DISTRIBUTION OF ELEMENTS IN STREAM WATER

B. De Vivo[1], E.L. Ander[2], M. Bidovec[3], A. Lima[1], S. Pirc[4],
S. Reeder[2], U. Siewers[5], B. Smith[2]

with contributions by

S. Albanese[1], M. Batista[6], A. Bel-lan[7], M. Birke[5], N. Breward[2], A. Demetriades[8], W. De Vos[9],
M. Duris[10], P. Gravesen[11], V. Gregorauskiene[12], J. Halamic[13], G. Jordan[14], K. Lax[15],
J. Locutura[7], P.J. O'Connor[16], A. Pasieczna[17], I. Slaninka[18], T. Tarvainen[19]

[1]Dipartimento di Scienze della Terra, Universita' di Napoli "Federico II", Naples, Italy;
[2]British Geological Survey, Keyworth, Nottingham, United Kingdom;
[3]Geological Survey of Slovenia, Ljubljana, Slovenia;
[4]Geology Department, University of Ljubljana, Slovenia;
[5]Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany;
[6]Geological Survey of Portugal, Alfragide, Portugal.
[7]Geological Survey of Spain, Madrid, Spain;
[8]Institute of Geology and Mineral Exploration, Athens, Greece;
[9]Geological Survey of Belgium, Brussels, Belgium;
[10]Czech Geological Survey, Prague, Czech Republic;
[11]Geological Survey of Denmark and Greenland, Copenhagen, Denmark;
[12]Geological Survey of Lithuania, Vilnius, Lithuania;
[13]Institute of Geology, Croatia, Zagreb, Croatia;
[14]Hungarian Geological Institute, Budapest, Hungary;
[15]Geological Survey of Sweden, Uppsala, Sweden;
[16]Geological Survey of Ireland, Dublin, Ireland;
[17]Polish Geological Institute, Warszawa, Poland;
[18]Geological Survey of Slovak Republic, Bratislava, Slovak Republic;
[19]Geological Survey of Finland, Espoo, Finland;

For solid materials on the Earth's surface, water is principally the major weathering agent responsible for the release of chemical elements from rocks and for chemical changes in soils, sediments and vegetation. However, stream water is also the transporting and chemical medium that controls the composition of matter dissolved in it, in amounts usually well below 1%. Hydrogeochemistry of stream water considered in the global hydrological cycle is determined not only by the solid substrate, but also very strongly by climate and climate-related phenomena such as vegetation zones. Of particular importance to element distribution patterns are rainfall and temperature, not only at present, but also in the past, going back to the last ice age. Topography also plays an important role in the relation between surface water and ground water, because mountains are mainly infiltration areas of fresh rain and snow, whereas low-lying areas witness effluent seepage of groundwater, which has taken up dissolved ions during its residence underground.

Systematic geochemical mapping of stream water on the European scale shows marked differences in the spatial distribution of the analysed determinands. Most patterns appear to be controlled less directly by geology, but more by climate-related parameters such as rainfall, temperature, acidity and organic matter, in combination with topography and distance from the ocean, *i.e.,* the source of precipitation. In the interpretation of elemental distributions these complex controls of water chemistry are considered, but also the geological substrate is described, even when its control is not obvious, for the ultimate source of most elements is in the rocks within the drainage basins. Finally, anthropogenic influence is often visible or suspected.

There is a wide range of electrical conductivity (EC) values reflecting different ionic strengths and total dissolved solids. The range of EC covers two orders of magnitude from <3 mS m^{-1}

in stream water draining catchments associated with crystalline rocks throughout Scandinavia, northern Britain and Wales, the north west Iberian Peninsula and over the Massif Central, to values >500 mS m^{-1} in stream water associated with sedimentary rocks in Lithuania, south east England and over the Pannonian basin in Hungary, Croatia and Slovenia. The highest conducting stream water samples occur over southern Spain and Italy and may reflect the presence of evaporitic deposits, high rates of evapotranspiration or volcanic activity. Stream water pH, which represents the dominant control on solution speciation and trace hydrochemistry, varies from 2.2 to 9.8, with 90% of the values between 6.2 and 8.6. The most acidic conditions are found throughout Fennoscandia and are often associated with high concentrations of dissolved organic acids and geological environments of low buffering capacity. Highly alkaline stream water samples, consistent with carbonate dominated alkalinity, are found mainly in Austria and around the Mediterranean and are associated with the presence of sedimentary carbonate and marble.

Conductivity, pH, dissolved organic carbon (DOC) and the concentrations of major ionic species have been used to interpret data for individual elements. *For example*, pH, DOC and other important ligands, such as fluoride, control the distribution of aluminium, whilst other elements, including the rare earths, zirconium and titanium largely reflect the influence of climate and topography, and also regional geology. High chromium and, to a much lesser extent, nickel, reflect the presence of ultramafic rocks over the ophiolites of Albania and Greece.

The distribution of uranium in stream water differs in many respects from that in soil and sediment samples, in which the highest baseline levels occur over the northern Iberian Peninsula and the Massif Central. In stream water, however, there is a strong correlation between uranium and bicarbonate. This observation is consistent with the aqueous stability of hexavalent uranium carbonates and bicarbonates above pH 6 to 7. The highest uranium concentrations of >3 µg l^{-1} occur in carbonate-dominated stream water of southern Spain, the Baltic states, Hungary and parts of southern Italy.

There is a wide variation in the concentration of potentially harmful elements, such as arsenic, cadmium, nickel, chromium and lead. Levels of arsenic are consistently low (<0.05 µg l^{-1}) over

much of the Baltic Shield and the Caledonides, whilst the highest values (>8 µg l^{-1}) occur principally over the Rhine delta of the Netherlands, eastern France, the Pannonian basin and volcanic areas of central Italy.

The mapped distribution patterns of the elements in stream water were compared with distribution patterns of the solid sample media, but an attempt was made to recognise different types of dispersion, each one characterising several elements. This was achieved by Factor Analysis (FA, explained in Annex 4 to this volume, Pirc *et al*. 2006). This statistical analysis was performed as an exploratory data technique for obtaining preliminary objective information inherent in the structure of the data, without human interference. Eight distinct elemental patterns in stream water, expressed by 8 factors, were established by FA. Each of the factors represents a certain distribution pattern that is visualised on the map of scores of this factor. This pattern is followed approximately by every element loaded on the specific factor. Each factor may have an underlying meaning that can be interpreted from elemental associations and geochemical, geological, climatological and other relevant information. The eight distinct pattern types are:

1. Rare earth and associated elements in acid, high organic matter and low mineralisation waters, 31.0% variance explained.
2. Major ions and other elements high-mineralisation waters, 22.2% variance.
3. Chalcophile and lithophile elements, 4.55% variance.
4. Alkaline rocks elements, 4.18% variance.
5. Mostly lithophile elements, 3.56% variance.
6. Ultramafic and inversely felsic rocks elements, 3.24% variance.
7. Mn-Fe-dissolved organic carbon waters, 2.64% variance.
8. Sea influence elements, 2.56% variance explained

The patterns of the first, second, seventh and eighth type are determined largely by exogenic factors, such as climate, topography, vegetation, distance from sea, human activities, and only exceptionally by geogenic factors. The fourth, sixth and fifth type reflect primarily geology, and the third geology, mineralisation or pollution. The patterns are described in more detail in Annex 4

(Pirc *et al.* 2006).

The aqueous geochemistry of each of the minor and trace elements under consideration can be further understood by studying their abundance in relation to the major ions (*cf.* the importance of HCO_3^- concentration in controlling U solubility), dissolved organic carbon and physico-chemical conditions, such as conductivity and pH of the stream waters. Additionally, comparison with the wider natural and human-impacted environment may allow a greater understanding to be arrived at.

Comparison of the relative abundance of any particular analyte in stream waters with that in the soils and sediments can illustrate differences in the baseline concentration of that analyte between these media. Differences can be substantial and demonstrate further the value of such multi-media multi-element systematic datatsets, because prediction of the baseline concentrations of stream water using other media is frequently almost impossible. Good examples of this can be found by studying the interpolated images for As, Cu and U, but is not limited to these analytes. The aqueous chemistry, in examples such as these, is controlled not only by the natural abundance of the analyte in the near-surface environment within the catchment, but also by the pH, major ion chemistry and DOC concentrations, which in turn are controlled by the Solid and Quaternary geological environment. Thus, U mobility is enhanced in high HCO_3^- environments, with the natural abundance of HCO_3^- being dominated by the underlying geology. An example of a very strong inverse relationship in the relative abundance of a major ion in stream waters and the other analysed sample media can be seen in Na. Thus, although the subsoil and stream sediment, in particular, may be seen to be representative of the natural geochemical baseline environment in those media, aqueous concentrations and relative abundances may follow different distribution patterns as a result of entirely natural processes. The geological control may be that of catchment mineralogy, the effect on regional topography (and therefore temperature and rainfall) and soil development.

Other antagonistic patterns may reflect human perturbation of the natural geochemical environment, and some elements have a very strong connection to specific industrial, agricultural or even domestic, processes. Thus, although only analysed in stream waters, analytes such as B (detergents) and NO_3^- (fertilisers) may be studied in more detail to understand where this is influential. Such an understanding is important in the context of the value of the baseline data. If 'baseline' for an analyte in a sample media, is to be described for a natural region (*e.g.* geological environment or river catchment) or within an arbitary region (*e.g.* a national boundary), it is important to be able to exclude those data which are clearly acutely influenced by non-natural processes. The anomalous Ni values in south-east England are a good example of this human influence.

In the elemental description texts that follow the reader will find many examples of the usefulness of this approach of applying the objective information from the field to interpret the different sources of elements in stream water.