Source apportionment of organic matter by isotope analysis, AMS PMF and HNMR techniques

D. Ceburnis[1]* J. Ovadnevaite[1], A. Garbaras[2], S. Szidat[3] M. Rinaldi[4], S. Decesari[4], K.E. Yttri[5], V. Remeikis[2], M.C. Facchini[4] and C.D. O'Dowd[1]

[1]School of Physics and Centre for Climate and Air Pollution Studies, Ryan Institute, National University of Ireland Galway, Galway, Ireland
(*correspondence: darius.ceburnis@nuigalway.ie)
[2]Center for Physical Sciences and Technology, Institute of Physics, Vilnius, Lithuania
[3]Department of Chemistry and Biochemistry & Oeschger Centre for Climate Change Research, University of Berne, Berne, Switzerland
[4]Institute of Atmospheric Sciences and Climate, National Research Council, Bologna, Italy
[5]Norwegian Institute for Air Research, Kjeller, Norway

Particulate carbonaceous matter (PCM) is a significant contributor to ambient particulate matter originating from intervening sources which contribution is difficult to resolve due to chemical complexity of PCM and often internal mixture of aerosol particles.

Carbon isotope analysis of stable and radioactive carbon offers a method for quantitative source apportionment of three principal sources of PCM due to their unique isotopic signatures: i.e. marine, continental (non-fossil) and fossil fuel sources [1] while additional specific tracers will allow splitting into more specific sources or primary and secondary sources [2]. AMS PMF analysis allows splitting into PCM property specific sources based on degree of oxigenation and fragmentation markers of OM. HNMR factor analysis is based on common chemical structures – aromatic, aliphatic, mono, di-acids - arising from typical sources.

All three methods were applied to resolve PCM sources over the Northeast Atlantic ocean during common sampling periods demonstrating their convergence on sources and suggesting a more reliable albeit complex approach to source apportionment.

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An absorption method for porewater characterization in low-permeability sedimentary rocks

Magda Celejewski* and Tom Al

University of New Brunswick, Earth Sciences
*(correspondence: m.celejewski@unb.ca tal@unb.ca)

Determination of porewater geochemistry in low-permeability rocks is challenging due to small fluid volumes and the difficulty of extracting representative samples. Several porewater extraction techniques are available, but the ability of each to provide representative samples is suspect. The objectives of this study are to develop a method of extracting a representative sample of *in situ* porewater from low-permeability rocks using absorption into a cellulosic membrane, and to quantify porewater solute concentrations.

The feasibility of porewater extraction using absorption into cellulosic membranes has been demonstrated in trials with shale drill cores. Solute mass is measured with ICP-MS and water-content is measured with near infrared (NIR) spectrometry which together provide a measure of solute concentrations.

Interactions between the membrane and porewater solutes were investigated by assessing preferential adsorption of solutes to the membrane and the reversibility of solute leaching. The NIR spectrometer was calibrated to account for the influence of dissolved salt mass on the vibrational energies of H-O bonds in water. The method was tested by adding a known mass of synthetic porewater to membranes, and comparing the known solute concentrations to those determined from the leachable solute mass and the measured water-content.

Experimental results indicate that preferential adsorption of porewater solutes (Na, Cl, Mg, Ca, K, Sr, and Br) to the cellulosic membrane is statistically insignificant and that solutes are reversibly leachable. The relative error for NIR water-content based on the 95% confidence limits ranges from 2 to 7%. The relative difference in solute concentration between the known values and those calculated from solute-mass and water-content data range from 0 to 17%. The greatest relative differences occur when the measured water-content is very low and near the NIR detection limit.

Work to date has demonstrated that porewater can be extracted from low-permeability rock samples, and porewater solute concentration determinations are possible.

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