Chemical characterisation of the organic fraction of PM for an urban, rural and remote site of the North of Italy

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PM concentrations are measured in three sites of the North of Italy: an urban (Milan-MI; 45°31'19"N, 9°12'46"E), rural (Oasi Bine-OB; 45°13'33"N, 10°45'00"E) and high altitude remote site (Alpe San Colombano-ASC, m.2280 asl; 46°46'11"N 10°30'19"E). Daily PM2.5 samples are collected by using a low volume gravimetric sampler (38,33 l/min).

Samples are chemical characterised for the main inorganic ions (Na+, K^+, Ca^{++}, Mg^{++} NH_4^+ , F^-, Cl^-, NO_3^-, $SO_4^{2=}$,by IC) and carbonaceus fraction (EC and OC, by TOT).

Chemical speciation of the organic carbon is focuesed on certain compound classes. Low-molecular weight (C2-C7) carboxylic acids (mono and dicarboxylic acid) are analysed by IC; *n*-alkanes (C20-C32) and polycyclic aromatic hydrocarbons (PAHs) are analysed by GC-MS;.

Carboxylic acids are associated to atmospheric oxidation and they are known to be an important contribution to secondary organic aersol (SOA) [1]

The n-alkane pattern is investigated through the carbon precerence index (CPI) [2] and % Cwax to evaluate the contribution of vegetation during different seasons.

PAHs concentrations and relative mass contribution to fine PM are a tracer for contribution of combustion source in the three sites. During winter, when high altitude sites are above the mixing boundary layer of the polluted plan, PAHs mass contribution to PM2.5 at ASC site is up to 10 time lower compared with MI site.

[1] Rohrl A. and G. Lammel (2001) *Environ. Sci. Technol.,* **35**, 95-101. [2] Rogge W.F., *et al*. (1993) *Atmos. Env.* , **27**A, 1309-1330

Investigation of mercury methylation routes combining species-specific isotopic tracers and isotopic fractionation measurements

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Biotic or abiotic mercury methylation pathways remain a complete scientific challenge that has only been partially addressed. The development of new analytical speciation tools involving both natural and enriched stable isotopes measured by atomic mass spectrometry in single or multi-collector mode has recently demultiplicated the information level that can be obtained from experimental and field investigations on mercury transformations. Because methylation extent is often controlled by the reversible demethylation pathways, multiisotopic tracer studies (^{199}Hg(II), Me^{201}Hg) allow controlling the extent of both methylation and demethylation during the course of the same experiment. On the other hand, potential change in the isotopic composition of the mercury species as related with both methylation and demethylation could also probably be converted into distinct mass fractionation.

The aim of the proposed work is to present several results on the study of mercury methylation using either pure anaerobic bacterial strains or simple aqueous media incubation experiments. Enriched stable isotopes are used to discriminate both methylation and demethylation extent under the various conditions tested, while incubated natural Hg was used to evaluate the potential extent of mercury mass fractionation during such methylation pathways. Both experiments are based on the novel technologies and data treatment using the hyphenation between capillary gas chromatography and single collector ICP quadrupole MS or multicollector ICP sector field MS [1]. Preliminary results indicate that biotic mercury methylation by sulfate reducing bacteria in the dark conditions generate a significant mass dependent fractionation of mercury isotopes in the newly formed methyl-mercury, when no demethylation is occurring [2]. New results are expected to demonstrate the comparison of such methylation routes under various conditions and will be further discussed.

[1] Epov *et al*. (2008) *Anal. Chem.* **80**, 3530-3538. [2] Rodriguez-Gonzalez *et al*., in prep.