## Marine organic aerosol: Characterization by proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR)

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The water soluble and insoluble organic fraction of marine aerosols, collected under strict clean marine sector conditions, in the framework of the EU Project MAP, has been analyzed by proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR). Samples have been collected during a one-year-long sampling campaign at Mace Head (Ireand), covering the year 2006, and during a cruise in the East North Atlantic Ocean, that took place between June and July 2006.

The composition of water soluble organic carbon (WSOC) was characterized by  ${}^{1}H$  NMR analysis in D<sub>2</sub>O solution, while the water insoluble fraction (WIOC), mainly of primary origin [1], by a novel 1H NMR method in deuterated trifluoroacetic acid solution.

The <sup>1</sup>H NMR analysis of WSOC samples showed that during the spring-summer period the organic composition was characterized by a large contribution from methanesulphonate (MSA), associated with two additional components: a) one from nitrogen-containing species (mainly alkylammonium ions), and b) another from oxygenated compounds (mainly short chain carboxylic acids and polyols, possibly including carbohydrates). The <sup>1</sup>H NMR analysis highlighted also the different distribution of S-containing, N-containing and oxygenated compounds between different seasons and between fine and coarse aerosol particles. The main features of marine aerosol WSOC resulted compatible with a secondary origin.

The NMR spectrum of WIOC showed, instead, long chain aliphatic compounds as major components, similar to the insoluble organic compounds of biological origin found in laboratory-produced sea spray particles and described in Facchini *et al.* [1].

[1] Facchini et al. (2008) Environ. Sci. & Technol. 42, 9116-9121.

## Are glacials (interglacial) in the easternmost Pacific Ocean drier (wetter) during the last 300 000 years?

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How precipitation patterns on the western area of South America and Central America behaved according to high latitude glaciations and deglaciations is still not well known. Eastern equatorial Pacific (EEP) sedimentary records of past sea surface temperatures (SSTs), productivity and water column stratification have been interpreted as El Nino-like, La Nina-like, or as simply a oceanographic response linked to high latitude climate during the ice ages. In this study we analyze organic and inorganic sediment composition of marine sediments from ODP Site 1239, located 120 km off Ecuadorian coast, in order to reconstruct climatic changes in western tropical South America and EEP during the western tropical South America and EEP during the glacial/interglacial climate variability of the last 300 000 years.

Alkenones derived-SST showed a difference of ~3°C between the last glacial maximum and the Holocene and ~2°C between termination II and the Eemian. The patterns of siliciclastic elements (Fe, Ti, Al) input, measured by X-Ray fluorescence (XRF) scanning, and SST in the eastern tropical and subtropical Pacific reveal a generally good correlation with the 100-kyr-cycles. During this time-span, maxima in siliciclastic elements deposition correspond to inter-glacials, suggesting higher terrigenous input and thus increased tropical precipitation during warm-phases. Higher input of terrigenous material is also supported by terrestrial plant biomarker abundances (i.e. long-chain [C25 to C33] n-alkanes). Modern rainfall changes over the coast of Ecuador are closely coupled to offshore SSTs and intertropical convergence zone (ITCZ) seasonal migration. We suggest a strong link between EEP atmosphere and high latitude climate, expressed as latitudinal migrations of the ITCZ. Then during ice-ages, hydrological deficit in the coastal area of Ecuador might respond to shifts on the mean annual position of the ITCZ; while during interglacial times, the ITCZ had a similar spatial distribution to the one it has today.