Mg – Magnesium

Introduction

Magnesium belongs to group 2 of the periodic table, along with Be, Ca, Sr and Ba. The element has an atomic number of 12, an atomic mass of 24, one main oxidation state (+2) and three naturally occurring isotopes (^{24}Mg, ^{25}Mg and ^{26}Mg), of which ^{24}Mg is the major isotope at 79% of the total mass. Magnesium is the seventh most abundant element in the Earth's crust with a quoted average of 2.76% (Fyfe 1999), and the Mg^{2+} ion is the second most abundant cation in sea water, after Na^+. Its chemistry is intermediate between that of Be and the heavier alkali earth elements.

Magnesium is a lithophile metallic element and a major constituent of many mineral groups, including silicates, carbonates, sulphates, phosphates and borates. It forms several important minerals, including magnesite $MgCO_3$, dolomite $CaMg(CO_3)_2$, pyrope garnet $Mg_2Al_2(SiO_4)_3$ and kieserite $MgSO_4.H_2O$. It is a major component of many mafic rock-forming minerals, such as olivine, *e.g.,* forsterite Mg_2SiO_4, pyroxene, amphibole, spinel $MgAl_2O_4$, biotite mica, chlorite, serpentine, talc, and clay minerals, such as montmorillonite, as well as less common mineral groups, such as arsenates, halides, nitrates and oxalates (Wedepohl 1978).

In magmatic systems, Mg is concentrated in high temperature minerals like olivine and pyroxene, which precipitate relatively early. However, if water and oxygen fugacity reach critical limits, the precipitating phases are more likely to be amphibole or mica. Magnesium displays a steady decrease in concentration within the calc-alkali rock series, with MgO concentrations ranging from >40% in some ultramafic rock types, *e.g.,* dunite, through to <0.5% in calc-alkali rocks, such as calc-alkali rhyolite (Wedepohl 1978).

Magnesium is a significant component of phyllosilicate minerals, such as chlorite, montmorillonite and glauconite, although it is low in illite, so shale (1.5% Mg) has higher concentrations than sandstone (0.7% Mg). Magnesium carbonate minerals, commonly dolomite, are generally more soluble than Ca-carbonate and form around 30% of all carbonates. Magnesium occurs in sediments either as a solute in porewater or as an important component in the formation of late stage diagenetic chlorite and dolomite (Wedepohl 1978). The average concentration of Mg in loess is 0.68% (McLennan and Murray 1999). High Mg values indicate mafic or ultramafic rocks (in association with Cr, Ni, V, *etc.*) or calcareous rocks (with Ba, Ca and Sr).

As many Mg compounds are very soluble, Mg is highly mobile after its release by weathering, under all environmental conditions. Under the pH, redox and conductivity regimes typically found in streams, Mg is likely to be present almost exclusively as Mg^{2+}. This ion is one of the major cationic species in stream water, exceeding Na^+ and Ca^{2+} in some areas. $MgSO_4$ is more soluble than $CaSO_4$, so Mg^{2+} may be more prevalent in streams fed by sulphate- rich mine drainage, derived from the oxidation of sulphide minerals. Most limestone contains significant amounts of Mg, so streams draining limestone, and other carbonate-rich rocks, are likely to have high Mg^{2+} concentrations. The average value of Mg in river particulates is 1.2% (McLennan and Murray 1999).

Magnesium in fresh water is typically present at concentrations ranging from <10 to 50 mg l^{-1} (Hem 1992). Sea water contains approximately 1350 mg l^{-1} Mg (Hem 1992), where it is the second most common cation after sodium. The ratio of Mg:Ca is much higher in sea water (*ca.* 5.0) than a typical fresh water (*ca.* 0.5) (Wedepohl 1978). Much of the Mg^{2+} in rain is of marine origin although a small, but significant, input comes from soil dust. Adsorption on negatively charged clay-mineral surfaces may reduce the concentration of Mg^{2+} ions more than Ca^{2+} and univalent cations, since Mg^{2+} is more strongly bound to these surfaces.

Anthropogenic sources of magnesium include fertilisers and liming (Reimann and de Caritat 1998). Because of its low weight and ability to form mechanically resistant alloys, it is widely used as a structural metal in the building industry and is essential in airplane and missile construction. It is also used in flashlight photography, flares and pyrotechnics, including incendiary bombs, as well as a reducing agent in the production of pure uranium and other metals from their salts. Magnesium hydroxide (milk of magnesia), chloride, sulphate (Epsom salts) and citrate are used in medicine.

Magnesium is essential for all organisms and is not toxic under normal circumstances. Deficiencies of magnesium are much more common than problems concerned with toxicity. The adult daily requirement of magnesium is about 300 mg day^{-1}. Magnesium is a key plant nutrient and is essential for photosynthesis in plants, where it forms the active site in the chlorophyll enzyme molecule.

Table 43 compares the median concentrations of Mg in the FOREGS samples and in some reference datasets.

Table 43. Median concentrations of MgO in the FOREGS samples and in some reference data sets.

Magnesium (MgO)	*Origin – Source*	*Number of samples*	*Size fraction mm*	*Extraction*	*Median %*
Crust[1)]	Upper continental	n.a.	n.a.	Total	2.48
Subsoil	**FOREGS**	**788**	**<2.0**	**Total (XRF)**	**0.98**
Topsoil	**FOREGS**	**845**	**<2.0**	**Total (XRF)**	**0.77**
Soil[2)]	World	n.a.	n.a	Total	1.49
Water *(Mg)*	**FOREGS**	**808**	**Filtered <0.45 µm**		**6.02 (mg l^{-1})**
Water *(Mg)*[3)]	World	n.a.	n.a.		2.9 (mg l^{-1})
Stream sediment	**FOREGS**	**852**	**<0.15**	**Total (XRF)**	**1.20**
Floodplain sediment	**FOREGS**	**747**	**<2.0**	**Total (XRF)**	**1.20**

[1)]Rudnick & Gao 2004, [2)]Koljonen 1992, [3)]Ivanov 1996.

MgO in soil

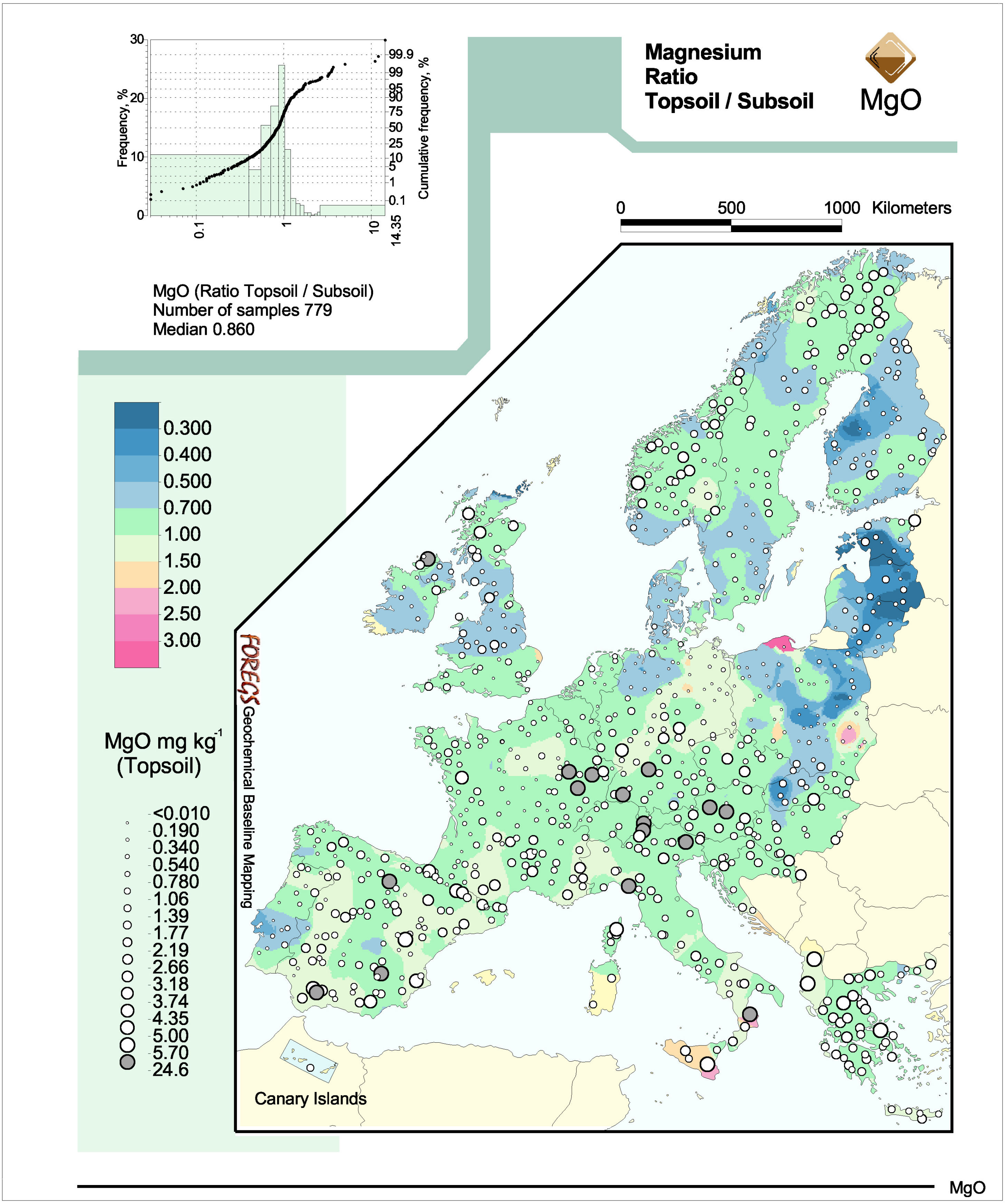
The median MgO content in subsoil is 0.98% and in topsoil 0.77%. MgO values range from <0.01 to 18.7% in subsoil and from <0.01 to 24.6% in topsoil. The average ratio topsoil/subsoil is 0.796.

Low MgO values in subsoil (<0.54) occur in southern Sweden, in the glacial drift area from the Netherlands to Poland, in central Ireland, central France, and in the western Iberian peninsula.

High MgO values (>1.66%) are observed on the subsoil map over northern Fennoscandia (greenstone belts), central Norway, Latvia and western Estonia (Devonian dolomitic clay and dolomite), a zone from western Slovakia over the Austrian Alps up to Graubünden in Switzerland, some isolated anomalies in the Vosges and Black Forest, central and northern Greece and Albania, the north-western Appenines, Corsica, the eastern Pyrenees, and the mountains of southern Spain (Jurassic dolomite in Sierra de Segura, amphibolite and amphibole gneiss in Nevado-Filábride unit of Baetic Cordillera). The distribution of MgO is geologically controlled, with greenstone belts, ophiolitic belts, and crystalline mafic rocks causing most of the anomalies, but there are also high values over some dolomitic areas (*e.g.,* Greece), and also magnesite mineralisation (Austria, Greece).

The MgO topsoil map is very similar to the subsoil map, but shows no anomaly in Latvia-Estonia (leaching of dolomite), and more enrichment in Calabria-Sicily (Italy) and southern Spain just north of Gibraltar. The ratio topsoil/subsoil is on average 0.796 for MgO, the lowest ratio except for CaO; also the correlation between topsoil and subsoil is high, 0.83. This expresses a systematic tendency of MgO to be leached during pedogenesis (Map 8).

Magnesium in both subsoil and topsoil has a weak positive correlation (>0.3) with Fe, Sc, V and Co. With Ca, there is a weak correlation in topsoils (0.32), and a very weak one (0.21) in subsoils. Magnesium has a good negative correlation with SiO_2 (-0.49 in subsoil and -0.57 in topsoil).



Map 8. Ratio of MgO in topsoil vs subsoil.

Mg in stream water

Magnesium values in stream water range over four orders of magnitude, from 0.05 to 230 mg l^{-1}, with a median value of 6.02 mg l^{-1}. Magnesium data tend to correlate with pH, conductivity, bicarbonate and calcium for most areas.

Lowest Mg values in stream water (<1.9 mg l^{-1}) are found throughout Fennoscandia, Scotland and Wales, north-west Iberian Peninsula, eastern Switzerland and over the Massif Central. The low values are predominantly associated with granitic and felsic igneous and metamorphic rocks.

Enhanced Mg concentrations in stream water (>21 mg l^{-1}) are found in the Baltic states, central-eastern Britain, southern and eastern rim of the Iberian Peninsula (dry climate with intense evapotranspiration causing concentration of ions), southern Germany, western Slovakia, Hungary and northern Croatia, Albania, parts of Greece, Sardinia, Sicily and most of continental Italy. High Mg in water is derived from dolomitic carbonate rocks in southeastern Spain, Italy with Sardinia and Sicily, Austria, and southern Germany. In Greece and Albania, and probably parts of Italy, Mg is released in stream water by weathering of ophiolite and dolomitic limestone. In south-west Spain, Triassic clastic rocks with evaporitic salt release Mg.

High Mg in stream water in Hungary and Croatia is derived from loess containing calcareous dust, deposited in the last ice age, when the region was in periglacial position, and dolomitic carbonates of the Transdanubian Range were exposed to wind erosion. Isolated high Mg anomaly in the north-eastern England is related to Carboniferous sandstone, mudstone and limestone. In Lorraine (France), the high Mg values in stream water are correlated with Sr, Br, Cl, SO_4^{2-} and are related to natural salt dissolution (Nancy area) of the Keuper salt layers (halite and anhydrite) and sewage, from past and present industrial extraction by *in situ* brining method (Nancy and Sarralbe districts).

Magnesium in stream water is distributed according to the “Major-ions” water pattern dominated primarily by exogenic factors and less by geology, and partly inversely proportional to the “REEs high-DOC” model.

A more detailed description on the chemistry of Mg 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 cation predominance).

MgO in stream sediment

The median MgO content in stream sediment is 1.20%, with a range from <0.1 to 24.5%.

The MgO distribution map shows low values in stream sediment (<0.50%) occurring in Poland, Denmark, southern Norway, south-central Sweden, most of France and southern Britain.

A highly anomalous MgO zone in stream sediment occurs over the northern and southern calcareous Alps belonging to the eastern Alps in Austria and northern Italy (upper Triassic dolomite and limestone); this is a well-known Mg-rich geochemical province with economic Mg-deposits. Further anomalies are in the ophiolite belt and on magnesian carbonate rocks (dolomitic limestone) in Albania and Greece, with occasional magnesite mineralisation. High values (>2.1%) occur in northern Fennoscandia (greenstone belts in Lapland and central Norway), the Baltic states, and in eastern Spain and Slovenia (dolomite).

MgO in stream sediment has a weak positive correlation with CaO (0.33), and a good negative correlation with SiO_2 (-0.54).

MgO in floodplain sediment

Total MgO values in floodplain sediment show a marked variation from <0.1 to 17.20%, with a median of 1.20%. About 10% of the MgO values are below the detection limit.

Low MgO values in floodplain sediment (<0.5%) are found over a variable lithology in southernmost Norway, central Sweden, the glacial drift covered plain extending from northern Germany through Poland to the Baltic countries, over most parts of Britain and Ireland, northern France and the alluvial Garonne river basin.

High MgO values in floodplain sediment (>2.2%) occur over the greenstone rocks of central and northern Norway, the greenstone belt in north-east Finland, Stockholm region in Sweden, southern Spain with dolomitic limestone, dolomitic marble and ophiolites. There are two extensive belts with very high to highly anomalous MgO values (2.68 to 17.2%) in floodplain sediments. The first extending from Bavaria in south Germany into the Alpine System rocks covering most of Switzerland, almost the whole of Austria and northern Italy down to Slovenia, an area with variable lithology, including mafic-ultramafic rocks, dolomitic limestone and magnesite mineralisation (*e.g.,* Hochfilzen, Radentheim and Breitenau mines in Austria), and the second starting from Albania and into Greece with ophiolite rocks, dolomitic limestone, and magnesite mineralisation in many parts of Greece (*e.g.,* Mantoudi-Limni, northern Euboea island). In Hungary, dolomitic carbonates of the Transdanubian Range were exposed and eroded by wind during the last ice age; wind-blown dolomitic particles accumulated in sands and loess, contributing to high Mg contents in floodplain sediments. Total MgO content in this loess ranges from 1.66 to 4.76% (Galovic 2005).

The highest MgO anomalous floodplain sediment samples are in northern Euboea, Greece (17.2%), related to mafic-ultramafic rocks and magnesite mineralisation, and Austria (15.3 and 13%), which are associated with both magnesite mineralisation and dolomite of the northern calcareous Alps. The point MgO anomalies in southern Italy (8.9 and 12%) are related to alkaline volcanics and dolomitic limestone.

The total MgO spatial distribution in floodplain sediment and the element associations suggest that it is directly related to the underlying lithology, and mineralisation.

Magnesium in floodplain sediment shows a good correlation with Ni, and a weak, but significant, correlation with Ca, Cr and Co. Magnesium has a good negative correlation with SiO_2 (-0.52).

In conclusion, mafic and ultramafic lithologies, and ophiolite masses, together with their metamorphic equivalents (greenstone) and mineralisation, show the highest MgO concentrations in floodplain sediment. Greece and Albania appear to represent a geochemical province with respect to MgO, but also Cr, Ni, Co, Cu and Mn. The distribution map of total MgO in floodplain sediment shows, therefore, the geochemical differences of the geological substratum and mineralised areas quite well, and no distinguishable influences from anthropogenic activities are recognised.

Mg comparison between sample media

Patterns in Mg distribution between all solid sample media are broadly similar, with highest concentrations in northern Fennoscandia, western Norway, over the ophiolite belt and dolomitic limestone of Greece and Albania, and in an area throughout northern Italy and western Austria and Slovenia, and lowest concentrations throughout the Quaternary sediments of northern mainland Europe and parts of central and eastern France. The main differences in solid sample media occur throughout parts of the Baltic states, in which Mg concentrations are relatively high in subsoil and stream sediment (dolomite), but much lower in topsoil and floodplain sediment (leaching of dolomite).

A boxplot comparing MgO variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 27.

Stream water data show some similarities to the solid sample media, although Mg values are enhanced in the southern and eastern Iberian Peninsula, southern Italy, throughout the Pannonian basin of Hungary, in the Baltic states (possibly weathering effects) and central-eastern Britain (magnesian limestone), and significantly depleted throughout all of Fennoscandia and Scotland (limited weathering of relatively newly exposed silicate minerals) and to the north-west of the Iberian Peninsula (possibly dilution by rainwater).

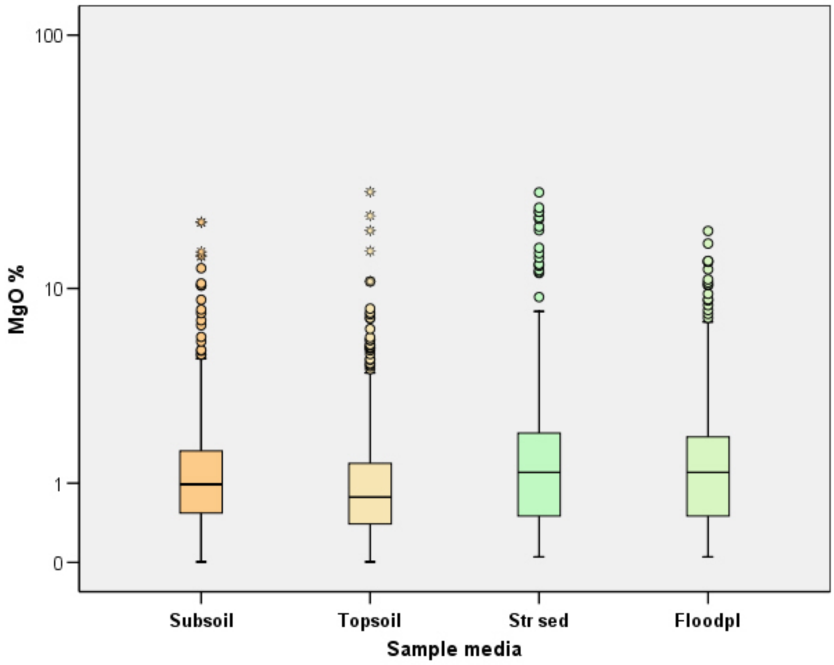


Figure 27. Boxplot comparison of MgO variation in subsoil, topsoil, stream sediment and floodplain sediment.