

PM_{2.5}, PM₁ and PM_{0.4} acidity during spring and summer at one Po Valley site.

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Nitrate, sulphate and ammonium are the three main important water-soluble inorganic ions of PM. Typically, they account for 30-60% of the total PM mass (Seinfeld and Pandis, 2006; Lonati *et al*, 2005). In the Po Valley, they show a typical seasonal trend: during the summer sulphate is the dominant inorganic ion (13% of PM₁ and PM_{2.5}; Perrone *et al*, 2010) because of the strong atmospheric photochemistry, while during the winter nitrate becomes the most abundant inorganic ion (23-29% of PM₁ and PM_{2.5}; Perrone *et al*, 2010). This seasonal pattern affects the characteristics of aerosol acidity, because sulphuric and nitric acids are two of the most important aerosol precursors. Typically, ammonia is the main neutralizing species. The goal of this study is to expand the knowledge about aerosol acidity characteristics.

PM_x samples (Table 1) were collected at Sannazaro de' Burgondi (Pavia, Italy), a rural site located in the middle of the Po Valley (North of Italy). Three dimensional sizes of PM were sampled: PM_{2.5} (4-h filters), PM₁ (8-h filters) and PM_{0.4} (24-h filters). The sampling period was 24 March – 19 April (spring) and 10 June – 2 July 2010 (summer). All the collected filters were extracted in ultra-pure water and analyzed by IC to determine the concentration of water soluble inorganic ions (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺; F⁻, Cl⁻, NO₃⁻, PO₄³⁻, SO₄²⁻) and mono-/dicarboxylic acids (acetic, propionic, formic, glutaric, succinic, malonic, maleic, oxalic acids).

Table 1. Mean ± standard deviation of PM_x concentration (µg/m³).

| | PM _{2.5} | PM ₁ | PM _{0.4} | PM ₁ /PM _{2.5} | PM _{0.4} /PM ₁ |
|--------|-------------------|-----------------|-------------------|------------------------------------|------------------------------------|
| SPRING | 21±14 | 12±8 | 3±1 | 0.61±0.12 | 0.23±0.05 |
| SUMMER | 13±8 | 12±7 | 5±1 | 0.64±0.13 | 0.35±0.08 |

While the ammonium concentration was at the same level during spring (e.g., PM₁=1.2±1.1 µg m⁻³) and summer (e.g., PM₁=1.4±1.0 µg m⁻³), nitrate and sulphate showed the typical seasonal pattern described above. For example in PM₁, NO₃⁻ was three times higher during spring (spring: 2.9±3.2 µg m⁻³; summer: 0.8±1.0 µg m⁻³); on the contrary, SO₄²⁻ was three times higher during summer (spring: 1.0±0.8 µg m⁻³; summer: 2.9±2.3 µg m⁻³).

All the samples (regardless of season, time of the day, and PM size) were ammonium-rich, i.d. [NH₄⁺]/[SO₄²⁻] molar ratio was always >1.5. Moreover, it was clearly visible that the ammonium concentration increased at the increasing of the nitrate concentration,

suggesting that nitrate formation was a consequence of the gas-phase reaction between ammonia and nitric acid.

However, the spring strong correlation between excess of NH₄⁺ (excess NH₄⁺=[NH₄⁺]-[SO₄²⁻]) and NO₃⁻ (R²≥0.98) was lost during the summer (R²≥0.46) (Figure 1), suggesting that the presence of ammonium in PM samples could not be attributed to this inorganic ion.

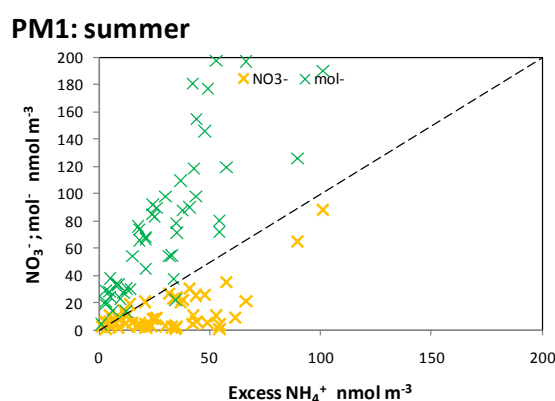


Figure 1. Relationship between excess of NH₄⁺ and NO₃⁻ concentration.

The summer higher level of ammonium in PM_x could be explained by the increased concentration of mono- and dicarboxylic acids, due to stronger photochemical processes than in spring. In fact, the concentration of these acids was double in summer (e.g., PM₁=0.20±0.19 µg m⁻³) than in spring (e.g., PM₁=0.11±0.10 µg m⁻³).

In addition to strong acidity (i.e., H⁺ derived from strong acids in an aqueous extract of PM samples; Pathak *et al*, 2004), also free acidity (i.e., the actual concentration of free H⁺; Pathak *et al*, 2004) is an important parameter to describe the aerosol acidity characteristics. Then, a thermodynamic model (*E-AIM*) will be used to determine free acidity for the collected samples.

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