Hourly composition of gas and particle phase pollutants at a central urban background site in Milan, Italy

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ABSTRACT

A comprehensive range of gas and particle phase pollutants were sampled at 1-hour time resolution in urban background Milan during summer 2012. Measurements include several soluble inorganic aerosols (Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, Ca^{2+}, K^+, Mg^{2+}, Na^+, NH_4^+) and gases (HCl, HNO_2, HNO_3, NH_3, NO, NO_2, O_3, SO_2), organic, elemental and black carbon and meteorological parameters. Analysis methods used include mean diurnal pattern on weekdays and Sundays, pollution roses, bivariate polar plots and statistical models using backtrajectories. Results show how nitrous acid (HONO) was mainly formed heterogeneously at nighttime, with a dependence of its formation rate on NO_2 consistent with observations during the last HONO campaign in Milan in summer 1998, although since 1998 a drop in HONO levels occurred following to the decrease of its precursors. Nitrate showed two main formation mechanisms: one occurring through N_2O_5 at nighttime and leading to nitrate formation onto existing particles; another occurring both daytime and nighttime following the homogeneous reaction of ammonia gas with nitric acid gas. Air masses reaching Milan influenced nitrate formation depending on their content in ammonia and the timing of arrival. Notwithstanding the low level of SO_2 in Milan, its peaks were associated to point source emissions in the Po valley or shipping and power plant emissions SW of Milan, beyond the Apennines. A distinctive pattern for HCl was observed, featured by an afternoon peak and a morning minimum, and best correlated to atmospheric temperature, although it was not possible to identify any specific source. The ratio of primary-dominated organic carbon and elemental carbon on hourly PM$_{2.5}$ resulted 1.7. Black carbon was highly correlated to elemental carbon and the average mass absorption coefficient resulted MAC $= 13.8 \pm 0.2 m^2 g^{-1}$. It is noteworthy how air quality for a large metropolitan area, in a confined valley and under enduring atmospheric stability, is nonetheless influenced by sources within and outside the valley.

1. Introduction

The interactions between gaseous and aerosol phase pollutants have long been studied due to their impact on air quality (Penkett et al., 1979; Ravishankara, 1997) and on human health (World Health Organization, 2006). In order to investigate processes leading to atmospheric pollutants formation and ageing in densely populated areas with large emission load (i.e. hotspots), time resolved composition of both gas and particle phase atmospheric compounds are needed. Po valley (Northern Italy) is one of the most important hotspot regions in Europe (Putaud et al., 2010), with Milan metropolitan area exhibiting one of the poorest air qualities within the valley (Bigi and Ghermandi, 2014).

Very few 1-hour time resolution campaigns were accomplished in Milan urban area. Three noteworthy studies resulted from the Limitation of Oxidant Production/Pianura Padana Produzione di Ozono (LOOP/PIPAPO) campaign held in May and June 1998 in Milan urban background (Neftel et al., 2002). In one of these

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studies Baltensperger et al. (2002) analysed data by several continuous instruments sampling aerosol physical properties (number size distribution, volatility, hygroscopicity, mass), aerosol chemical composition (BC_E, nitrate, sulphate) (NH_3, HNO_3). This same study showed the large contribution to airborne particles smaller than 40 nm by primary emissions rich in soot content and the increase in secondary and hygroscopic aerosol for particles larger than 50 nm. The second study within PIPAPO, Putaud et al. (2002) collected samples of size-segregated aerosol with 4- and 7-hour time resolution and analysed them for elemental carbon (EC), organic carbon (OC), particulate organic matter (POM) and major ionic species; their results showed the large contribution (¿30%) to PM mass by POM, by ammonium nitrate (29% of PM mass) and ammonium sulphate (22% of PM mass). Putaud et al. (2002) found also a diurnal and weekly pattern for traffic-related pollutants (e.g. EC and resuspended mineral dust), the influence of traffic emissions on nitrate formation and of industrial emissions on sulphate formation. In the third study of PIPAPO Alicke et al. (2002) investigated hydroxyl radical formation by measuring several gas phase pollutants by DOAS (differential optical absorption spectroscopy): HCHO, HONO, NO_2, NO, O_3 and SO_2. Their results identified HCHO as the primary source of OH˙ radicals (up to 40% of total OH˙ on clear days), while photolysis of nitrous acid and of ozone provides similar contribution to atmospheric OH˙ (15–30% of total OH˙ each), with the former compound dominating during early morning and the latter during the afternoon. In addition to the above mentioned studies, the aerosol elemental composition and sources were investigated with hourly resolution in Milan by D'Alessandro et al. (2003, 2004) during wintertime and summertime 2001 evidencing quasi-periodical and episodic pollution sources.

Several sources influence the sampling site: Bernardoni et al. (2011) used positive matrix factorization to apportion 4-hour PM_{10} measurements and showed the diurnal pattern in the relative contribution by resuspended dust, construction works and industry, which altogether account for 48% to total PM_{10} in summer. These results were confirmed by the a detailed source apportionment exercise in Milan urban background by Perrone et al. (2012), where three years of daily $PM_{2.5}$ and PM_{10} samples were analysed. This latter study also showed how 60% of summer daily $PM_{2.5}$ derives from traffic and secondary inorganic ions (sulphate, nitrate and ammonium) and contribution of resuspended dust to summer daily $PM_{2.5}$ is only to 3.8%. Consistently emission inventory for the only municipality of Milan assessed Road Traffic (SNAP 7) to be the main source of NO_x and EC for the city of Milan, SNAP 2 (non-industrial combustion) is the main source of OC and the second most important of NO_x, and SNAP 6 (solvent use) is the main source of NM-VOC. Notwithstanding these studies, in Milan there is no available analysis of simultaneous characterization of atmospheric pollutants in both gas and particle phase sampled at a 1-hour resolution. The present article is based on a thorough analysis of measurements of several gas phase pollutants and main chemical composition of $PM_{2.5}$ sampled at 1-hour time resolution. Formation process of $PM_{2.5}$ in Milan will be presented along with the influence of meteorological conditions and air mass trajectories. Observations include HCl, HONO, HNO_3 and NH_3, i.e. the first published measurement of hydrochloric acid in the Po valley and the first 1-hour resolution measurements of nitrous and nitric acids in the last 15 years in Milan. Details on the instrumentation and methods used are presented in Section 2. Results and conclusions are found in Sections 3 and 4 respectively.

2. Data and methods

Milan (45° 28′N; 9° 13′E) urban area counts about 1,500,000 inhabitants and is the second largest town in Italy, after Rome, and considering the whole Milan province the population rises up to about 3.1 millions inhabitants.

The data here presented were collected on the roof of the Department of Chemistry, University of Milan, at a ∼10 m a.g.l. within the University campus, a site representative of central urban background conditions for the city. Sampling was performed from June 5th until July 23rd 2012.

Hourly resolution composition of $PM_{2.5}$ for soluble inorganic ions composition and for gases was determined using a commercially available Ambient Ion Monitor (AIM) URG-9000D (URG Corp, USA). In particle phase five anions (Cl^-, F^-, NO_2^-, NO_3^-, SO_4^{2-}) and five cations (Ca^{2+}, K^+, Mg^{2+}, Na^+, NH_4^+) were determined. F^-, Ca^{2+}, K^+, Mg^{2+} and Na^+ were often below the detection limit and therefore not analysed in details. The gases determined include hydrochloric acid (HCl), nitrous acid (HONO), nitric acid (HNO_3), ammonia (NH_3) and sulphur dioxide (SO_2). The AIM consists of a sampling system for both gas and particles, coupled with two ion chromatographies for the analytical determination. Gases are collected by a liquid diffusion denunder with H_2O_2 5 mM running continuously at 10mLh^{-1} flow rate. Particles are collected in a chamber supersaturated with ultrapure water vapour: water soluble particles are allowed to grow and then inertially separated and injected into the ion chromatographies. Further instrumental details and the calibration procedure used in this study can be found in Markovic et al. (2012). AIM data were compared to off-line daily data from $PM_{2.5}$ samples collected during 22 days throughout the campaign by denuded filter-pack setup (Vecchi et al., 2009): the system consisted in two dry annular denuders removing both acidic and basic gases, followed by a filter pack made of a quartz fibre front filter and a nylon fibre backup filter. Once the campaign ended, AIM blank values for particle-phase aerosol were estimated by inserting a quartz fibre filter between the denuder and the filter pack over 5 full days.

Comparison of AIM and denuded filter pack showed statistically significant (by ANOVA test) and large coefficients of determination for linear regression models between off- and on-line data for all species (Fig. S1), supporting the reliability of the patterns observed by AIM. Regression coefficients were close to unity for HNO_2 + HNO_3 and NH_3, while some difference occurred between particle-phase compounds, with lower NO_2^- + NO_3^- levels observed by AIM and lower values for SO_4^{2-} and NH_4^+ observed by denuded filter-pack. Assuming that the denuded filter pack reported in Vecchi et al. (2009) is artefact-free for nitrogen compounds, some bias likely affects ammonium in AIM measurements, preventing a fully-correct estimate of ion balance for the experimental dataset. Part of the offset between the two measurement sets might also be due to the possibly different transmission efficiency curve between respective size-selective inlets: AIM uses a custom $PM_{2.5}$ cyclone, while denuded filter pack used a US-EPA equivalent $PM_{2.5}$ inlet equipped with a PM_{10} sampling head and a WINS $PM_{2.5}$ impactor downstream.

Gaseous precursors levels during AIM blank test resulted similar to their respective mean observed during the campaign, indicating an efficient collection of gas and a complete transmission of particles by the denuders. Significant particulate sodium was observed during blanks and ascribed to contamination in the ultrapure water used in the supersaturated chamber during the blank test. The low particulate nitrite, nitrate and ammonium observed during blank testing (i.e. < 1μgm^{-3}) can be considered negligible. Slightly larger blank for particulate sulphate was observed (∼1.5μgm^{-3}), but considered sufficiently low to support the reliability of the AIM measurements for this compound.

Elemental carbon (EC) and organic carbon (OC) measurements were collected by a Model-4 Semi-Continuous ECOC Field Analyser by Sunset Laboratory, USA (Bae et al., 2004). The carbon analyser was provided with a $PM_{2.5}$ cyclone and operated at a 24L min^{-1} flow rate. Measurement had 1-hour time resolution, comprising 45 min