Introduction

Chlorine is one of the halogen elements belonging to group 17 of the periodic table, which also includes F, Br and I. It is a lithophile element with an atomic number of 17, an atomic mass of 35, five oxidation states (–1, +1, 3, 5 and 7), of which the -1 state is most common in nature, and two naturally occurring isotopes (^{35}Cl and ^{37}Cl), of which ^{35}Cl comprises 76% of the total mass.

More than 75% of the Cl in the Earth's rocks, atmosphere and hydrosphere occurs in the ocean as Cl^- ions. Its average crustal abundance is 180 mg kg^{-1} (Kaufmann 1999b). Most igneous rocks contain 100–200 mg kg^{-1}, dolomite 660 mg kg^{-1}, other sedimentary rocks 20–130 mg kg^{-1} and most metamorphic rocks 200–350 mg kg^{-1}. The Cl bearing minerals of igneous rocks include sodalite $Na_8[Al_6Si_6O_{24}]Cl_2$ and the phosphate mineral apatite $Ca_5(PO_4)_3(Cl,F,OH)$. Chlorine can substitute for hydroxide in common rock-forming minerals such as biotite and amphibole, but concentrations are generally very low and most rocks release very little Cl^- into circulating water. Chlorine can occur in the cement of some sedimentary rocks, as a consequence of the trapping of connate brine. Porous rocks that are submerged under the sea are impregnated with soluble salts containing chlorine, predominantly halite NaCl. Brines derived from halite-rich evaporitic deposits typically have Cl^- concentrations greater than 1000 mg l^{-1}; sea water contains 19,000 mg l^{-1} Cl (Hem 1992). Because of its high concentration in sea water, Cl may be enriched in marine-derived drift.

A very large proportion of the Cl released during weathering of these rocks is highly soluble in water. The chloride ion (Cl^-) is the only significant form of chlorine in natural water. The behaviour of Cl^- is described as conservative, *i.e.,* its circulation through the hydrological cycle is determined by physical rather than chemical processes. It has been termed a cyclic element, being derived from the sea, either directly or indirectly via evaporate sediments or brines, and ultimately carried back to the sea by surface run-off. It is not strongly adsorbed to mineral surfaces; it does not enter into oxidation or reduction reactions; it does not form complexes, unless its concentration is extremely high, and it forms only a few low-solubility salts. In areas where there is very little Cl derived from bedrock and overburden, the most significant sources of Cl in stream water are rain and marine aerosols. European river water concentrations average 6.9 mg l^{-1} (Wedepohl 1978).

The Cl:Br ratio is an important factor for defining different geological environments, and is dependent on the hierarchy of salt precipitation from evaporation of ocean water; it is assumed that the modern average Cl:Br ratio of approximately 300:1 has not changed significantly with time (Kaufmann 1999a):

- Cl/Br = 300, oil fluid, brine or formation water derived directly from ocean water;
- Cl/Br >300, oil fluid, brine or formation water derived from halite salt, and
- Cl/Br <300, oil fluid, brine or formation water derived from residual solutions produced by partial precipitation of halogen salts.

The concentration of chloride in surface and groundwater can be influenced by human activities, such as the application of salt for the de-icing of roads, leaching from landfill sites, discharges from sewage treatment works, and the intrusion of saline water following the pumping of fresh water from coastal aquifers. Chlorine is used in treating drinking water, swimming pools, hot tubs, *etc.*, to kill bacteria and other microorganisms. It is also a building block for polyvinyl chloride (PVC) and numerous other chemicals such as antifreeze, pesticides (DDT and chlordane), refrigerants, anti-knock compounds and industrial cleaners (carbon tetrachloride). As sodium hypochlorite, or bleach, it is widely used as a disinfectant and in bleaching.

Chloride is an essential anion and constitutes approximately 0.15% of human body weight. It is primarily found in cerebrospinal fluid and gastrointestinal secretions and is also present in small amounts within bone. It is the major anion in plasma and interstitial fluid, where it aids in the maintenance of osmotic pressure and electrolytic balance. It is also essential in maintaining the acid/base balance of body fluids. Chloride has no known toxicity, since excess chloride is excreted from the body through urine, sweat, vomit and diarrhoea. The use of diuretics, as well as

excessive diarrhoea or vomiting, can deplete the body of chloride ions resulting in metabolic alkalosis, a condition which leads to an elevated blood pH, disrupted muscle function, difficult respiration and swallowing and, on occasion, death. High levels of Cl^- in water used for irrigation have a deleterious effect on agricultural production.

Table 19 compares the median concentrations of Cl^- in the FOREGS samples and in some reference datasets.

Table 19. Median concentrations of Cl^- in the FOREGS samples and in some reference data sets.

Chloride (Cl)	*Origin – Source*	*Number of samples*	*Size fraction mm*	*Extraction*	*Median*
Crust[1)]	Upper continental	n.a.	n.a.	Total	370 mg kg^{-1}
Water	**FOREGS**	**808**	**Filtered <0.45 µm**		**8.81 (mg l^{-1})**
Water[2)]	World	n.a.	n.a.		7.8 (mg l^{-1})

[1)]Rudnick & Gao 2004, [2)]Ivanov 1996.

Cl in stream water

Chloride values in stream water range over four orders of magnitude, from 0.14 to 1077 mg l^{-1} (excluding three outliers up to 4560 mg l^{-1}) with a median value of 8.8 mg l^{-1}. Chloride data tend to correlate most closely with sodium and to a lesser extent, potassium and sulphate.

Lowest Cl values in stream water (<2.6 mg l^{-1}) are found throughout Fennoscandia and western Scotland on Precambrian Shield and Caledonian terrains, northern Spain, across the Pyrenees, over the Massif Central to south-east France on Variscan, and throughout the Alpine belt of eastern France, northern Italy, Switzerland, Austria, Slovenia and Croatia. Low values also occur over Albania and northern Greece, all on the Alpine Orogen. Some of these regions are characterised by high rainfall that might lead to dilution of stream water. Further, mountain areas are generally low in Cl, because this is where water infiltrates in the ground before much interaction with rocks has taken place.

Enhanced Cl concentrations in stream water (>36 mg l^{-1}) are encountered within a belt extending from central and eastern Britain through Belgium and western France on Variscan, the Netherlands on Quaternary deposits, northern Germany, western Poland and western Hungary associated with complex inter-bedded loessic aeolian sand, soil, till and fluvial glacial sediment. High values are also observed in the south-western rim of the Iberian Peninsula and on Sardinia on Variscan terrains, and in most parts of Italy and Sicily, as well as north-east tip of Greece on Alpine Orogen. In Italy, high chloride (as well as fluorine) is typical for stream water of volcanic areas. Elsewhere, high chloride values indicate the presence of evaporates, coalfield brines and of anthropogenic pollution with NaCl, as seen from comparison with the Na distribution. A highly anomalous value in Denmark could be related to saltwater intrusion. In southern Portugal, high chlorine is the result of slow-flowing groundwater with long residence time in marine sediments, which picks up easily dissolved ions before feeding stream water. In southern Spain, high values are related to outcrops of the Triassic Keuper facies containing evaporitic layers of gypsum and halite, and of resedimented Triassic materials during the Alpine orogeny in olisthostromic units. An isolated high Cl^- value in the Ebro River basin in northern Spain can be explained by evaporite (gypsum, halite) in Miocene sediments. Anomalous Cl^- values on the southern Mediterranean coast of Spain are probably enhanced by the warm and dry climate, evapotranspiration and rise of salinity from groundwater.

Chloride as one of the major anions in stream water correlates closely with the Major-ions pattern, which characterises the distribution of total dissolved solids in European stream water. This type of stream water reflects climatic and geographical/topographic conditions of the continent to a higher degree than its lithological composition. The other association of Cl is with sea spray and evaporates pattern, which explains

the coast related patterns by cyclic supply from the ocean, and some high areas in the Mediterranean by evaporate deposits. A clear correlation with Na can be observed for high chloride values.

A more detailed description on the chemistry of Cl 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 sections on anion predominance, and sodium and chloride ratios).

Cl comparison between sample media

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