Copper addition by organic matter degradation in the freshwater reaches of a turbid estuary (Gironde Estuary, France)

M. MASSON[1], G. BLANC[1], J. SCHÄFER[1], E. PARLANTI[2], P. LE COUSTUMER[3] AND A. DABRIN[1]

[1]University Bordeaux1, UMR 5805 EPOC, Géochimie et Ecotoxicologie des Métaux dans les Systèmes Aquatiques (GEMA), France (m.masson@epoc.u-bordeaux1.fr; g.blanc@epoc.u-bordeaux1.fr)

[2]University Bordeaux1, UMR 5472, Physico et Toxico Chimie des Systèmes Naturels (LPTC), France

[3]University Bordeaux1, Géosciences HYdrosciences MAtériaux et Construction (GHYMAC), France

The Gironde Estuary is a macrotidal estuary with a permanent maximum turbidity zone (MTZ) that moves upstream and downstream depending on hydrologic conditions. In 2004, monthly samples have been conducted in the freshwater reaches of the estuary (from the limit of the tidal zone to the beginning of the salinity gradient). In May and September 2005, longitudinal profiles of surface water have been sampled in the freshwater reaches. Additionally, sampling was carried out in the salinity gradient of the estuary in May 2005. Dissolved Cu (<0.2 µm and <0.02 µm) concentrations and C18-Sep-Pak extracted metal-organic complex fractions were analysed. The organic matter (OM) was quantified by measuring dissolved and particulate organic carbon, the dissolved OM was then characterized using 3D-fluorescence and transmission electronic microscopy.

The presence of the MTZ in the freshwater reaches of the estuary induces significant Cu addition, mainly in the "truly" dissolved phase (<0.02 µm). In addition, major transformations of OM (e.g. humification index) were observed in the MTZ which suggests that degradation of fluvial OM plays a strong role in Cu addition. In 2004, dissolved Cu addition (~5 $t.a^{-1}$) represented ~25% of the annual dissolved Cu fluxes entering into the estuary (~21 $t.a^{-1}$). Copper addition occurred mainly in the "truly" dissolved (<0.02 µm) phase, increasing fluxes of hydrophobic (C18-extracted) metal-organic Cu complexes.

Experimental simulations of freshwater inputs into the MTZ were performed by mixing river water with different concentrations of MTZ particles. Important and rapid (inferior to tidal period) Cu desorption followed pseudo-second order kinetics and depended on particle concentration. The amount of Cu desorbed (q_e) represented ~40% and ~2% for particle concentrations of 20 $mg.l^{-1}$ and 2000 $mg.l^{-1}$, respectively. The relationship between Cu desorption and particle concentration can be described as follows: log (Cu) = a*log(MES) + b. The coefficients a and b obtained for both, the experimentation and in-situ observations were found to be similar. This supports the hypothesis that Cu addition is closely related to particulate OM degradation in highly turbid estuaries.

Origin, migration, fate and impact of hydrocarbon gases from mud structures in the Nile deep sea fan (eastern Mediterranean)

V. MASTALERZ[1], G. J. DE LANGE[1], A DÄHLMANN[1], T. FESEKER[2] AND THE NAUTINIL, THE MIMES, AND THE BIONIL SCIENTIFIC PARTIES

[1]Faculty of Geosciences, Department of Earth Sciences, Utrecht University, P.O. Box 80021, 3538 TA Utrecht, The Netherlands (v.mastalerz@geo.uu.nl)

[2]Ifremer, Géosciences Marines, B.P. 70, 29280 Plouzané, France (Tomas.Feseker@ifremer.fr)

At all investigated mud volcanoes in the Nile deep sea fan, not only methane but also heavier hydrocarbons have been measured in the sediment column. At Isis and Amon MV's the origin of CH_4 is mainly thermogenic with variable microbial contribution. However, in regards to the stable carbon isotopic composition of the heavier hydrocarbons, two distinct thermal source are found for Isis and Amon MV's.

Gas advection occurs mainly at the centre of the mud structures, while at off centre sites. Moreover, another important process occurring at those mud volcanoes is a downward flow of seawater following each gas expulsion, as indicated by the compositional and isotopic signature of the pore water indicating a pure seawater signature within the upper sediment column.

In the upper sediment section, anaerobic oxidation of methane occurs within the Sulfate-Methane Transition Zone (SMTZ). In addition, major shifts in the $\delta^{13}C$ and δD of propane and *n*-butane have been observed in the upper 20 cm of the sediment column. This indicates that these hydrocarbons are also efficient terminal electron donors for sulfate reducing bacteria.

Finally, and despite that microbial filter, enhanced fluxes of hydrocarbons are encountered in the water column, with up to several tens of µmol/L. These gas plumes can extend to several hundreds of meter up in the water column and, for the shallowest mud structures, can even reach the sea surface.