# CHEMICAL AND ISOTOPIC CHARACTERIZATION OF PARTICULATE ORGANIC MATTER

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Estuaries form an interface between marine and fluviatile water masses where riverine water is flowing into the sea and complex processes of mixing of water masses, deposition and resuspension of particulate matter and production and mineralization of organic matter take place. A better understanding of these processes is important for acquiring insight in the carbon flux from land to ocean.

Particulate Organic Matter (POM) in estuaries is a mixture of terrestrial, fluviatile and marine components, consisting of phytoplankton cells, organic debris and eroded material from soils, peats and sediments. A distinction between marine, fluviatile and terrestrial originated components can be made based on their different stable carbon isotope ratios. The material can also be characterized by radiocarbon dating as fresh phytoplankton is distinguished from eroded material by its lower $^{14}C$ age. The $^{14}C$ activity is measured using Accelerator Mass Spectrometry (AMS), a technique that enables the measurement of much smaller samples than by conventional methods because not the radioactive decay is measured but the $^{14}C$ and $^{12}C$ atoms are directly counted based on mass spectrometry principles.

Besides the isotopic signature also the molecular characterization could give information about the origin and history of organic matter. We primarily use Pyrolysis-GC-MS to study the composition and structure of the bulk samples and non-volatile fractions while more volatile components are analyzed by means of GC-MS.

*Washington coast*

Three samples of recent sediments from the shelf and slope west of the state Washington, USA, were separated in hydrodynamically sorted size fractions. All three samples showed different patterns for $\delta^{13}C$ and $^{14}a$ of the fractions. In the sample closest to the coast $^{14}a$ decreased with increasing particle size, while in the more seaward sample $^{14}a$ increased with increasing sample size. This can be explained assuming that terrestrial OM consists mainly of eroded material which is older than marine OM. Coarse particles from the river settle close to the coast, thus giving a low $^{14}a$ in the coarser fractions in the sediment, while fine terrestrial particles can be transported more far off shore, thus giving relative low $^{14}a$ values in the finer fractions of the more off shore sample.

*North Sea*

Four suspended matter samples from a sampling station 10 miles from the coast of the Netherlands taken in the different seasons of 1994 were analyzed. $^{14}a$ values were high in spring and summer, caused by phytoplankton blooms. In winter and autumn the $^{14}a$ value was much lower, indicating that the fresh organic material almost disappeared from the water column or was heavily diluted with old organic material. $\delta^{13}C$ values are were between –17 and –19‰ in spring and summer, values typical for phytoplankton, and ca. –23‰ in winter.

*Ems-Dollard*

**1. Time series suspended matter**

Of suspended matter samples taken every three months for two years both bulk and isolated chemical fractions were analyzed. The spring phytoplankton bloom caused an increase in the $^{14}a$ value of suspended matter in spring, which in 1993 was paralleled by an increase in the $\delta^{13}C$. Hot water extracts, consisting mainly of carbohydrates and some protein, and hydrochloric acid hydrolysates, consisting mainly of amino acids, have much higher $^{14}a$ values than the bulk. The residues after hot water extraction, HCl hydrolysis, lipid extraction and saponification have much lower values. Lipids, saponification extracts and the final residue have the same $\delta^{13}C$ values for all the samples.

**2. Size fractions**

A sample of surface sediment was fractionated by sieving and settling. There is a large difference in $^{14}a$ between fractions finer and coarser than 20 μm (ca. 80 pMC and 50 pMC respectively). The organic material in the coarse fractions originates from eroded old deposits. It could not be determined with certainty if these were terrestrial or marine. The OM in the finer fractions probably consists of marine, terrestrial and locally produced material.