C – Carbon

Introduction

Carbon is a group 14 element of the periodic table, along with Si, Ge, Sn and Pb. The element has an atomic number of 6, an atomic mass of 12, two main oxidation states (-4 and +4) and two naturally occurring isotopes (^{12}C and ^{13}C), of which ^{12}C is the most abundant at 99%. Carbon is unique because of the vast number and variety of compounds it can form. In combination with hydrogen, oxygen, nitrogen and other elements, it forms a very large number of organic compounds, as well as inorganic compounds such as bicarbonate (see section on alkalinity).

Carbon is a siderophile element, but it has also lithophile and atmophile properties (Long 1999). The two most abundant natural sources of organic carbon found on Earth are coal and kerogen, accounting for over 95% of all organic carbon (Wedepohl 1978). Kerogen is a diagenetically formed, highly polymerised, complex organic material that serves as a major source of crude oil (Abelson 1963). Coal is fossilised plant matter and the end product of the coalification process, in which plant matter is transformed through changes in pressure and heat. Peat and humic substances are formed during the first stages of coalification (Karwail 1966, Van Krevelen 1961).

The terrestrial biosphere and soil represent a large pool of carbon that is relatively easily altered by humans or by climate change. Carbon storage in the terrestrial biosphere and soil is highly inhomogeneous in space, ranging from <0.5 kg m^{-2} in poor desert systems and rock or ice covered areas, to about 30 kg m^{-2} in tropical forests (Bawkin 1999). Approximately one-third of terrestrial biosphere carbon is contained in plant biomass, and the remainder is dead and decomposing plant material in soil. Forest and woodland ecosystems hold about 60% of carbon contained in the terrestrial biosphere, including 40% of the soil carbon and 90% of plant biomass (Schlesinger 1991).

Dissolved organic carbon (DOC) is present in all natural water. Hem (1992) gives the average DOC concentration of river water as 5.75 mg l^{-1}, with rivers of the subarctic zone containing an average of 19 mg l^{-1}, tropical regions 6 mg l^{-1} and temperate and semiarid or arid zones 3 mg l^{-1}. The total organic carbon transported to the ocean by rivers is estimated to be 1 to 2% of the primary production (photosynthesis) of organic carbon. DOC concentrations in groundwater are usually less than those in surface water.

Most DOC is derived from naturally occurring organic materials formed from the degradation of biological materials. These are complex mixtures of heterogeneous macromolecules that are virtually impossible to separate into their component materials. In many water bodies, particularly highly coloured upland water, the majority of the DOC is present in the form of high molecular weight humic and fulvic acids, but smaller molecular weight carbohydrates and amino acids may also be present. Humic substances have properties typical of weak electrolytes and carry weakly acidic functional groups such as carboxylic or phenolic acids; fulvic acids may contain hydroxyl aromatic methoxy carboxylic acids. In lowland surface water, which suffers from high turbidity rather than colour, natural organic materials are more likely to be in the form of lower molecular weight, hydrophilic materials.

Although the amount of DOC in natural water is small compared with inorganic solutes, naturally occurring organic materials are very effective complexing agents for metals, such as Al, Cu, Pb, Zn and Cd, and influence the solubility and transport of these metals. Natural organic materials also participate in redox reactions and provide substrates for microbial growth.

High DOC concentrations in groundwater are likely to be characteristic of leachate from landfill sites and, in some water types, organic solutes can be major constituents. For example, short chain aliphatic acid anions, such as acetate, proprionate and butyrate, can occur in water associated with petroleum contamination. Halogenated organics, *e.g.,* PCBs and pesticides, such as DDT, are among the more stable species in water. The chemical industries of the developed nations produce huge quantities of synthetic organic carbon materials, waste and by-products, many of which do not occur naturally. These products are widely dispersed into the hydrosphere during production, end-use and waste disposal.

Many synthetic organic carbon chemicals found in natural water are harmful or potentially harmful; some are known carcinogens. Some naturally occurring DOC species, especially humic and fulvic acids, can complex with other toxic metals and thus reduce bioaccessibility.

Table 15 compares the median concentrations of C in the FOREGS samples and in some reference datasets.

Table 15. Median concentrations of C in the FOREGS samples and in some reference data sets.

Carbon (C)	*Origin – Source*	*Number of samples*	*Size fraction mm*	*Extraction*	*Median %*
Subsoil *(TOC)*	**FOREGS**	**763**	**<2.0**	LECO	**0.40**
Topsoil *(TOC)*	**FOREGS**	**819**	**<2.0**	LECO	**1.73**
Soil, C-horizon[1)]	Barents region		<2.0	Thermal conductivity detector	0.15
Water *(DOC)*	**FOREGS**	**803**	**Filtered <0.45 µm**		**4.99 (mg l^{-1})**
Stream sediment *(TOC)*	**FOREGS**	**847**	**<0.15**	Pyrolytic determination after HNO_3 digestion	**1.71**
Floodplain sediment *(TOC)*	**FOREGS**	**750**	**<2.0**	Pyrolytic determination after HNO_3 digestion	**1.39**
Stream sediment[2)]	Canada	50 684	<0.18	Total (L.O.I.)	6.9

[1)]Salminen *et al.* 2004, [2)]Garret 2006.

Total organic carbon (TOC) in soil

The FOREGS field manual prescribes separate collection of the organic layer (forest litter or peat) before sampling the topsoil (Salminen, Tarvainen *et al.* 1998). This humus sample (and not the mineral soil) should account for the representativity of the geochemistry of the pure organic layer. This layer is well developed in northern and north-central Europe, but less widespread elsewhere.

The FOREGS soil analyses show that most soil samples contain some organic carbon, and a few even have exceptional (>20%) total organic carbon (TOC) content. Organic matter in the mineral soil layer (topsoil sample) is the result of normal soil forming processes, and TOC content increases with soil maturation. Soil organic matter is usually well decomposed and is distributed as fine particles or as coatings on the mineral particles; in any case, it is intimately associated with the mineral fraction. It can be assumed, therefore, that the TOC distribution maps for soil generally reflect the regional TOC content irrespective of soil type.

The measured Total Organic Carbon content in the FOREGS samples ranges in subsoil from 0.00 to 48.5% with a median at 0.401%, and in topsoils from 0.07 to 46.6% with a median at 1.73% TOC. The average ratio topsoil/subsoil is 2.585 for TOC, which, although very high, is quite natural.

Low TOC values (<0.17%) in subsoil occur in Sweden, Finland, most of Poland and the Baltic States, and north-eastern Greece where soil is generally young. It should be noted that only residual minerogenic soil was selected for sampling in the FOREGS mapping programme. Other soil types, such as biogenic histosols, which are common in northern Europe, but were not sampled, have high content of TOC.

The subsoil TOC distribution map shows high values (>0.84%) in highland areas in Scotland, northern Ireland, western England, the Cantabrian Mountains in northern Spain, the Alps, and the Norwegian Caledonides. Isolated high values also occur in the Netherlands, Denmark, eastern Germany, south-eastern Spain, Slovenia, southern Italy, and Kefallonia (Greece).

The topsoil TOC distribution pattern shows higher contents in Britain and Ireland, the Netherlands, the eastern Alps, northern Portugal and Slovakia, in addition to scattered point anomalies elsewhere. The resulting high values are frequently associated with wet climates and/or mountainous areas with vegetation cover.

The highest TOC content in soil was measured in a sample from north-western England (Lancashire), where the subsoil contains 48.5%

TOC, and the topsoil sample 46.6% TOC. Some other high values are in a topsoil sample in south-central Switzerland containing 39.35% TOC (no subsoil sampled in this location); a topsoil sample in northern Ireland with 36.27% TOC over a subsoil containing 9.24% TOC; a topsoil sample in central Norway with 26.19% TOC over a subsoil containing 9.59% TOC; and in the Netherlands a subsoil with 23.1%, while the overlying topsoil contains 16.11% TOC.

In subsoil, TOC has a good positive correlation with S and Hg, and a weak correlation with I; there is also a weak negative correlation with Si.

In topsoil, TOC shows a strong correlation (>0.6) with S, a good correlation with Hg, a weak correlation with Pb, I and P_2O_5, and a weak negative one with Si.

The association of sulphur with TOC, and the fact that a high TOC content (making TOC a major constituent of soil) is logically compensated by smaller amounts of silica and other elements, makes it necessary to take TOC into account when interpreting soil geochemical data.

Dissolved organic carbon (DOC) in stream water

Dissolved organic carbon (DOC) concentrations in stream water range over two orders of magnitude, from <0.5 to 72 mg l^{-1}, with a median value of 5.00 mg l^{-1}. The distribution patterns of TOC were found to be characteristic for low mineralisation acid stream water, and TOC is associated with the REE pattern and partly also with those of Alkaline rocks, Mn-Fe and Felsic elemental associations in stream water.

Lowest DOC values in stream water (<2 mg l^{-1}) are found throughout southern mainland Europe and the Mediterranean, and are related to the more arid climate, but also to mountain climates (*e.g.,* the Alps). Norway has low DOC levels compared to the rest of Fennoscandia, particularly along its west coast; this could be a dilution effect due to heavy rains and rapid water flow in mountain areas.

Highest DOC values in stream water (>14.5 mg l^{-1}) are generally found in northern Europe, especially throughout Ireland, southern Sweden and Finland, but not within Norway and England. The high levels are associated with humic substances derived from flat, boggy topographies, especially in Finland, northern Poland, northern coastal Germany, Denmark and Ireland. An exception to this general trend are the high DOC concentrations found in Sardinia, which may be derived, especially in the south, from swampy areas. In the lowland of the Charente river and the other rivers on the western coast of Brittany (France), both peaty Quaternary swamps and manure sludge contribute to the DOC of the present-day rivers and sediments.

The DOC trends in stream water closely resemble the distribution observed in stream sediment, and to a lesser extent floodplain sediments throughout southern Europe, except in Sardinia. However, distribution patterns of highest DOC concentrations in Ireland, Fennoscandia and the north of mainland Europe are opposite to those observed in subsoil and, to a lesser extent, topsoil. This is probably a result of the sampling strategy in northern countries. TOC maps for subsoil and topsoil represent the distribution of organic carbon in residual soil selected for the FOREGS mapping project. Other soil types, such as biogenic soil, are far more important sources of organic carbon in the surface environment of northern Europe.

A more detailed description on the influence of DOC on the speciation of metals 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 Fe and Cu speciation).

Total organic carbon in stream sediment

The median total organic carbon (TOC) content in stream sediment is 1.71%, and the range of values varies from 0.06 to 34.5%.

Low TOC values in stream sediment (<0.84%) are found in the whole Mediterranean area (dry climate) except Corsica and Sardinia; also in the Alps, the Netherlands, and central Finland.

Stream sediment shows high TOC values (>2.88%) in a belt from Denmark over eastern Germany to the western Czech Republic, in northern Portugal and adjacent parts of north-west Spain, Corsica, the south of Sardinia, the Dalmatian coast of Croatia, western and north-west Ireland (bogs), northern Scotland (bogs), northern and south-eastern England, southern Norway, south-east, central and northern Sweden, south-east and northern Finland, Lithuania, eastern Poland, the Loire basin and southern Brittany in France. Isolated TOC anomalies occur in northern Netherlands, eastern Poland, and northern Norway.

TOC in stream sediment has a good positive correlation with sulphur (0.40) and phosphate (0.46).

Total organic carbon (TOC) in floodplain sediment

Total organic carbon (TOC) values in floodplain sediment vary from 0.08 to 24.3%, with a median of 1.40%.

Low TOC contents in floodplain sediment (<0.79%) are distributed on the continent over three regions: in Fennoscandia, Poland, and in the Mediterranean countries. In Fennoscandia, the low values occur in western, central and northern Norway and adjacent parts of Sweden, northern Finland, and a small part of eastern and southern Finland. Low TOC values are found in the central and south-eastern parts of Poland. In the Mediterranean region, low TOC values occur over central, eastern and southern Spain, and lower part of the Rhône valley in France, most of southern half of Italy and Sardinia, all of Sicily; in Albania, and part of central Greece and Crete.

High TOC values in floodplain sediment (>2.5%) are found in the central and northern parts of the continent, *i.e.,* in south-western Norway, the Oslo rift area, and southernmost Sweden, south-central Finland, the whole of Estonia and Latvia, and parts of Lithuania, north-western Poland and northern and south-eastern parts of Germany. High TOC values cover most of Ireland, western Scotland and most of central England; northern part of Portugal, north-eastern part of the Paris basin, the lower Charente river basin in France; parts of the Czech Republic, part of western Slovakia, central Hungary, eastern and coastal Croatia and Slovenia.

Highly anomalous TOC values in floodplain sediment occur in Latvia (24.3%), south-central Slovenia (22.4%), north-west Germany (18.5%), north-east Germany (17.0%), and Estonia (17.2 and 16.6%). Point anomalous TOC values are found in the Kiruna area of northern Sweden (12.9%), to the east of Lublin in central-eastern Poland (14.5%), and in the Linares area of south-central Spain (14.08%).

Total Organic Carbon in floodplain sediment shows a good positive correlation with P_2O_5 (0.41), see scattergram (Figure 6), and with S (0.52), see scattergram (Figure 7).

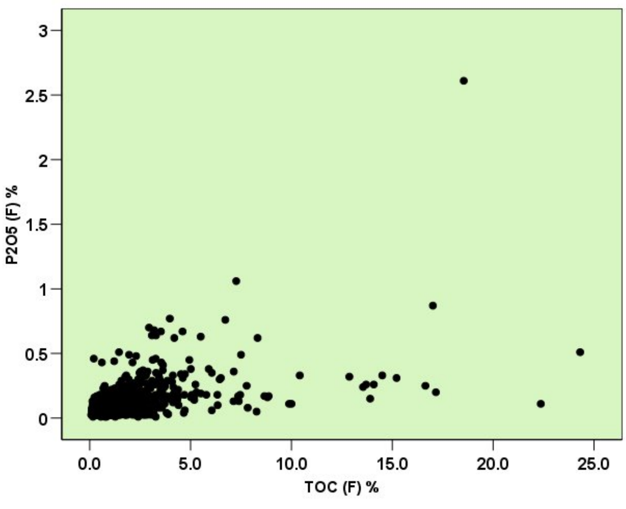

Figure 6. Scattergram of TOC and P_2O_5 values in floodplain sediment.

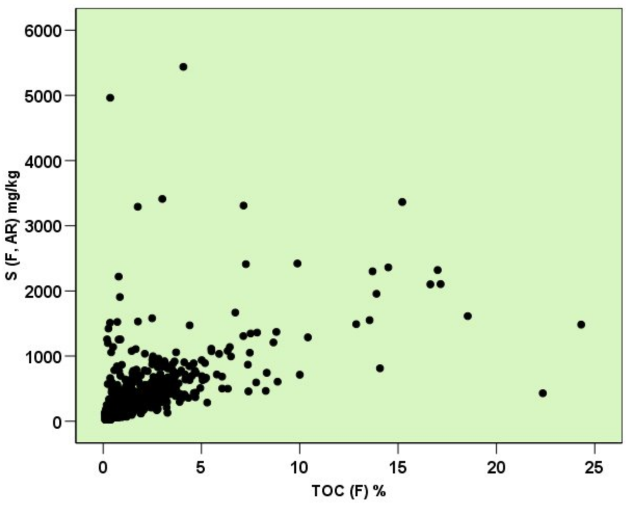

Figure 7. Scattergram of TOC and S values in floodplain sediment.

In conclusion, low TOC values in floodplain sediment are generally found in areas with young undeveloped soil, such as the Mediterranean region, mountainous areas and intensively glaciated areas in Scandinavia. Whereas high TOC values in floodplain sediment occur in areas with developed soil or peat bogs, such as Ireland, Britain, France, Germany and the Baltic states.

Organic carbon comparison between sample media

Patterns in subsoil and topsoil distribution are similar in parts, although topsoil is generally enriched compared to subsoil by a factor of 2.6. There are some significant differences; in particular, topsoil is enhanced relative to subsoil in Ireland, northern Netherlands, coastal Norway, Slovakia, southern France and parts of Spain. There are major differences between sediment and soil TOC distribution. In particular, sediments are significantly depleted in TOC, especially compared to topsoil, around the whole of the Mediterranean area, except Corsica. Stream sediment in northern Britain and Ireland, the eastern Alps in Italy, Switzerland and southern Germany, the Netherlands and adjacent northern Germany are also depleted relative to soil. Higher values are observed in stream sediment compared to topsoil in southern Norway, parts of Finland, Denmark, south-east England and Lithuania, reflecting the low TOC content of the sampled residual soil, in contrast to the higher TOC content in biogenic soil that was not sampled in the framework of this FOREGS survey, but which contributes to a generally high content of organic matter in the environment of northern Europe. Soluble organic matter is taken out of the soil in humid climate conditions, and also washed out of organic matter from soil in hilly areas with subsequent redeposition in incised streams. Floodplain sediment values show similar patterns to stream sediment, although higher TOC contents occurs in Latvia and Estonia, central Norway, Ireland, northern France, northern Germany and parts of Hungary. A boxplot comparing TOC variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 8.

DOC in stream water most closely resembles the distribution observed in stream, and to a lesser extent floodplain, sediments throughout southern Europe, especially the Mediterranean areas, with the exception of Sardinia. However, highest DOC concentrations are observed throughout Ireland, southern Sweden, most of southern and central Finland and the northern area of mainland Europe,

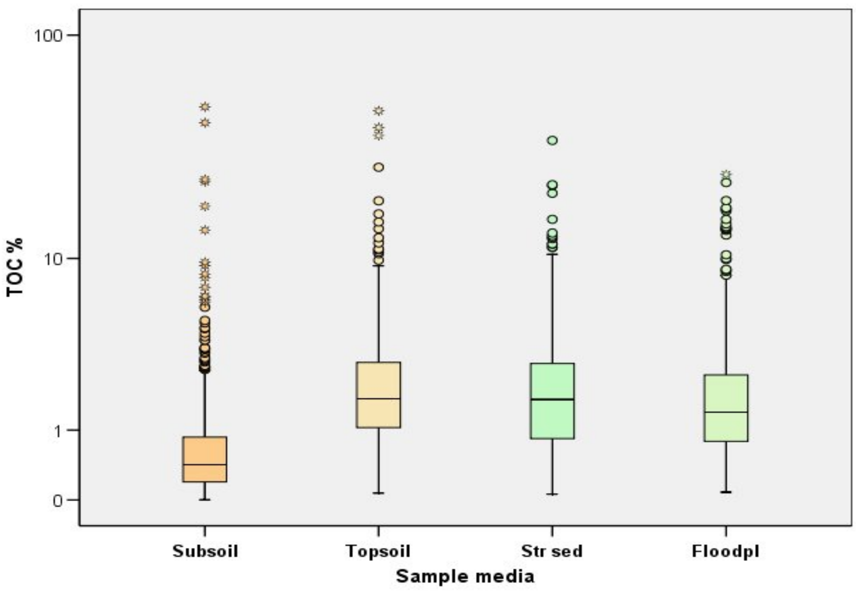

Figure 8. Boxplot comparison of TOC variation in subsoil, topsoil, stream sediment and floodplain sediment.

in a belt extending from the Netherlands, Denmark, northern Germany and Poland to the Baltic states. This distribution pattern is opposite to that observed in the minerogenic residual subsoil and, to a lesser extent, topsoil. A better correspondence between soil TOC and stream water DOC distribution could have been expected if biogenic soil types had been included in the soil-sampling programme.