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The fractionation of the elements in river waters with respect to the continental crust: a UK perspective based on a river enrichment factor approach

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Abstract

The fractionation in chemical elements for UK river waters is described relative to the continental crust based on data collected within studies of upland acidic catchments in mid-Wales and major eastern-UK rivers. Four types of river are examined (upland, rural, agricultural and industrial/urban) together with an average for the UK based on a 'river enrichment factor', REF. Here, the REF is defined as the ratio of the median river water concentration to the average abundance for the upper continental crust for each element. For this purpose, graphical representations of the logarithm of the REF are presented sequentially in increasing order of magnitude. The results demonstrate vividly the high fractionating of the more volatile, anionic and 'sea-salt' elements to the aqueous phase and the retention of transition elements of high charge due to solubility controls with intermediate controls for the divalent base cations of intermediate solubility. They also show the increasing significance of pollutants in the agriculturally and industrially/ urban impacted environments.

Keywords: Elements; major elements; trace elements; nutrients; river; hydrochemistry; enrichment factor; river enrichment factor; LOIS; Plynlimon; River Severn; Afon Hafren; River Tweed; River Aire; River Thames

Introduction

Understanding the geochemistry of the elements within the hydrosphere remains of major research importance within the environmental sciences. The need relates to many issues and time frames ranging from the evolution of surface water quality on geologic timescales, to the subjects of ecological change within rivers, lakes, estuaries and the open-ocean and human health within a contemporary setting (Edmunds and Smedley, 1996; Stumm and Morgan, 1996; Drever, 1997). The introduction of new analytical chemistry technology means that there is much greater accuracy and much lower detection limits for the measurement of dissolved substances. This feature coupled with rapid multi-element procedures, means that, within recent years, much more reliable and much more wide-ranging information is available for natural waters.

In this paper, two of the most extensive datasets available in the United Kingdom (UK) have been examined. These datasets cover the main surface water types within the UK and provide information on major, minor, nutrient and trace elements. One of these datasets relates to almost 20 years of data for an acidic and acid sensitive region of the British Uplands (the Afon Hafren, Plynlimon in mid-Wales; Neal *et al.*, 1997a). The other dataset comprises up to six years of data for rural, agricultural and industrial/urban river basins draining to the eastern UK coast collected as part of a major community programme, the Land Ocean Interaction Study (LOIS; Leeks and Jarvie, 1998). The presentation is made to gain a general overview of the element attenuation through catchments and the transport within the surface waters of the region. The work provides a stimulus for more detailed studies on partitioning of the elements between dissolved and lithogenic/sedimentary material and it utilizes a novel graphical way of representing the information within a simple format that it is hoped will be of broad applicability.

Study area and datasets

The data focus on two regions, the Plynlimon area of mid-Wales and the Eastern-UK river basins. This provides 'endmember groups' for the four principal water types in the UK: an upland acidic and acid sensitive system, a rural river basin, an agriculturally impacted river basin and an industrial/urban impacted river basin.

AN UPLAND RIVER: THE UPPER RIVER SEVERN, PLYNLIMON, MID-WALES

A major hydrochemical programme on catchments at Plynlimon was undertaken to characterise the effects of forestry management on stream water quality starting in May 1983. For these catchments, the soils are relatively thin (<1m thick); they are of podzolic and gley types and they are acidic. The underlying bedrock is of hard-rock geology and comprises Ordovician to Silurian age mudstones, grits and shales. From the onset, the underlying approach was to study a wide range of chemical constituents to assess both the hydrological flow pathways at the catchment level and the impacts of land use change for the headwaters of the River Severn in the Hafren forest (the Afon Hafren and the Afon Hore). The water is of variable chemistry with a systematic change between baseflow and stormflow (Neal et al., 1997a). Under baseflow conditions, the waters are approximately circumneutral and bicarbonate bearing owing to the predominant drainage of shallow groundwater from the inorganic weathering zone of the lower soil and bedrock. Under highflow conditions, the waters are of poorer quality: they are acidic and aluminium bearing since they are supplied primarily from the acidic soil zones.

For the present study, data for only one of the tributaries, the Afon Hafren, are examined. This tributary represents the Upper Severn (the Afon Hafren is the Welsh name for the River Severn). It has a catchment area of about 3.6 km^2 and comprises approximately equal areas of acid moorland (on the upper part) and conifer plantation forest (on the lower part). Major, minor and trace elements as well as the nutrients were monitored on a weekly basis using the methodologies described by Neal et al. (1997a).

The reader is directed to a special Issue of Hydrology and Earth System Sciences (Neal, 1997a,b) and to Neal et al. (1997a) for details of the hydrological, sedimentological and water quality functioning of the Afon Hafren and the associated tributaries.

RURAL, AGRICULTURAL AND INDUSTRIAL/URBAN RIVERS: THE EASTERN UK RIVERS

The study area comprises the major eastern-UK lowland rivers draining into the North Sea: it extends from the borders of England and Scotland, through the English midlands to the south and south east of England. This represents about a fifth of the UK. The data examined is part of the detailed core-monitoring programme from the Land Ocean Interaction Study (LOIS, Leeks and Jarvie, 1998) undertaken by CEH groups at Wallingford, Windermere and Dorset. It relates to both the main channels of the rivers and, in some cases, tributaries and covers a variety of rural, rural/urban, rural/mining, industrial/urban and agricultural catchments.

For the present analysis, three rivers/river-types are examined

1. **The Tweed: a rural river.** The Tweed is located in the eastern borders between Scotland and England. The catchment is large (about 4400 km^2) and mainly of a low-intensity agricultural character, ranging from upland areas of moorland and rough pasture for hill sheep farming to arable tilled regions in the lowlands. The geology of the catchment comprises mainly sedimentary and metamorphosed sedimentary rocks (Ordovician and Silurian age greywacke, shale and mudstone, Old Red Sandstone and Carboniferous age shale, greywacke and limestone). Further, Old Red Sandstone age igneous rocks (intrusive granites and extrusive basic lavas) occur to the south of the area in the Cheviot Hills. Three sites have been monitored and are of similar water quality. For the present study, data for the monitoring site furthest downstream at Norham, on the main-stem of the river, towards the non-tidal estuary were chosen as the site characterises the Tweed basin as a whole. The catchment to this point may still be categorised as rural and the water is of good quality (Neal et al., 1997d; Robson and Neal, 1997a).

2. **The Thames: an agricultural river.** The Thames is the major river draining southern-central and southeast England. The data presented here relate to water quality monitoring of the upper Thames at a site about half way along its length, mid-way between the towns of Oxford and Reading. The Thames basin to this point represents a large mixed-farming catchment; the only major population centres upstream are the market/light-industrial towns of Oxford (at the junction of the main stem of the Thames and a tributary, the Cherwell) and Aylesbury on a tributary of the Thames, the Thame. The area of the catchment to the monitoring point is about 3500 km^2 The bedrock comprises mixed sedimentary geology of Oolitic limestone in the headwater areas and Oxford clays and minor Cretaceous age sedimentary rocks in the lower parts of the catchment. The water quality of the area is moderate to good; it is influenced by calcium bicarbonate bearing groundwater sources and agricultural inputs of nutrients and micro-organics (Neal et al., 2000c).

3. **The Humber Rivers: the Aire, an industrial/urban river.** The Humber Rivers drain into the North Sea at the Humber estuary in northern England. The Humber catchment divides unto an upland region to the east and north and a lowland region to the west. The bedrock varies from sedimentary rocks of Carboniferous and Permo-Triassic age (primarily sandstone, grit and limestone) in the upland areas to Jurassic and Cretaceous age sandstone and limestone to the lowlands. The northern Humber Rivers drain essentially moorland areas near their sources to agricultural land in the lowland areas. The southern Humber Rivers drain from moorland source areas through the industrial/urban heartland of

north eastern and central England. For the present study, one of the southern rivers is examined, the river Aire. The Aire may be classed as an industrial/urban river; the water quality is poor in relation to point sources of pollutants of nutrients, micro-organics and metals (Neal et al., 1997c; Jarvie et al., 1997).

The study sites have all been monitored on a weekly basis for a wide range of major, minor and trace elements and for nutrients. In most cases, the monitoring programme lasted for about two to four years: the sampling and analytical chemistry methodologies used are described by Leeks et al. (1997). For details of the hydrology and water quality functioning of the area, the reader is directed to several sources listed above. Reference is also given to three volumes of Science of the Total Environment (Neal et al. (eds), 1997b, 1998a, 2000a), to overviews by Robson and Neal (1997b) and Neal et al. (2000b) and to the data summary of Neal and Robson (2000).

Data analysis: a river enrichment factor approach

For the present analysis, the full data record is considered for each of the four rivers. As average conditions are being examined, median values are used for each chemical determinand: this is employed instead of the average value to avoid the influence of skewed data and outlier points that are characteristic of all the datasets. In addition, the average of these median values of the four types of river studied in this paper is used to represent an averaged case.

For the analysis, the partition between dissolved and particulate phases is examined in terms of an enrichment factor, the River Enrichment Factor (REF), which is the ratio of the concentration of an element in solution (μg-element l^{-1}), divided by the concentration in the crust (μg-element/g-rock). For the crustal values, the average concentration of the upper continental crust is used. The values taken are based on the data collated by Wedepohl (1995). These values include allowance for magmatic, metamorphic and sedimentary rocks of the top 20 km of crust. Further, the crustal composition used is very similar to one of the major sedimentary types, greywacke. This division has been chosen because it probably is representative not only of the upper continental crust as a whole but also of the average geologic material to which the hydrosphere relates.

The REF data was converted to logarithmic form and plotted in a sequence from lowest REF (the greatest retention in the solid phase) to the highest REF (the highest degree of leaching to solution). This approach was used to gain a measure of the relative attenuation of chemicals from the solid to the solution phase.

The dissolved component comprises two sources for the elements: the atmosphere and the upper continental crust.

However, the important elements derived from the atmosphere (e.g. wet deposited sea-salts and gaseous inputs of carbon as carbon dioxide) ultimately come from the upper continental crust (and deeper) and separation is not strictly appropriate. For the discussion of the results presented below, reference is given to this aspect where atmospheric inputs to the rivers are important to clarify matters.

The crustal concentration unit used in this study is μg-element gm^{-1} rather than μg-element kg^{-1} so that REF spanned a uniform positive to negative logarithmic range. The utility of this approach becomes apparent later in this paper. If the reader prefers a most rigorous unit, namely μg-element/kg-rock, which maps directly to the dissolved phase, namely μg-element l^{-1}, the logged REF values in the graphs must be reduced by three.

Results

The results of the study are presented in four figures. Figure 1 shows the averaged REF values for the four rivers so that an overview can be provided of the general features. This is important for the UK, as diverse water types are present across the country. Indeed, no part of the UK can really be classed as pristine. Figure 2 provides the same plot but it includes the data for all four of the river types to set against the averaged data. This figure thus provides an indication of the 'scatter' within the REF across the river types. Two other figures are provided in an appendix (Appendix Figs. 1 and 2). They show the variations in the REF for the individual rivers (upland/rural and agricultural/industrial/urban, respectively).

Broadly, there are eight main features discernible (from Fig. 1).

1. There is a large variation in REF: nine orders of magnitude when a non-logarithmic scale is used.
2. Hydrogen and oxygen have the highest REFs as they make up the bulk of the water phase: hydrogen has a higher REF than oxygen owing to the stability of oxide phases in the crust.
3. The highest REFs occur for the elements that are primarily present in solution as soluble anions (apart from hydrogen and oxygen) and/or occur in gaseous form (either as hydrides or oxides). These elements are those related to the life cycle (hydrogen, oxygen, carbon, nitrogen and sulphur).
4. Sodium, chlorine and bromine also have high REFs. These elements occur in ionic form, they are of high solubility and they are associated with 'sea-salts' that have both a major atmospheric source (enrichment by sea-spray) and an urban component.
5. The soluble anions have high REFs, even in comparison with the major cations (e.g. sodium, calcium and magnesium) while silicon and aluminium have low REFs. This occurs because of two factors. Firstly, the soluble
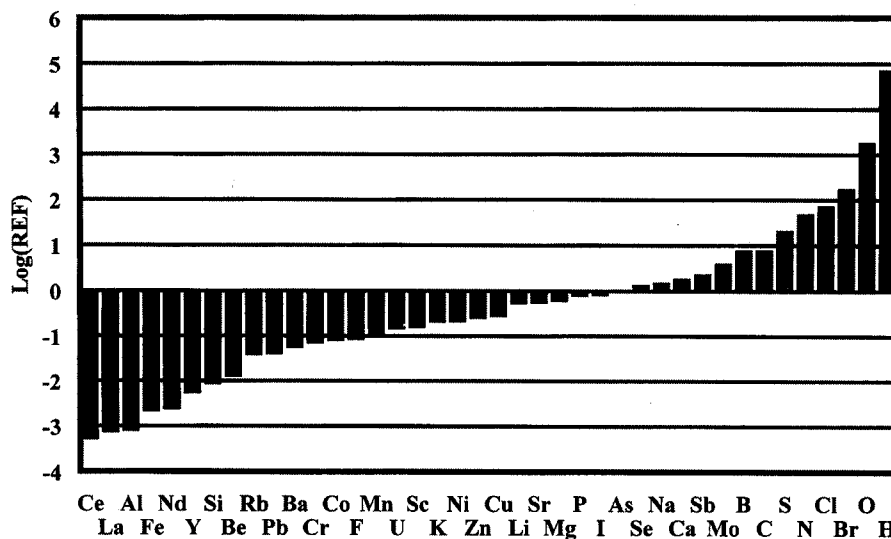
River Enrichment Factor: UK average

Fig. 1. *A sequential plot of log(REF) for averaged UK river data. The data are presented in elemental sequence from low to high REF.*

anions provide the major negative charge in the aqueous phase. Secondly, the anionic charge is associated primarily with silicate, aluminosilicate and oxide/hydroxide counterparts in the crust. Thus, the pattern represents the major difference in anionic components between the dissolved and solid phases.

6. The lowest REFs occur for the elements which are of high charge and which are most prone to solubility controls associated with the precipitation of oxide, hydroxide (aluminium, lanthanides, silica, iron and manganese) and

layer silicate weathering products (e.g. clay minerals for aluminium, silica and iron).

7. The intermediate REFs occur for components with moderate to high solubility but where ion exchange (e.g. potassium), biogenic (e.g. iodine) and solubility/weathering (e.g. calcium, magnesium and fluoride) come into play.

8. For carbon and phosphorus, the total concentrations comprise both inorganic and organic species that are often determined analytically separately. For both com-
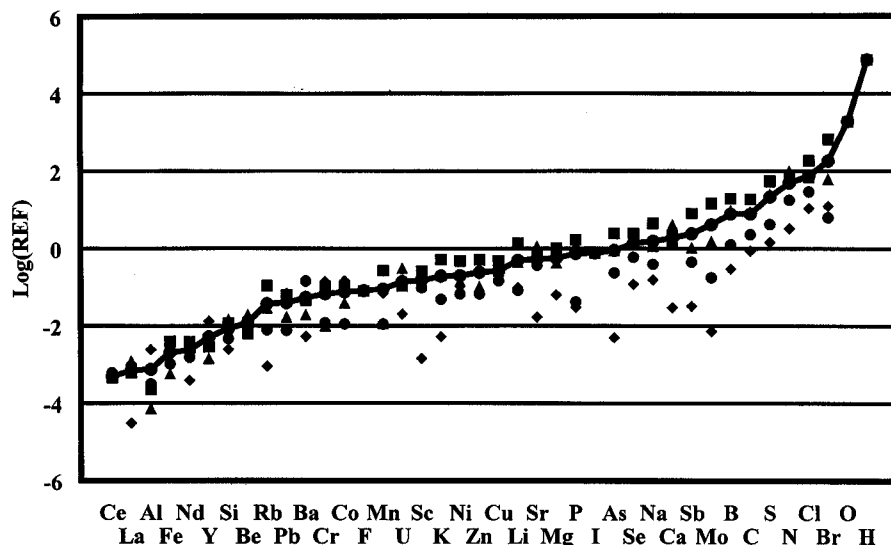
River Enrichment Factor: UK

Fig. 2. *A sequential plot of log(REF) for averaged UK river data as compared with information for the individual river types. Within the plot, the averaged data is represented as a solid line while the solid figures of diamonds, circles, triangles and squares, represent upland-acidic, rural, agricultural and industrial/urban rivers, respectively. The data are presented in elemental sequence from low to high REF.*

ponents, the inorganic forms represent over 40% of the total concentrations in solution, average about 90% (Table 2). For the present study, to simplify matters, only the totals are provided.

Against this broad backdrop, there are both similarities and clear differences in REF for the different types of river examined (Fig. 2 and Table 1).

In general terms, the patterns of REF variation for each type of river system are similar for all the elements. Nonetheless, there are some differences. In particular, the agricultural and industrial/urban REF data are higher or near to the average while the upland and rural catchments are below the average for many elements. Thus, for pollutant components such as molybdenum, phosphorus, arsenic and many of the transition metals, the REF values

Table 1. The attenuation in UK river waters: data structured on the basis of the River Enrichment Factor in descending order with respect to an average UK river. Reference is also provided for global values for average river water and seawater.

Rank	UK Average	UK Upland	UK Rural	UK Agriculture	UK Ind./Urban	River	Seawater
1	H	H	H	H	H	H	H
2	O	O	O	O	O	O	Br
3	Br	Br	Cl	N	Br	Cl	Cl
4	Cl	Cl	N	Cl	Cl	Br	O
5	N	N	Br	Br	N	N	S
6	S	S	S	S	S	I	Na
7	C	C	C	B	B	Sb	B
8	B	I	Ca	C	C	S	Mg
9	Mo	B	B	Ca	Mo	Se	I
10	Sb	Zn	I	Se	Sb	C	Sr
11	Ca	Cu	Mg	Mo	Na	B	N
12	Na	Na	Se	P	As	As	Ca
13	Se	Co	Sb	Na	Se	Ca	K
14	As	Cr	Na	Sr	Ca	Zn	C
15	I	Se	Sr	Sb	P	Cu	Li
16	P	Ni	As	As	Li	Li	Mo
17	Mg	Li	Mo	I	Mg	Mg	F
18	Sr	F	Cu	Li	I	Mo	As
19	Li	Mn	Ba	Mg	Sr	Na	U
20	Cu	Pb	U	U	K	Sr	Se
21	Zn	Mg	Sc	Cu	Zn	F	Rb
22	Ni	Sb	Li	Sc	Cu	Ni	Sb
23	K	P	F	K	Ni	Ba	P
24	Sc	Ca	Ni	Ni	Mn	Pb	Zn
25	U	U	Zn	Zn	Sc	U	Cu
26	Mn	Sr	K	F	Rb	P	Ni
27	F	Be	P	Co	Co	Cr	Ba
28	Co	Y	Cr	Rb	U	K	Si
29	Cr	Mo	Co	Ba	Cr′	Co	Cr
30	Ba	Ba	Mn	Be	F	Mn	Co
31	Pb	K	Rb	Pb	Pb	Rb	Be
32	Rb	As	Pb	Si	Ba	Be	Pb
33	Be	Fe	Be	Mn	Si	Si	Mn
34	Si	Si	Si	Cr	Be	Y	Nd
35	Y	Al	Y	Nd	Fe	Fe	Fe
36	Nd	Sc	Nd	Y	Nd	Nd	Sc
37	Fe	Rb	Fe	La	Y	Al	La
38	Al	Ce	La	Fe	La	Sc	Y
39	La	Nd	Ce	Ce	Ce	Ce	Ce
40	Ce	La	Al	Al	Al	La	Al

503

Table 2. The inorganic and organic fractionation of carbon and phosphorus in UK river waters: concentrations provided in μg-element l^{-1}.

Species	Average	Upland	Rural	Agriculture	Industrial/Urban
C—inorg.	28258	1000	29944	56064	28024
C—organic	4765	1450	3490	4200	9920
C—% inorg.	86	41	90	93	74
P—inorg.	500	20	28	818	1134
P—organic	56	20	21	8	175
P—% inorg.	90	50	57	99	87

are relatively low for the upland and rural rivers and this simply reflects the less polluted nature of these rivers. The differences in REF between the upland and rural rivers as opposed to the agricultural and industrial/urban rivers can be as high as about three hundred fold (i.e. about 2.5 on the logged scale used in the diagrams). However, for many pollutant components, the difference is about 30 fold (i.e. about 1.5 on the logged scale used in the diagrams). In general, the upland and rural data points show the greatest deviations from the averages. This feature represents (i) the relatively low dissolved concentration for the pollutant elements, (ii) the use of arithmetic rather than geometric averages and (iii) the use of a logarithmic transformation of the REF values. With regard to trends within the patterns for REF in the different river types, the following is discernible.

1. **Hydrogen, oxygen, nitrogen, carbon, sulphur, chlorine and bromine.** These have uniformly high REFs with values greater than zero. For this group, the sequence is generally in the order H > O > Br ≈ Cl > N > C > S. Br, Cl, C and S all occur primarily in ionic form (i.e. Br^-, Cl^-, HCO_3^- and SO_4^{2-}). There are minor differences in REF for this group. For example, nitrogen concentrations are higher for the agricultural and industrial/urban rivers due to agricultural and urban pollutant inputs.

2. **Boron.** This is relatively high on the list across the sites (rank number 7 to 9). Boron is so highly placed as (i) it is present as a soluble and chemically unreactive anionic species (borate) and (ii) there are marked anthropogenic sources across all the rivers. In the case of the upland and rural rivers, most of the boron probably comes from atmospheric sources and there is a significant contribution from both 'sea salt' (sea-spray transferred to the atmosphere and deposited as rain) and from pollutant sources such as fly ash (Neal, 1997c). Correspondingly, the highest REF values occur for the agricultural and industrial/urban rivers where inputs from sewage sources are particularly high (Neal *et al.*, 1998b).

3. **Molybdenum.** This is relatively high for the industrial/urban river (rank number 9) and there is a sequence in

REF of industrial/urban > agricultural > rural > upland. This reflects the relative importance of pollutant sources in the industrial/urban river: there may also be pollutant sources on the agricultural river that is downstream of car-industry works where molybdenum is utilized within the processing. The enhanced inputs of molybdenum from the anthropogenic sources are probably not lost from solution owing to its presence as a relatively unreactive oxy-anion, molybdate, within the water column. The high molybdenum level in the industrial/urban river may well distort the averaged data graphed in Fig. 1 to a higher value.

4. **Lead and zinc.** These have relatively high REF values for the upland river (rank number 10 and 20, respectively) compared to other water types (rank numbers 25 and 32, 25 and 31, 22 and 25, for the rural, agricultural and industrial/urban rivers, respectively). This reflects the presence of minor lead-zinc mineralisation in the bedrock of the Plynlimon area and the mobilisation in the soil due to its acidic character (Neal *et al.*, 1997a). For all the catchments, zinc is of higher rank than lead, even though the elements are often associated within the bedrock and the pollutant sources. The difference reflects the lower solubility of lead carbonate and hydroxide phases in the environment.

5. **Aluminium.** Although aluminium is of particularly low REF (typically the bottom of the list at rank number 40), it is higher for the upland catchments were acidic waters increase its mobilization to solution to rank number 35. Thus, the upland REF for the aluminium is one order of magnitude higher than the less acidic rural and industrial/urban rivers and two orders of magnitude higher than the more alkaline agricultural river examined. N.B. the enrichment factor may actually be higher than this; for the agricultural and industrial/urban rivers examined, a significant micro-particulate component may well be present (Neal *et al.*, 1997c).

6. **The divalent base cations.** These occur within a REF sequence Ca > Sr > Ba > Be with magnesium ranking between highest (upland) and third (agriculture) in the rank. For calcium, strontium and, to a lesser extent, barium, these components are relatively soluble and

associated primarily with the weathering of carbonate phases. Thus, the calcium and strontium REFs are relatively high for the agricultural catchments with a high calcite, strontium bearing, component in the aquifer matrix, but low for the base depleted bedrock of the acidic upland sites. Magnesium, while still of high solubility, is associated with two sources, sea-salt inputs from the atmosphere (particularly important for the upland river where it has the highest rank of the divalent base cation group) and from weathering of silicate minerals. Beryllium has the lowest REF and this reflects hydrolysis reactions and a low solubility for $Be(OH)_2$.

7. **The halogens.** These occur within the REF sequence $Br \approx Cl > I > F$. Of these elements, chlorine, bromine and iodine are enriched owing to the atmospheric input from sea salts. Iodine particularly is enriched above the level of sea salts due to enrichment at the air-sea boundary from which the sea salts in rainfall are derived. In hydrochemical terms, the order expected might be $Cl > Br > I > F$, in order of increasing chemical reactivity. This would be anticipated because chloride is a relatively unreactive ion while bromide and iodide are expected to have increasing biological uptake while fluoride is associated with strong sorption onto aluminosilicate phases common within the soil and bedrock zones. However, bromine seems to have an approximate input-output balance while iodine is retained within the catchment, for the uplands at least (Neal et al., 1997a). This aspect may well explain the similarity in REF between chlorine and bromine and lower REF for iodine. Clearly, the deviation in enrichment factor is related to the levels of atmospheric and pollutant inputs for the halogens and the biological and inorganic processing of these inputs within the catchment and the soil/bedrock-matrix.

Discussion

The approach provides graphically in both senses of the word, a simple means of describing the fractionation between riverine and lithogenous phases for the chemical elements. The work fits well within contemporary understanding of element mobility within the hydrosphere (c.f. Stumm and Morgan, 1996; Drever, 1997).

The approach is akin to the use of distribution coefficients (K_d) to describe dissolved-particulate interactions within natural waters (Schnoor et al., 1987).

$$K_d = [Element_{dissolved}] / ([Element_{particulate}] / SS)$$

where $[Element_{dissolved}]$ and $[Element_{particulate}]$ refer to the dissolved and particulate concentrations in the water column, respectively, and SS refers to the total suspended sediment concentration.

Like the K_d approach, the REF values vary from site to

site and catchment to catchment due to the variability of the solid phases involved and the variable extent of chemical reactivity (Neal et al., 1997c; Tipping et al., 1998). In addition, they are dimensionally similar. However, unlike the K_d approach, the REF methodology represents a much more integrated picture of reactivity. Thus, the REF approach allows a qualitative means of examining chemical reactivity for different types of catchment and river systems. This approach complements broad based mass balance techniques and mathematical approaches where detailed process information is often lacking.

In terms of this paper, the information provided represents only a start to interrogate the within-catchment reactions that determine river water quality and there are several avenues to take for progress. Within the framework of newly developing statistical and GIS based methodologies, the approach needs to be extended to examine REF variations within a spatial (sub-catchment) and a temporal/hydrological (event based) context. For this purpose, focus can be put on an analysis of hydrochemically distinct typologies, a method based on the well established method of examining 'endmember' mixing relationships and an understanding of the varying compositions of the bedrock chemistries. In particular, the REF values need to be more directly related to the chemistry of the specific bedrock and soil type/types rather than to the global average used in this paper. For example, in the case of calcium and carbon, their REFs would be lowered for the rivers that have calcite rich bedrock and this would reduce the variations between the various river types examined. Thus, the types of relationship that might be examined include comparisons of

1. Area weighted bedrock chemistry versus average baseflow chemistry: i.e. a mapping of geology against water chemistry under the situation where streamflow is mainly derived from bedrock sources.
2. Area weighted soil chemistry versus average highflow chemistry: i.e. a mapping of geology against water chemistry under the situation where streamflow is mainly derived from soil sources.
3. Area weighted bedrock and soil chemistry against flow weighted average chemistry. This is used to examine riverine chemical flux transfers and there is a need to use chemical hydrograph splitting to identify the individual fluxes from the bedrock and the soil. This must be undertaken in conjunction with (1) and (2).
4. (1), (2) and (3) with an estimate of the atmospheric input as modified in the catchment by evaporation and transpiration.

For the present, it suffices to provide a flag to encourage the use of this technique in three ways. Firstly, the approach is of use as a teaching aid. In this regard, the approach may be used in the study of element mobility within aquatic systems under the disciplines of hydrogeochemistry and environmental chemistry. For example, Fig. 3 is provided to show the REF sequence at a more 'global level' for both river and
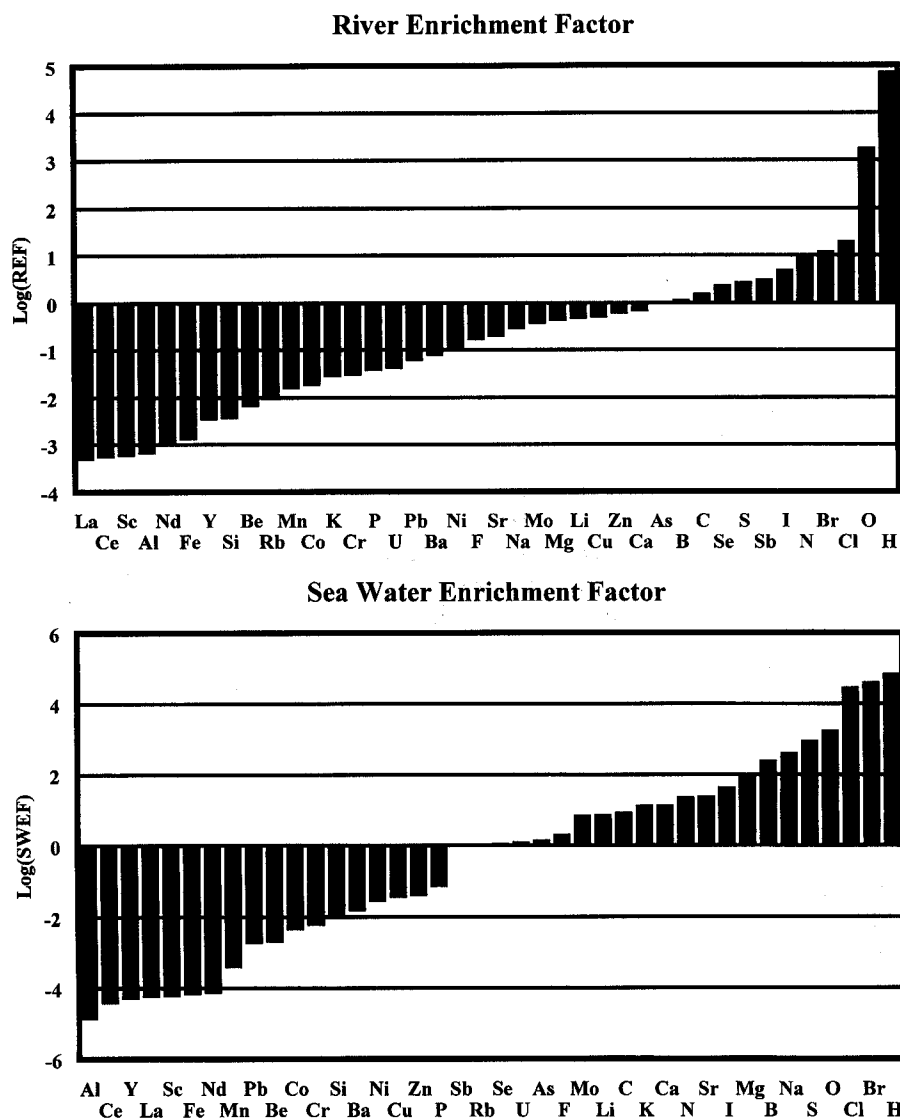
River Enrichment Factor

Sea Water Enrichment Factor

Fig. 3. *A sequential plot of log(REF) for average river and seawater chemistry based on the data presented primarily in Drever (1997). For the river case, the few elements not summarised in Drever (1997) are infilled using the UK data presented in this paper for the least polluted area (the upland system). For the seawater case, the Drever (1997) data is supplemented by rare-earth information taken from Brooklins (1989). The data are presented in elemental sequence from low to high REF.*

marine systems. In essence, the results indicate features similar to that described above although there is of course a higher enrichment for the sea-salt elements in seawater that leads to higher REF values for these elements. The reader is directed to excellent textbooks in the hydrogeochemistry field such as Stumm and Morgan (1996) and Drever (1997) for a wide-ranging account of the determinative reactions for the elements. Secondly, the approach is of use for hydrogeological data interrogation for wide-ranging and proactive initiatives that are developing to determine hydrogeochemical variability of surface waters at the regional and international scale (BGS, 1999). Thirdly, the approach may be of use to expand K_d methodologies to

incorporate geological as well as sedimentological interactions with the dissolved phase.

References

BGS, 1999. *Regional Geochemistry, stream waters, Wales*. British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK, 110 pp.

Brooklins, D.G., 1989. Aqueous geochemistry of rare earth elements. In, *Geochemistry and mineralogy of rare earth elements:* Lipin, B.R. and McKay, G.A. eds. Reviews in Mineralogy, 21, Min Soc Amer., 201–225.

Drever, J.I., 1997. *The geochemistry of natural waters*. Prentice Hall, Upper Saddle River, NJ 07458, USA: 436 pp.

Edmunds, W.M. and Smedley, P.L., 1996. Groundwater geochemistry and health: an overview. In *Environmental geochemistry and health*: Appleton, J.D., Fuge, R. and McCall, G.J.H eds Geol. Soc (London) special pub. **113**, 91–105.

Jarvie, H.P., Neal, C., Leach, D.V., Ryland, G.P., House, W.A. and Robson, A.J., 1997. Major ion concentrations in the Humber rivers. *Sci. Tot. Environ.*, **194/195**, 285–302.

Leeks, G.J.L., Neal, C., Jarvie, H.P., Casey, H. and Leach, D.V., 1997. The LOIS river monitoring network: strategy and implementation. *Sci. Tot. Environ.*, **194/195**, 101–110.

Leeks, G.J.L. and Jarvie, H.P., 1998. Introduction to the Land-Ocean Interaction Study (LOIS): Rationale and international context. *Sci. Tot. Environ.*, **210/211**, 5–20.

Neal, C., (ed.) 1997a. Water quality of the Plynlimon catchments (UK). *Hydrol. and Earth System Sci.*, **1**, 381–764.

Neal, C., 1997b. A view of water quality from the Plynlimon watershed. *Hydrol. Earth System Sci.*, **1**, 743–754.

Neal, C., 1997c. Boron water quality for the Plynlimon catchments. *Hydrol. and Earth System Sci.*, **1**, 619–626.

Neal, C. and Robson, A.J., 2000. A summary of river water quality data collected within the Land Ocean Interaction Study: core data for Eastern UK rivers draining to the North Sea. *Sci. Tot. Environ.*, **251/252**, 587–668.

Neal, C., Wilkinson, J., Neal, M., Harrow, M., Wickham, H., Hill, L. and Morfitt, C., 1997a. The hydrochemistry of the headwaters of the River Severn, Plynlimon. *Hydrol. Earth System Sci.*, **1**, 583–617.

Neal, C., House, W.A., Leeks, G.J.L. and Marker, A.H., (eds.) 1997b. U.K. fluxes to the North Sea, Land Ocean Interaction Study (LOIS). *Sci. Tot. Environ.*, **194/195**, 490 pp.

Neal, C., Robson, A.J., Jeffery, H.A., Harrow, M., Neal, M., Smith, C.J. and Jarvie, H.P., 1997c. Trace element inter-relationships for the Humber rivers: inferences for hydrological and chemical controls. *Sci. Tot. Environ.*, **194/195**, 321–343.

Neal, C., Robson, A.J., Harrow, M., Hill, L., Wickham, H., Bhardwaj, C.L., Tindall, C.I., Ryland, G.P., Leach, D.V., Johnson, R.C., Bronsdon, R.K. and Cranston, M., 1997d. Major, minor, trace element and suspended sediment variations in the River Tweed: results from the LOIS core monitoring programme. *Sci. Tot. Environ.*, **194/195**, 193–206.

Neal, C., House, W.A., Leeks, G.J.L., Whitton, B.A. and Williams, R.J., (eds.) 1998a. Water quality of UK rivers entering the North Sea (LOIS). *Sci. Tot. Environ.*, **251/252**, 697 pp.

Neal, C., Fox, K.K., Harrow, M. and Neal, M., 1998b. Boron in the major UK rivers entering the North Sea. *Sci. Tot. Environ.*, **251/252**, 41–52.

Neal, C., House, W.A., Leeks, G.J.L., Whitton, B.A. and Williams. R.J., (eds.) 2000a. The water quality of UK rivers entering the North Sea. *Sci. Tot. Environ.*, **251/252**, 696 pp.

Neal, C., House, W.A., Leeks, G.J.L., Whitton, B.A. and Williams, R.J., 2000b. Conclusions to the special issue of Science of the Total Environment concerning 'The water quality of UK rivers entering the North Sea'. *Sci. Tot. Environ.*, **251/252**, 559–576.

Neal, C., Jarvie, H.P., Willams, A.J., Neal, M., Bhardwaj, L.C., Wickham, H., Harrow, M. and Hill, L., 2000c. The water quality of the River Thames at a rural site downstram of Oxford.'. *Sci. Tot. Environ.*, **251/252**, 441–458.

Robson, A.J. and Neal, C., 1997a. Regional water quality of the Tweed. *Sci. Tot. Environ.*, **194/195**, 173–192.

Robson, A.J. and Neal, C., 1997b. A summary of the water quality of Eastern UK rivers. *Sci. Tot. Environ.*, **194/195**, 15–38.

Schnoor, J.L., Sato, C., McKechnie, D. and Sahoo, D., 1987. *Processes, coefficients and models for simulating toxic organics and heavy metals in surface waters*. Environmental Protection Agency Report, EPA/600/3-87/015. Environmental Research Laboratory, Athens, GA 30613, USA. 303 pp.

Stumm, W. and Morgan, J.J., 1996. *Aquatic Chemistry* (3rd edition). Wiley, New York, 1022 pp.

Tipping, E., Lofts, S. and Lawlor, A.J., 1998. Modelling the chemical speciation of trace metals in the surface waters of the Humber system. *Sci. Tot. Environ.*, **210/211**, 63–78.

Wedepohl, K.H., 1995. The composition of the continental crust. *Geochim. et Cosmochim. Acta*, **59**, 1217–1232.

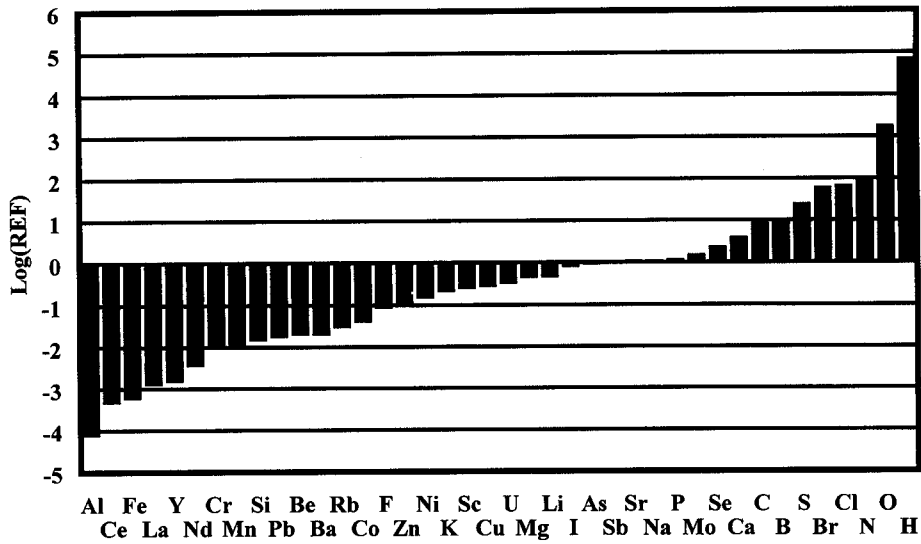# Appendix

River Enrichment Factor: UK upland
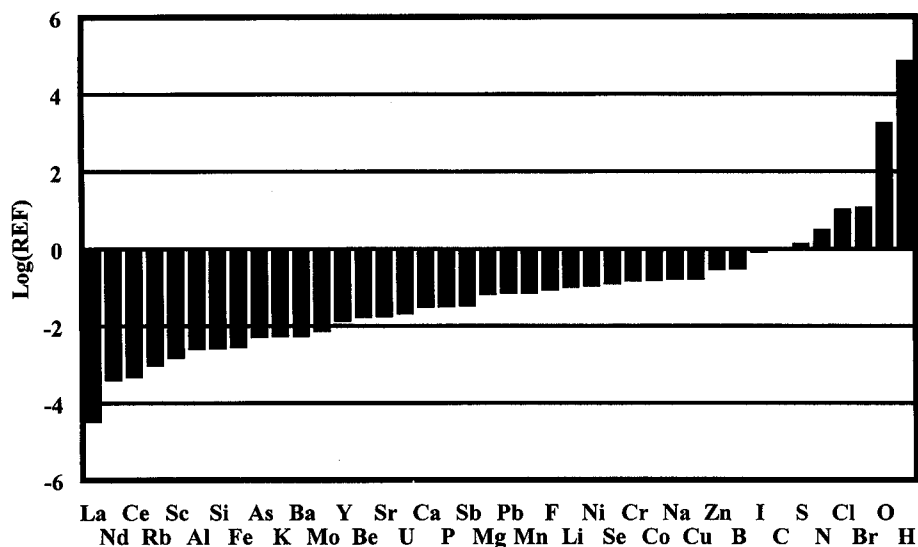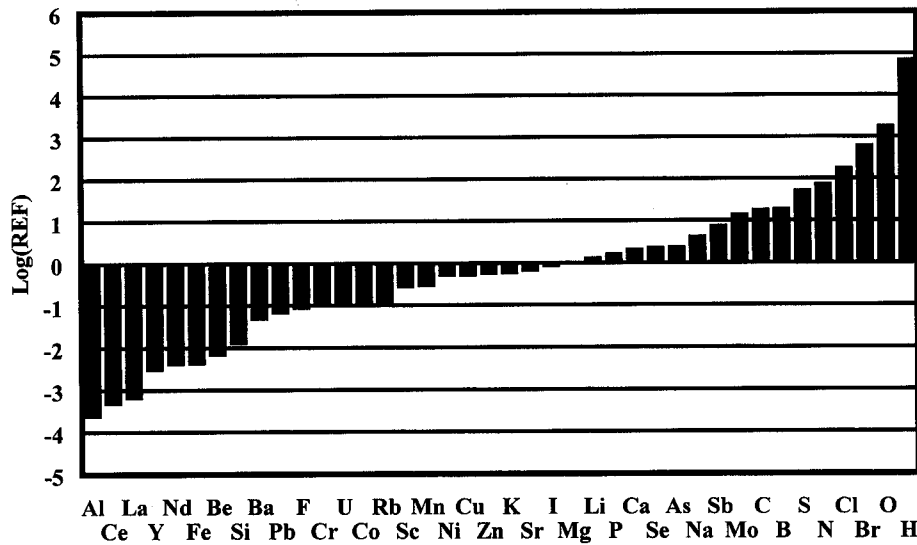

River Enrichment Factor: UK rural
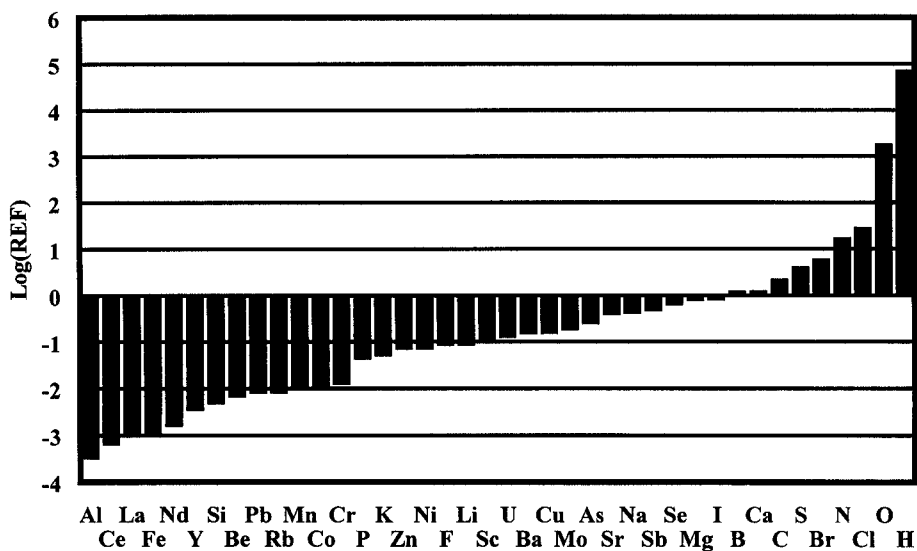
Appendix Figure 1. *A sequential plot of log (REF) for upland and rural UK river data. The data are presented in elemental sequence from low to high REF.*

Appendix *(continued)*

River Enrichment Factor: UK agricultural

River Enrichment Factor: UK Industrial/urban

Appendix Figure 2. *A sequential plot of log(REF) for agricultural and industrial/urban UK river data. The data are presented in elemental sequence from low to high REF.*