

PM formation processes in the urban atmosphere: comparison between South and North Italy

P.R. Dambruoso¹, G. de Gennaro¹, A. Di Gilio¹, P. Fermo², R., Gonzalez Turion³, A. Piazzalunga³

¹Department of Chemistry, University of Bari, Bari, Puglia, via Orabona, 4, 70126, Italy

²Department of Inorganic, Metallorganic and Analytical Chemistry, University of Milan, Milan, via Celoria, 18, 20133 Milano, Italy

³Department of Chemistry, University of Milan-Bicocca, Milan, Piazza della Scienza, 3, 20126 Milano, Italy

HNO₃, HONO, PM formation processes, AIM 9000D

alessia.digilio@uniba.it

The determination of inorganic fraction in PM is very important to define the effective contribution of each source to fine PM. This fraction and the ions in particular, which constitute about 30-40% of total mass of PM_{2.5}, can be used as markers of different sources. Moreover, time resolved information about ions and inorganic gases allow to study the chemical reactions and the chemical physical processes occurring in atmosphere. Nowadays, the disadvantages of this approach are the limited time resolution of the chemical characterization of PM filter samples and the simultaneous collection of inorganic gases concentrations data.

The AIM9000D is an automatic instrumentation that provides time-resolved direct measurements of anion and cation both in particulate (NO₃⁻, SO₄²⁻, Cl⁻, NH₄⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺) and gases phases (such as HCl, HNO₃, HNO₂, SO₂ and NH₃) and it is an useful tool that allows to investigate the chemical process leading to the formation of ionic fraction of PM_{2.5} but also physical transformations and subsequent gas-particle partitioning of its semi-volatile inorganic constituents.

The main goal of this work was the study of PM formation processes using high time resolved information about ions and inorganic gases concentrations. For this purpose, two monitoring campaigns have been performed in Bari and in Milan. In particular, the first sampling campaign took place at the urban background station in the Campus of University of Bari from 1st to 20th October 2011, while the second one on the roof of the University of Milan from 6th June 2012 to 26th July 2012.

In this work the preliminary results about the nitrous (HONO) and nitric (HNO₃) acids concentrations in atmosphere have been reported. The data analysis showed that nitrous acid concentrations were well correlated with NOx concentrations and humidity percentage both at Milan (for example only a few days in fig. 1) and Bari, confirming that heterogeneous reactions between NO₂ and H₂O on particle surface occurred (Stutz et al., 2004). Even if this reaction determines also the nitric acid formation, despite of Bari site, the nitrous and nitric acids hourly concentrations determined at Milan showed an uncorrelated behavior. Moreover, the hourly HONO concentrations peak between 06:00 and 08:00 am, during morning traffic rush hours. These findings suggested that HONO formation at Milan was probably due to the homogeneous recombination of the NO and OH radicals,

that contributes to significant HONO amounts under conditions of elevated NO concentrations (Wong et al., 2011). However, this process competes with HONO photolysis occurring in the morning (Harrison et al., 1996; Carr et al., 2009), that determines a decrease of HONO concentrations in daytime.

As concern nitric acids, higher photoreactivity, more vehicular traffic emissions and atmospheric stability in Milan determined a photochemical production of HNO₃. The hourly mean concentrations of HNO₃ in fact, showed a clear daytime peak when high ozone concentrations were registered (fig 2a). On the contrary, the hourly concentrations of nitric acid were related to humidity percentage and NOx concentrations. In particular high concentrations were determined in the night hours between 3:00 and 6:00 a.m (fig.2b). This result suggested that the main formation process of HNO₃ in Bari was due to heterogeneous reaction occurring in the dark, between nitrate radical (NO₃) and water on particle surface (Spataro et al., 2013).

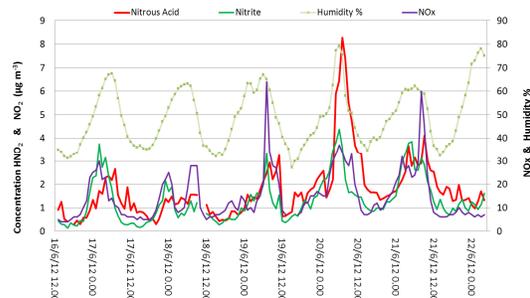


Fig. 1: Hourly concentrations of Nitrous acid, nitrogen oxides and nitrite with RH% determined at Milan

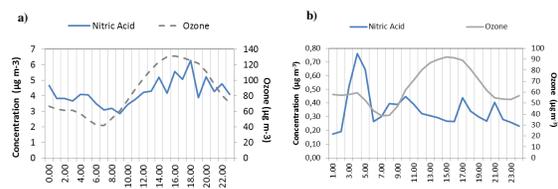


Fig. 2: Hourly trends of Ozone and Nitric acids concentrations at Milan (a) and Bari (b)

Reference

- Carr et al., 2009. Science 324:336b.
- Harrison et al., 1996. J Geophys Res 101:14429–39.
- Spataro et al., 2013. Sci. Tot. Env. 447 210–224
- Stutz et al., 2004. J Geophys Res 109:D03307.
- Wong et al., 2011. Atmos Chem Phys 11:3595–609.