

Origin of PM_{2.5} and Secondary Inorganic Aerosol (SIA) and relationship with gaseous pollutants in the Venice area

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Fine particles ($AD \leq 2.5 \mu\text{m}$) mainly derive from industrial and residential combustion processes, motor-vehicle emissions and conversion of gaseous compounds to particulate phase. The particle mass deriving from gas-to-particle conversion is defined as secondary aerosol (SIA – secondary inorganic aerosol, SOA-secondary organic aerosol).

In the Venice area, PM_{2.5} and NO_x emission are mainly related to road transport and combustion processes (combustion in energy and transformation industries and non industrial combustion plants) whereas SO₂ emission mostly derive from combustion in energy and transformation industries (ISPRA, 2012).

In this work, PM and major inorganic ions (NH₄⁺, NO₃⁻, SO₄²⁻) are studied in relation to environmental conditions and gaseous precursors (SO₂ and NO_x) to highlight SIA formation patterns and origin.

One-year PM sampling campaign has been carried out from January 2009 to January 2010 in three sites, representing different emission scenarios and environmental conditions: (i) SRC, semi-rural-background coastal site; (ii) UBG, urban background site; (iii) IND, industrial site. PM was collected simultaneously on 47 mm quartz fiber filters (Whatman QMA) using low volume automatic samplers equipped with PM_{2.5} cut-off inlets and set according to EN 14907 standard.

Four sampling periods were selected to represent the four seasons and ultrasonic method was used to extract all filters for determination of major inorganic ions (NH₄⁺, NO₃⁻, SO₄²⁻) by ion chromatography as proposed by Squizzato *et al.* (2012).

The concentrations of gaseous pollutants (SO₂, NO_x, NO, NO₂) in UBG and IND site were provided by local Environmental Protection Agency (ARPAV). Meteorological conditions (temperature, relative humidity, wind speed and direction) were recorded by Ente della Zona Industriale di Porto Marghera and ARPAV-Centro Meteorologico di Teolo.

The relationship between SIA and gaseous pollutant have been evaluated using SOR (Sulfur Oxidation Ratio) and NOR (Nitrogen Oxidation Ratio). SOR and NOR have been used to express the degree of atmospheric conversion of SO₂ to SO₄²⁻ and of NO₂ to NO₃⁻. Then, wind speed and direction and back-trajectories have been combined with chemical data to point out the influence of local and external sources of PM and SIA and the Lenschow approach (Lenschow *et al.*, 2001) was used to estimate local contribution as described by Squizzato *et al.* (2012).

The PM_{2.5} annual mean was 33 $\mu\text{g m}^{-3}$ for the two mainland sites (UBG and IND) and 26 $\mu\text{g m}^{-3}$ for SRC. PM_{2.5} concentrations were inversely correlated with air temperature, with higher levels during the cold period. On a yearly basis, SIA accounts for 9.5 $\mu\text{g m}^{-3}$ (27% of PM_{2.5} mass) in UBG, 9.6 $\mu\text{g m}^{-3}$ (28%) in IND and 9.5 $\mu\text{g m}^{-3}$ (36%) in SRC.

Strong correlations were observed between NO₃⁻, NO₂, NOR, NH₄⁺, temperature and relative humidity (Table 1). This suggests a local origin for ammonium nitrate related to an increase in NO_x levels and particular environmental conditions (low temperature and high relative humidity). Heavy pollution events occur in days characterized by low atmospheric dispersion and air masses coming from Po' Valley. During these events the local contribution on PM and SIA increases. Nevertheless, considering the mass percentage, no significant variations were observed for all periods and samples. In conclusion, heavy SIA events are mainly due to a regional contribution and are enhanced by scarce atmospheric dispersion that traps pollutants.

Table 1. Correlation matrix between NO₃⁻, NO₂, NOR, NH₄⁺ temperature and relative humidity.

| UBG | NO ₃ ⁻ | NO ₂ | NOR | NH ₄ ⁺ | T (°C) | R.H |
|------------------------------|------------------------------|-----------------|-------|------------------------------|--------|------|
| NO ₃ ⁻ | 1.00 | | | | | |
| NO ₂ | 0.59 | 1.00 | | | | |
| NOR | 0.96 | 0.48 | 1.00 | | | |
| NH ₄ ⁺ | 0.89 | 0.59 | 0.87 | 1.00 | | |
| T (°C) | -0.44 | -0.35 | -0.51 | -0.33 | 1.00 | |
| R.H | 0.35 | 0.04 | 0.43 | 0.33 | -0.25 | 1.00 |

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