Heartsease, Knighton, Powys (Radnor Hills)	Wales	SW	S08-01390	334560	272530	29/09/2008	PET	Devonian Sandstone
Love One	Love One Spring, Heartsease, Knighton, Powys (Radnor Hills)	Wales	SW	12349-015	334560	272530	20/02/2010	PET	Devonian Sandstone
Malvern	Primeswell Spring, Malvern	England	NMW	S07-00670	377700	244700	07/02/2007	glass	Granite
Malvern	Malvern	England	SW	12349-019	377700	244700	24/02/2010	PET	Granite
Montgomery Spring	Churchstoke	England	NMW	S07-01077	327300	294000	22/10/2007	PET	Ordovician/Silurian
Montgomery Spring	Churchstoke	England	NMW	12349-017	327300	294000	22/02/2010	PET	Ordovician/Silurian
Morrisons Still Spring Water	Shepley, Yorkshire	England	SW	S07-00700	420100	409800	18/03/2007	PET	Millstone Grit
Morrisons Still Spring Water	Shepley, Yorkshire	England	SW	12349-016	420100	409800	20/02/2010	PET	Millstone Grit
O'Briens Spring water	County Kerry	Ireland	SW	S07-00693			21/02/2007	PET	Devonian Sandstone
Pennine Spring	Huddersfield	England	NMW	S07-00687	414280	417860	16/02/2007	PET	Millstone Grit
Princes Gate	New House Farm, Narberth, Pembrokeshire	Wales	SW	S07-01024	215900	211600	12/08/2007	PET	Devonian Sandstone
Priory Falls (1)	Churchstoke, Montgomery, Powys	Wales	NMW	S07-00704	327300	294000	07/05/2007	PET	Ordovician/Silurian
Priory Falls (2)	Burnbrae, Lennoxtown	Scotland	NMW	12349-13	327300	294000	01/02/2010	PET	Ordovician/Silurian

Source name	Location	Country	Water category	Sample No.	Easting	Northing	Purchase date	Bottle type	Aquifer type
Purezza	Pitreavie Business Park, Dunfermline	Scotland	SW	S07-00682	310000	685500	14/02/2007	PET	Carb Limestone
Radnor Hills	Heartease, Knighton, Powys	Wales	NMW	12349-020	334560	272530	28/02/2010	PET	Devonian Sandstone
Royal Deeside	Upper East Spring, Pannanich Wells, Ballater	Scotland	NMW	S07-00675	338000	796800	07/02/2007	glass	Granite
Scottish Natural Mineral Water	Campsie Fells, Lennoxtown	Scotland	NMW	S07-00669	262800	692500	05/02/2007	PET	Carb Basalt
Shepley	Shepley, Yorkshire	England	SW	S07-00698	420100	409800	18/03/2007	glass	Millstone Grit
Shepley	Shepley, Yorkshire	England	SW	S07-00705	420020	409960	30/05/2007	glass	Millstone Grit
Silverbrook Falls	Churchstoke, Montgomery, Powys	Wales	NMW	S07-00707	327300	294000	31/05/2007	PET	Ordovician/Silurian
Speyside Glenlivet	Slochd Spring, Ballindalloch, Speyside	Scotland	NMW	S07-00689	324300	820900	17/02/2007	glass	Dalradian
Springbourne	Church Stoke, Montgomery, Powys	Wales	NMW	S07-00678	327300	294000	12/02/2007	PET	Ordovician/Silurian
Springhill	Springhill Farm, Fylingdales, North Yorkshire	England	SW	12349-018	493200	501600	22/02/2010	PET	Jurassic Sst
Still Perfectly Clear	Silver Spring, Folkestone, Kent	England	SW	S07-00708	622090	137550	05/06/2007	PET	Chalk
Strath Lomond	StrathLomond Spring, Campsie Fells	Scotland	NMW	S07-01026	262800	692500	06/10/2007	glass	Carb Basalt
Strathglen	Strathglen Spring, Campsie Fells, Lennoxtown	Scotland	NMW	S07-00684	262800	692500	14/02/2007	PET	Carb Basalt
Strathlomond Mountain Spring	Campsie Fells, Lennoxtown	Scotland	NMW	S07-00674	262800	692500	07/02/2007	PET	Carb Basalt
Strathmore	Forfar, Fife	Scotland	SW	S07-00696	345200	750400	03/03/2007	glass	Devonian Sandstone
Strathmore	Forfar, Fife	Scotland	SW	12349-014	345200	750400	20/02/2010	glass	Devonian Sandstone
Thirsty Planet	Harlow Hill, Harrogate, Yorkshire	England	SW	12349-011	428700	454600	01/02/2010	PET	Sand and gravel
Tipp Active	Barrisoleigh, County Tipperary	Ireland	NMW	S07-01020			31/07/2007	PET	Carb Limestone
Tipperary Kidz	Barrisoleigh, County Tipperary (Devil's Bit Mountains)	Ireland	NMW	S07-01023			11/08/2007	PET	Carb Limestone

Source name	Location	Country	Water category	Sample No.	Easting	Northing	Purchase date	Bottle type	Aquifer type
Total Fitness	Houlston Manor, Myddle, Shropshire	England	NMW	S07-01025	347800	324700	19/09/2007	PET	PT Sandstone
Ty Nant	Bethania	Wales	NMW	S07-00668	256200	263000	05/02/2007	PET	Ordovician/Silurian
Wenlock Spring	Wolverton, Church Stretton	England	SW	12349-002	346800	287800	01/01/2010	PET	Ordovician/Silurian

Carb: Carboniferous; PT: Permo-Triassic
NMW: natural mineral water; SW: spring water

Table 4. Summary data for the bottled waters; summary includes samples from each source represented only once (i.e. n=67), 3 sigma detection limits applied.

Element	**Units**	**n**	**ncens**	**min**	**10th**	**25th**	**median**	**75th**	**90th**	**max**
pH		67	0	6.46	6.89	7.37	7.74	7.97	8.09	8.49
Ca	mg/L	67	0	3.37	13.2	19.3	45.6	61	90.1	135
Mg	mg/L	67	0	1.88	2.96	4.44	7.58	15.4	23.4	58
Na	mg/L	67	0	4.57	5.78	6.83	17.6	32.6	57.8	91.6
K	mg/L	67	3	<0.5	0.54	0.86	1.92	2.9	6.62	19.5
Cl	mg/L	67	0	4.43	5.24	8.68	19.6	36.5	60	143
HCO_3	mg/L	67	0	17	40	95	218	271	352	417
SO_4	mg/L	67	0	0.31	5.14	7.23	10.2	24.5	48.7	145
NO_3-N	mg/L	67	7	<0.05		0.153	0.727	1.9	3.92	6.33
Al	µg/L	67	20	<0.2			0.64	1.97	5.38	14.6
As	µg/L	67	34	<0.05			0.091	0.54	2.34	4.22
B	µg/L	67	47	<20	6.75	14.4	34.2	90.4	212	483
Ba	µg/L	67	3	<2	8.6	31.6	59.5	195	407	1010
Br	µg/L	67	4	<20	22	34	62	105	222	513
Co	µg/L	67	11	<0.01	0.006	0.043	0.102	0.198	0.33	0.446
Cr	µg/L	67	39	<0.2	0.045	0.064	0.12	0.238	0.405	0.908
Cs	µg/L	67	26	<0.01	0.003	0.009	0.0182	0.164	0.659	1.5
Cu	µg/L	67	21	<0.1	0.057	0.233	0.567	1.15	1.78	32.2
Eu	µg/L	67	51	<0.004				0.004	0.015	0.09
F	mg/L	67	3	<0.02	0.044	0.058	0.094	0.214	0.338	0.577
Ge	µg/L	57	25	<0.05			0.07	0.141	0.549	1.34
I	µg/L	10	0	0.751	0.751	0.973	2.32	4.93		11
La	µg/L	67	39	<0.002				0.008	0.0199	0.035
Li	µg/L	67	4	<0.5	0.424	1.24	4.9	21	47.6	128
Mn	µg/L	67	26	<0.01		0.02	0.0615	0.474	2.12	17.2
Mo	µg/L	67	9	<0.02	0.023	0.039	0.096	0.336	0.773	2.62
Nd	µg/L	67	45	<0.001			0.003	0.008	0.013	0.033
Ni	µg/L	67	7	<0.1	0.091	0.364	0.723	1.71	2.75	4.12
Rb	µg/L	67	0	0.093	0.291	0.487	1.4	3.22	9.72	18.4
Sb	µg/L	67	1	<0.01	0.027	0.196	0.294	0.389	0.562	1.35
Se	µg/L	63	50	<0.01		0.018	0.055	0.182	0.477	2.03
Si	mg/L	67	0	2.9	3.71	4.29	5.12	6.51	8.35	12.4
Sr	µg/L	67	0	2.99	38.3	90.8	185	399	589	2070
Tl	µg/L	67	51	<0.001			0.001	0.004	0.01	0.152
U	µg/L	67	3	<0.002	0.004	0.023	0.108	1.38	2.39	13.4
V	µg/L	67	22	<0.02	0.02	0.028	0.113	0.226	1.13	13
Y	µg/L	67	2	<0.05			0.024	0.054	0.094	0.21
Yb	µg/L	67	52	<0.005				0.005	0.007	0.096
Zn	µg/L	67	36	<0.5	0.114	0.20	0.418	0.889	2.59	8.04
Zr	µg/L	67	26	<0.002			0.005	0.028	0.103	0.128

min, max: minimum and maximum observations; n: number of observations; ncens: number below detection limit

FIGURES

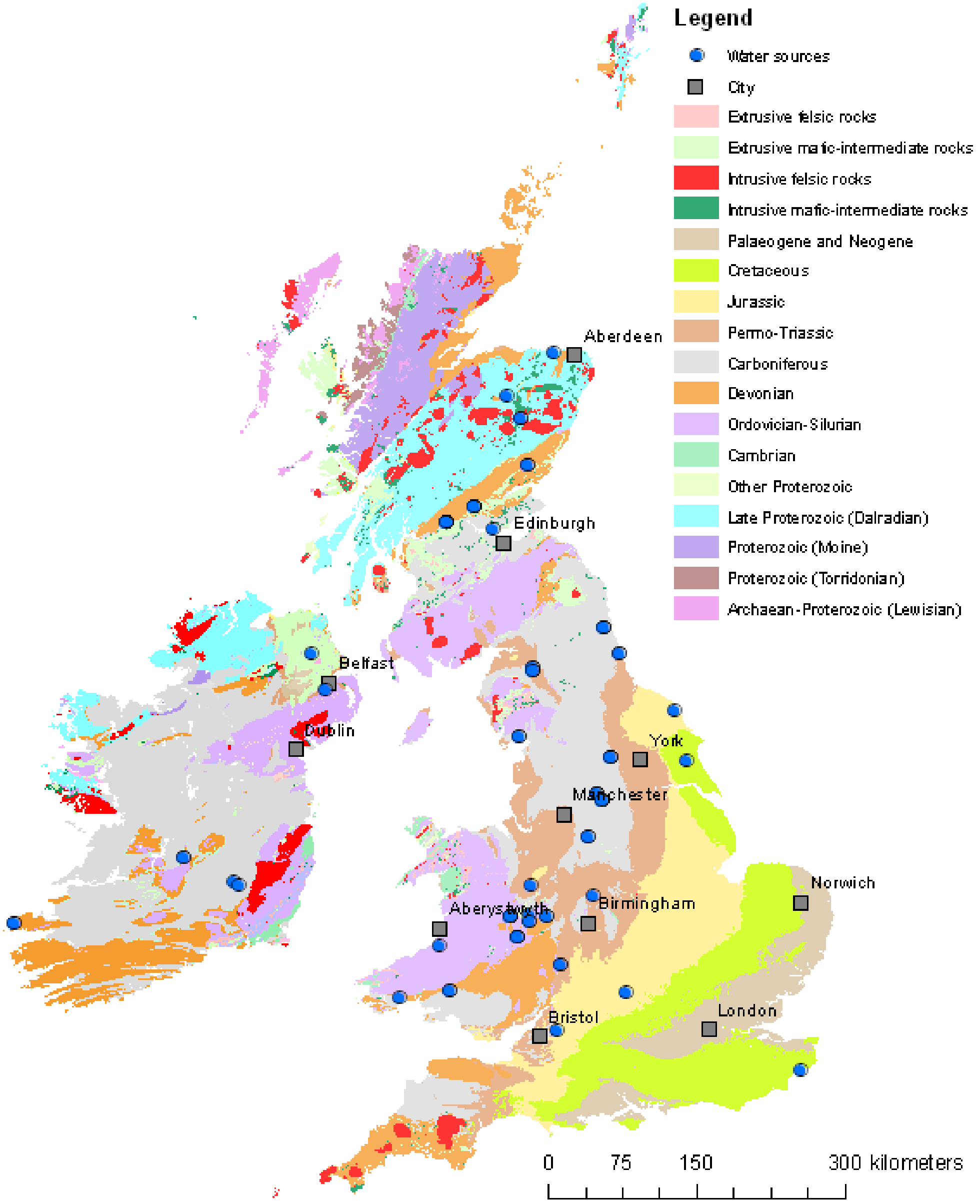

Figure 1

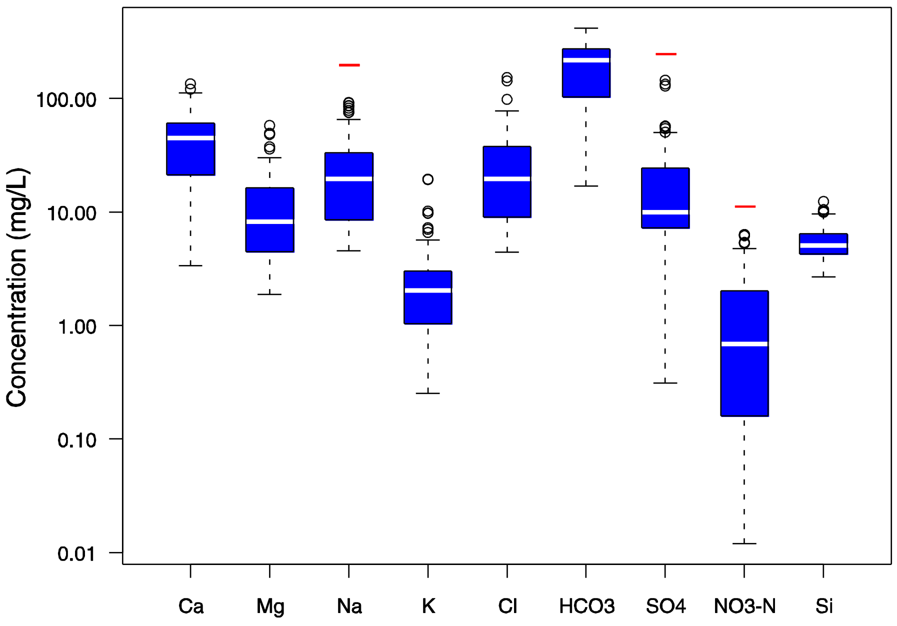

Figure 2

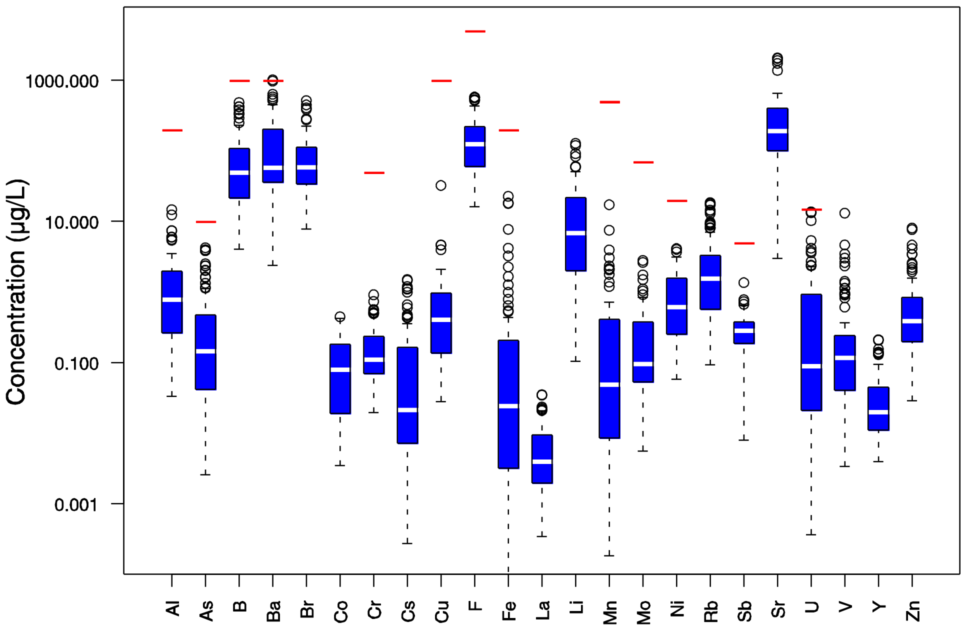

Figure 3

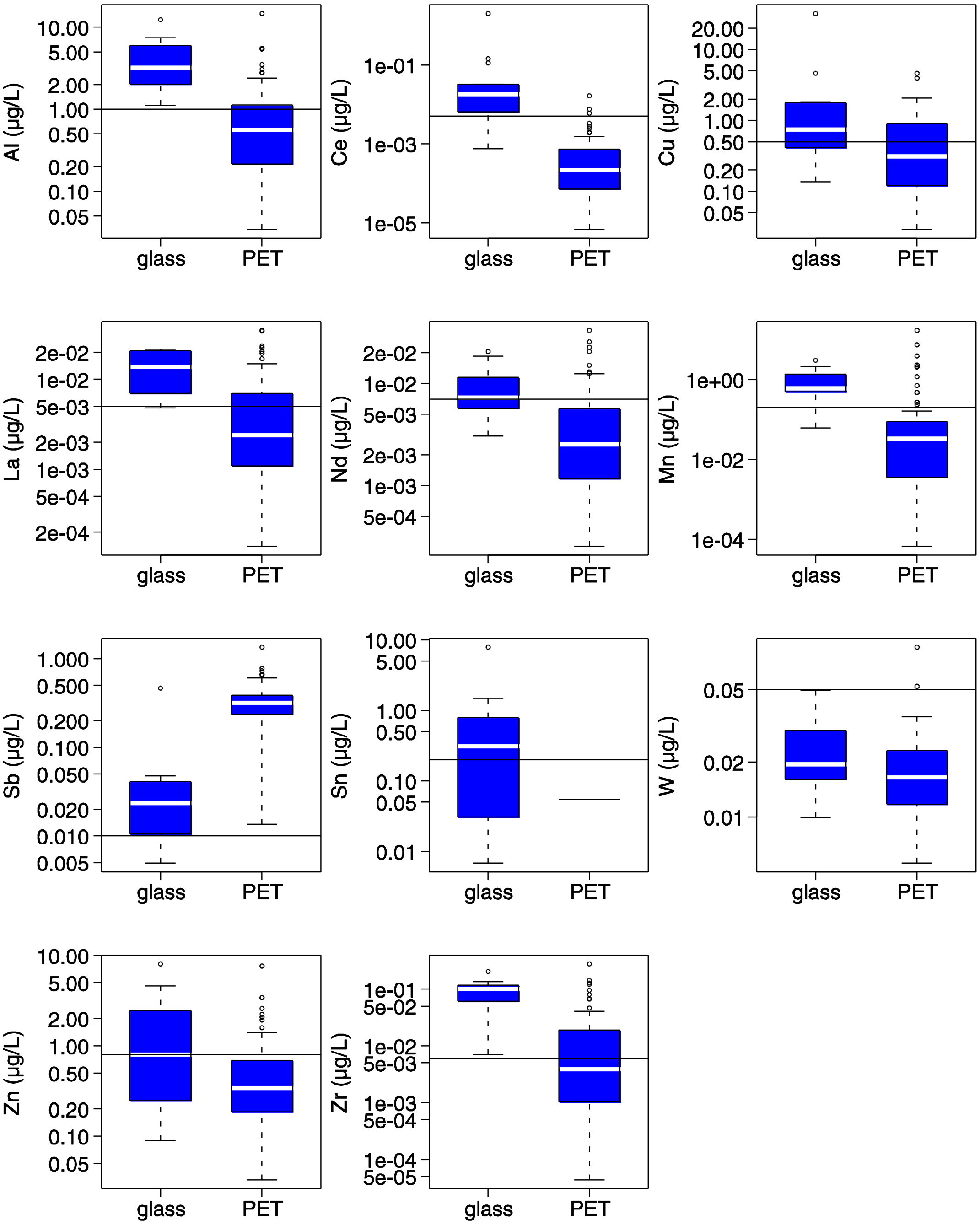
Al (µg/L)
10.00
5.00
2.00
1.00
0.50
0.20
0.10
0.05
glass
PET
Ce (µg/L)
1e-01
1e-03
1e-05
glass
PET
Cu (µg/L)
20.00
10.00
5.00
2.00
1.00
0.50
0.20
0.10
0.05
glass
PET
La (µg/L)
2e-02
1e-02
5e-03
2e-03
1e-03
5e-04
2e-04
glass
PET
Nd (µg/L)
2e-02
1e-02
5e-03
2e-03
1e-03
5e-04
glass
PET
Mn (µg/L)
1e+00
1e-02
1e-04
glass
PET
Sb (µg/L)
1.000
0.500
0.200
0.100
0.050
0.020
0.010
0.005
glass
PET
Sn (µg/L)
10.00
5.00
1.00
0.50
0.10
0.05
0.01
glass
PET
W (µg/L)
0.05
0.02
0.01
glass
PET
Zn (µg/L)
10.00
5.00
2.00
1.00
0.50
0.20
0.10
0.05
glass
PET
Zr (µg/L)
1e-01
5e-02
1e-02
5e-03
1e-03
5e-04
1e-04
5e-05
glass
PET

Figure 4

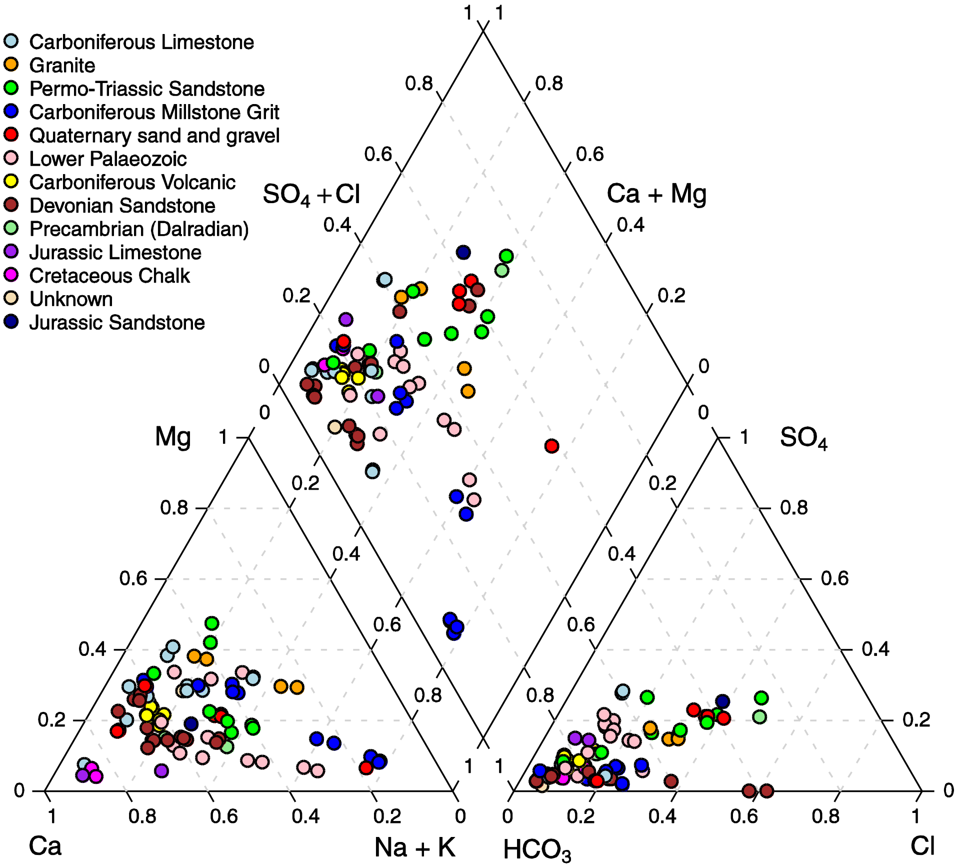
Carboniferous Limestone
Granite
Permo-Triassic Sandstone
Carboniferous Millstone Grit
Quaternary sand and gravel
Lower Palaeozoic
Carboniferous Volcanic
Devonian Sandstone
Precambrian (Dalradian)
Jurassic Limestone
Cretaceous Chalk
Unknown
Jurassic Sandstone
SO_4 + Cl
Ca + Mg
Mg
SO_4
Ca
Na + K
HCO_3
Cl
0
0.2
0.4
0.6
0.8
1

Figure 5

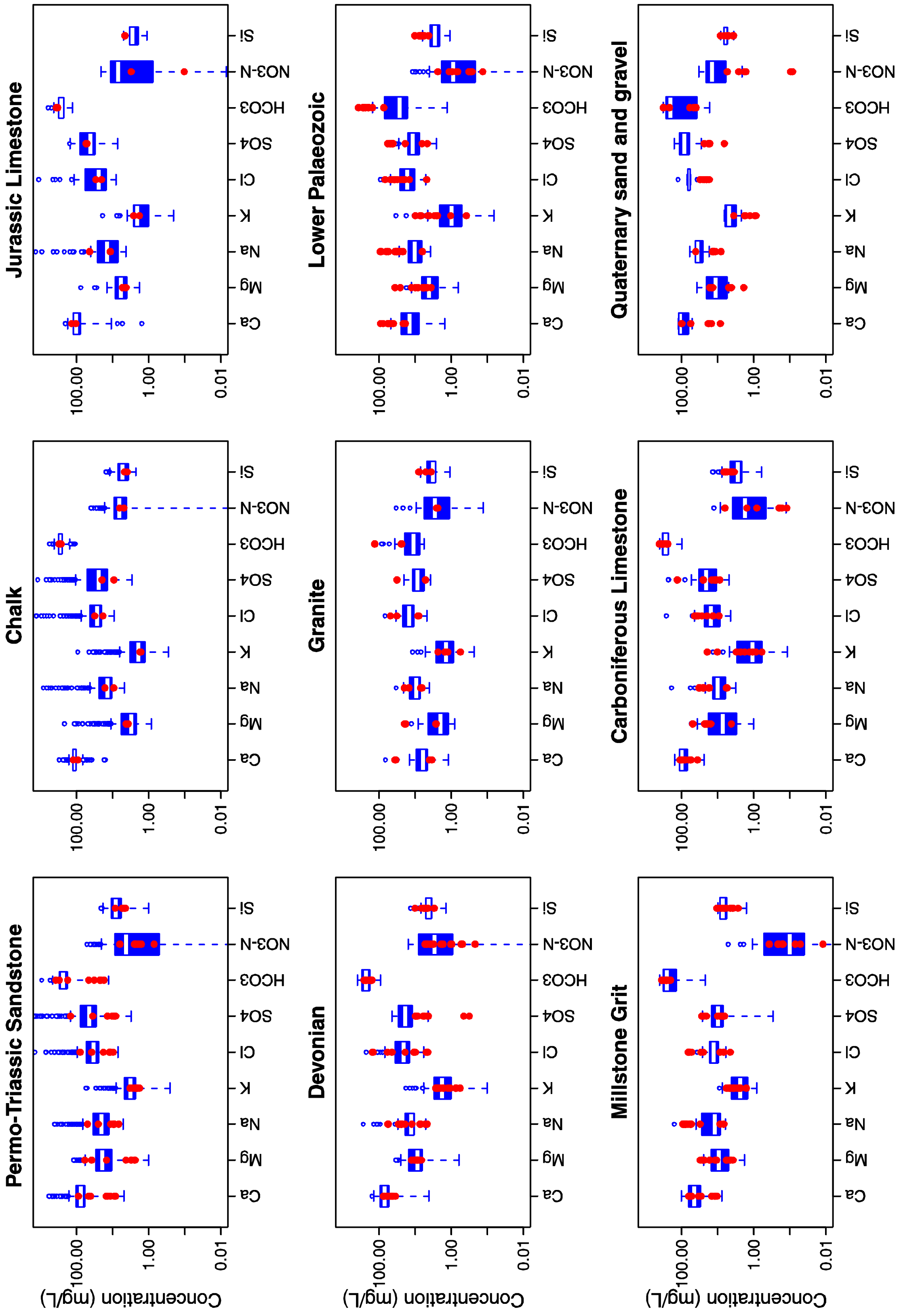
Permo-Triassic Sandstone
Chalk
Jurassic Limestone
Devonian
Granite
Lower Palaeozoic
Millstone Grit
Carboniferous Limestone
Quaternary sand and gravel
Concentration (mg/L)
100.00
1.00
0.01
Ca
Mg
Na
K
Cl
SO4
HCO3
NO3-N
Si

Figure 6

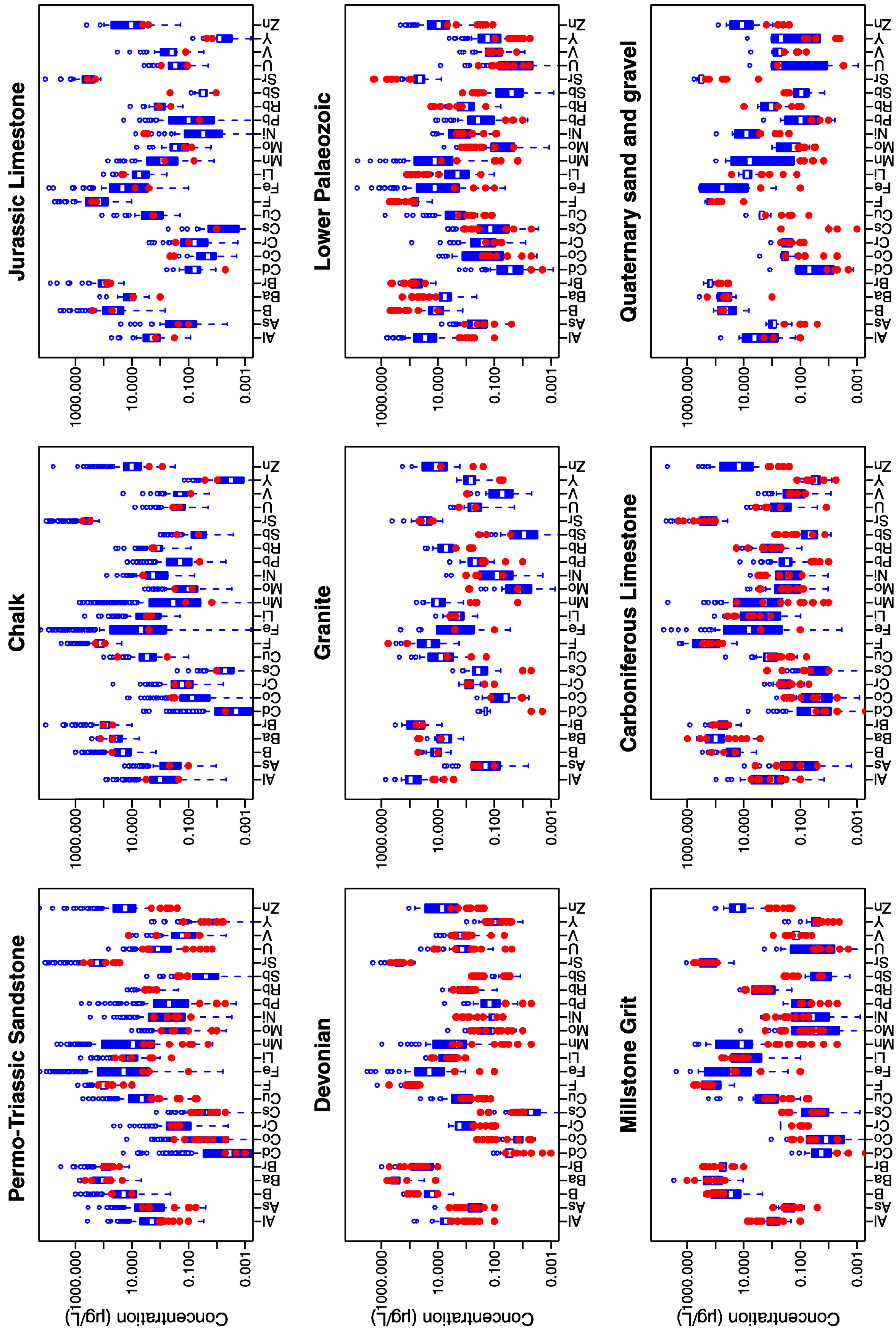
Permo-Triassic Sandstone
Chalk
Jurassic Limestone
Devonian
Granite
Lower Palaeozoic
Millstone Grit
Carboniferous Limestone
Quaternary sand and gravel
Concentration (µg/L)
1000.000
10.000
0.100
0.001
Al
As
B
Ba
Br
Cd
Co
Cr
Cs
Cu
Tl
Fe
Li
Mn
Mo
Ni
Pb
Rb
Sb
Sr
U
V
Y
Zn

Figure 7

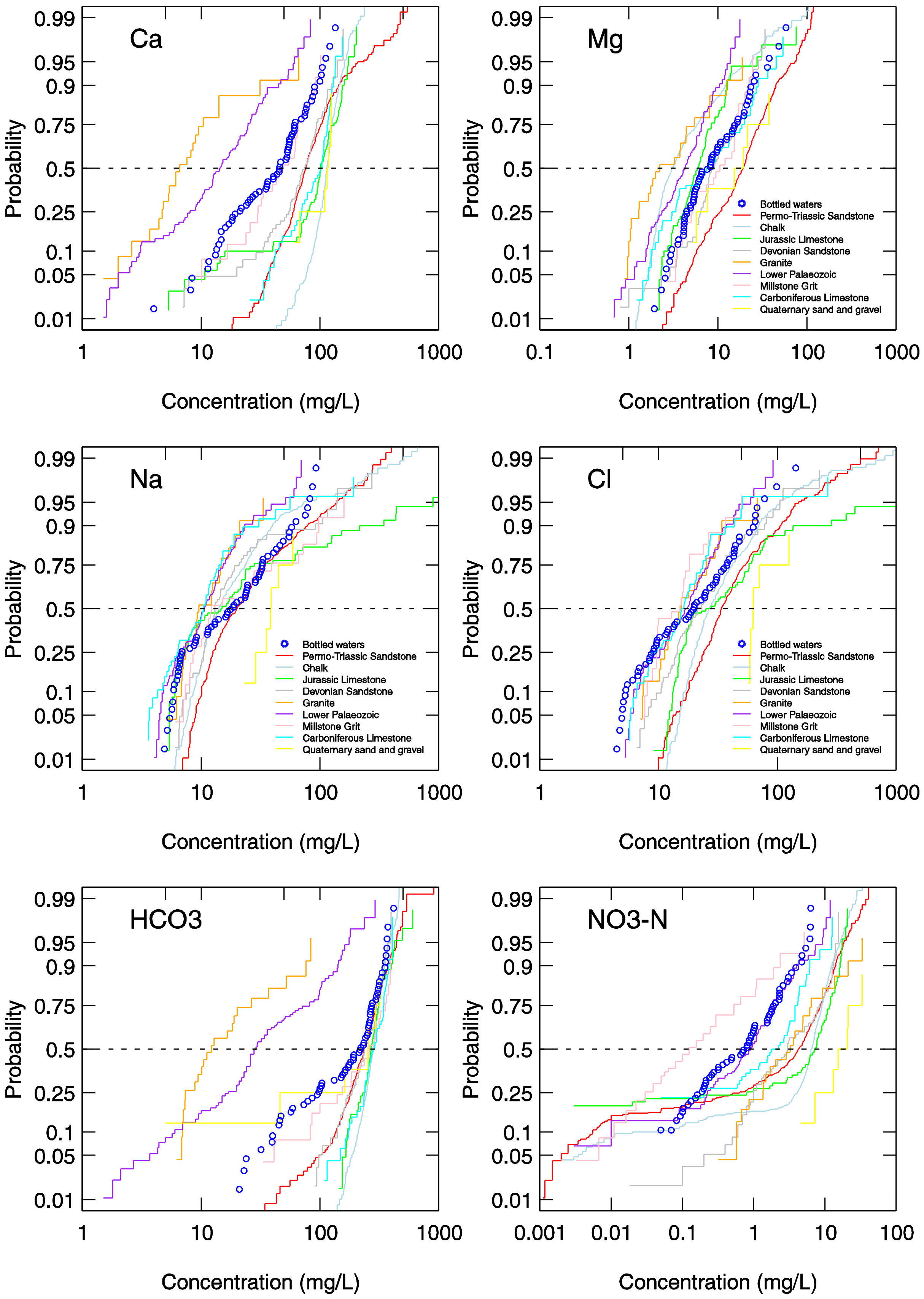
Ca
Mg
Na
Cl
HCO3
NO3-N
Probability
0.99
0.95
0.9
0.75
0.5
0.25
0.1
0.05
0.01
Concentration (mg/L)
1
10
100
1000
0.1
0.001
0.01
Bottled waters
Permo-Triassic Sandstone
Chalk
Jurassic Limestone
Devonian Sandstone
Granite
Lower Palaeozoic
Millstone Grit
Carboniferous Limestone
Quaternary sand and gravel

Figure 8

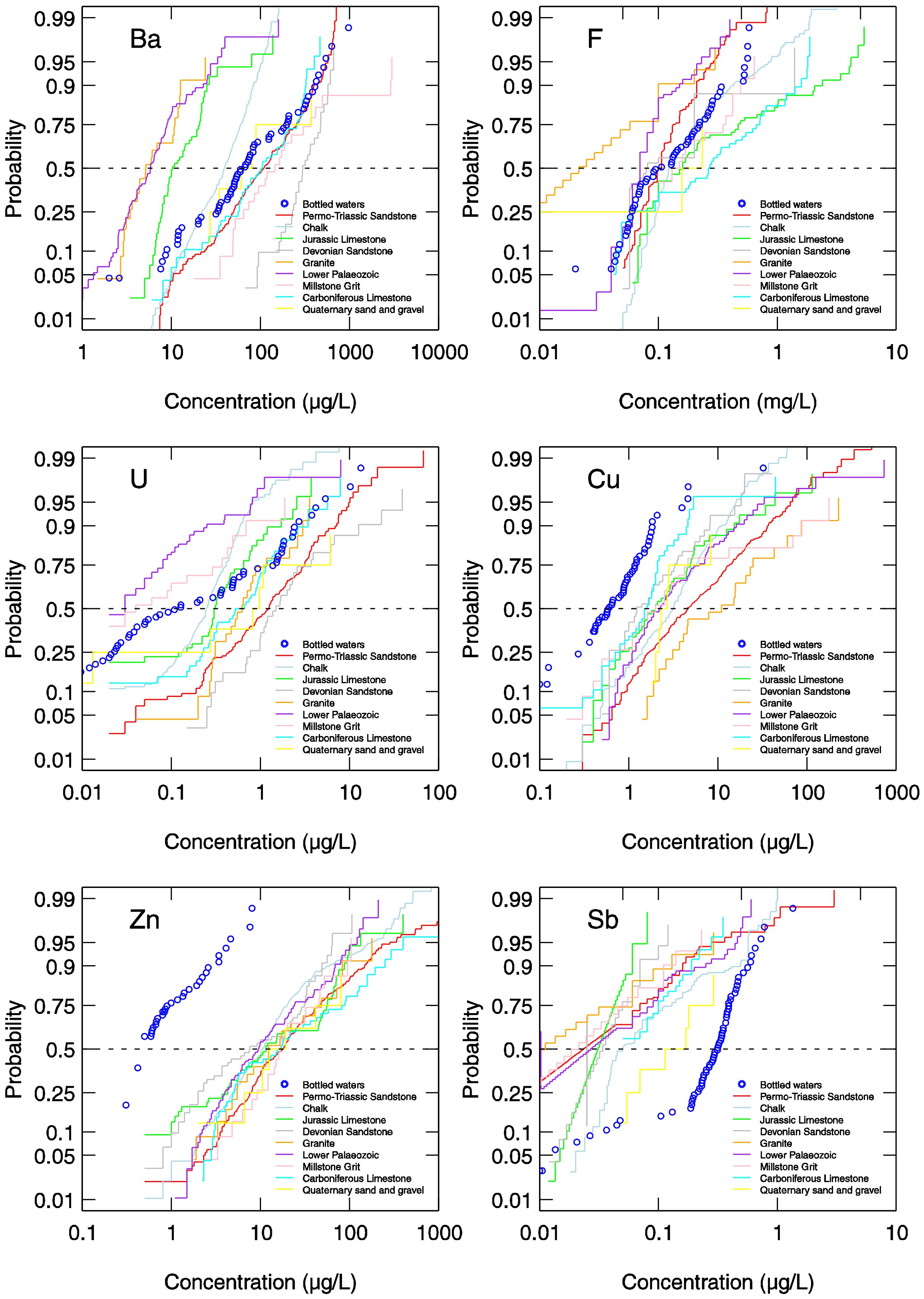Ba
Probability
0.99
0.95
0.9
0.75
0.5
0.25
0.1
0.05
0.01
1
10
100
1000
10000
Concentration (μg/L)
F
0.01
0.1
1
10
Concentration (mg/L)
U
0.01
0.1
1
10
100
Concentration (μg/L)
Cu
0.1
1
10
100
1000
Concentration (μg/L)
Zn
0.1
1
10
100
1000
Concentration (μg/L)
Sb
0.01
0.1
1
10
Concentration (μg/L)
Bottled waters
Permo-Triassic Sandstone
Chalk
Jurassic Limestone
Devonian Sandstone
Granite
Lower Palaeozoic
Millstone Grit
Carboniferous Limestone
Quaternary sand and gravel

Figure 9