N – Nitrogen (Nitrate)

Introduction

Nitrogen is a member of group 15 of the periodic table, along with P, As, Sb and Bi. The element has an atomic number of 7, an atomic mass of 14, three main oxidation states (-3, +3 and +5) and two naturally occurring isotopes (^{14}N and ^{15}N), of which ^{14}N is the most abundant at 99.6% of the mass. In its neutral state, nitrogen is a gas with the molecular formula N_2, making up about 78% of Earth's atmosphere by volume.

It is generally assumed that nitrogen in igneous rock-forming minerals occurs as NH_4^+, and in sediments and sedimentary rock-forming minerals as NH_3^+ (Wedepohl 1978). The NH_4^+ ion has a similar estimated ionic radius to that of K^+ (148 pm and 138 pm respectively), which tends to explain the presence of ammonium in minerals such as feldspar, clay and mica (Goldschmidt 1970). Examples of minerals in which N is a major constituent are rare, because of the ease with which they dissolve in water. However, niter KNO_3 and nitratine $NaNO_3$ are two N-rich minerals that fall under the carbonate classification based on their crystal structure.

Granitic and granodioritic rock types tend to have an average N concentration of around 20 mg kg^{-1}, with gabbroic and dioritic rocks containing roughly half that amount (Wedepohl 1978). Mafic rock types commonly contain less N, which is attributed to a general decrease in K and alkali earth metal concentrations within these rocks. Igneous rocks that have either been hydrothermally altered or have come into contact with sedimentary rock bodies often display signs of N enrichment (Mattiat 1960). Due to the rapid reduction of NO_3^- to NH_3^+ under anaerobic conditions, it has been suggested that most N in sediments occurs in an organic form, either as insoluble kerogen or soluble amino acids (Degens *et al.* 1963). Shale commonly contains the highest concentrations of N, up to 1,900 mg kg^{-1}, in Palaeozoic shale units (Stevenson 1962), whilst limestone with an average concentration of 4 to 200 mg kg^{-1} N, is significantly depleted.

TNitrogen may be present in stream water as nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+) ions, dissolved organic N, and in particulate form, which is usually organic, but may contain inorganic N. Factors that determine the speciation of N in surface water include pH, temperature and oxygen availability. Nitrate typically constitutes between 60 and 95% of the total dissolved N in stream water, except under acid anoxic conditions when NH_4^+ predominates. As N is closely linked to biological cycles, the concentration of NO_3^- in surface water is highly variable and dependent on productivity within the catchment, locality, water depth and season. Nitrogen concentrations in stream water typically rise to a maximum over the winter months, following soil water recharge during the autumn. Organic N in soil decomposes to form inorganic NH_4^+, which is subsequently oxidised to NO_3^-. Nitrate is not strongly absorbed, so any NO_3^- in excess of plant requirements is readily leached into groundwater and subsequently enters stream water. However, N generally accumulates within natural and semi-natural ecosystems, because it is an essential element for plant growth.

Nitrate concentrations in surface water vary considerably. The European average has been estimated as 3.7 mg l^{-1} (Wedepohl 1978), although nitrate concentrations as high as 1000 mg l^{-1} have been found in areas of unusually high biological activity (Hem 1992).

The amount of nitrate and nitrite in the environment continues to increase, mainly through the extensive use of agricultural fertilisers. Point sources of pollution, such as silage and liquid run-off from stored manure, as well as agricultural run-off, make a significant contribution to the total dissolved N in stream water. Nitrogen oxides emitted by the combustion of fossil fuels in power stations and vehicles are other important sources of nitrates and nitrites. Other sources of N in water include run-off from caves inhabited by large colonies of bats (Hem 1992).

Nitrogen is crucial to life. The nitrogen cycle is one of the most important processes in nature for living organisms and N is a component of all proteins. High concentrations of nitrates and nitrites are, however, known to cause several adverse health effects. The most common of these include: reactions with haemoglobin in blood, reducing the capacity of blood to carry oxygen (nitrite), decreased functioning of the thyroid gland (nitrate), shortages of vitamin A (nitrate), and the production of nitrosamines, which are known to be one of the most common causes of cancer (nitrates and nitrites).

Table 46 compares the median concentrations of NO_3^- in the FOREGS samples and in some reference datasets.

Table 46. Median concentration of NO_3^- in the FOREGS samples.

Nitrate (NO_3^-)	*Origin – Source*	*Number of samples*	*Size fraction*	*Extraction*	*Median mg kg^{-1}*
Water	**FOREGS**	**808**	**Filtered <0.45 µm**		**2.82 (mg l^{-1})**

Nitrate (NO_3^-) in stream water

Nitrate values in stream water show a very wide range of four orders of magnitude, from <0.04 to 107 mg l^{-1}, with a median value of 2.8 mg l^{-1}. Approximately 15% of data are below the limit of quantification (0.04 mg l^{-1}). It is noted that Tthe European average nitrate concentration Tfrom 808 stream water samples collected in the present study is 9.07 Tmg l^{-1}, which is considerably higher than the 1978 average value of 3.7 mg l^{-1} mentioned by Wedepohl (1978).

Lowest nitrate values in stream water (<0.4 mg l^{-1}) are found throughout Norway, northern Sweden and Finland, western Scotland, northern Ireland, parts of the west Iberian Peninsula, Sardinia and north-western Greece. The low values are predominantly associated with acid igneous and metamorphic rocks but they can be related to a wide variety of rock types. Low nitrate is also associated with high topographic relief and high rainfall, including the natural vegetation cover, which is highly efficient at recycling plant-available nitrate.

Enhanced nitrate concentrations in stream water (>20 mg l^{-1}) are found throughout most of central and southern England, northern Denmark, northern France (central Paris Basin, Brittany and Aquitaine) and Belgium, large parts of Germany and Poland, western parts of Hungary and parts of southern Italy. These data are generally associated with areas of intensive farming. An isolated anomaly in south-west Hungary is related to excessive fertiliser application, with some contribution from communal sewage, as no sewage treatment exists in the region. Nitrate data tend to correlate most closely with calcium in several areas. The isolated stream water nitrate point anomaly in central-eastern Greece is most certainly due to agricultural contamination, as are most other elevated values. In south-central Spain high nitrate values in stream water coincide very well with areas where nitrate fertiliser consumption in agriculture is very high.

From the above description it is apparent that nitrate, as a major anion, shows a distribution similar to the elemental patterns of the Major-ions group. The dependence upon climate and vegetation undoubtedly leads to the observed N-S zoning of nitrate abundances in stream water, with agricultural influences superposed on it.

A more detailed description on the chemistry of nitrate in stream water is given in Annex 1 of this volume by Ander *et al.* (2006), where the thematic interpretation of stream water chemistry is discussed (see section on anion predominance).

N - comparison between sample media

Nitrogen (nitrate) was determined only on stream water samples, so no comparison can be made between distributions in other sample media.