

Evaporation of ammonium nitrate in coastal sites

M. Catrambone¹, A. Ianniello¹, S. Dalla Torre¹, E. Rantica¹, T. Sargolini¹

¹CNR Institute of Atmospheric Pollution Research, Monterotondo St. (Rome), 00015, Italy

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Presenting author email: catrambone@ia.cnr.it

The presence of ammonium salts, especially volatile compounds (NH₄NO₃ and NH₄Cl) in the troposphere affect Earth's radiative balance and contribute to the long-range transport of their acid constituents. These acid compounds may cause an intense acid deposition, forest decline, and eutrophication on areas far from anthropogenic activities.

Since ammonium nitrate is a solid or liquid phase species, gas-to-particle conversion occurs. The equilibrium dissociation of ammonium nitrate is very sensitive to temperature, relative humidity, aerosol size, pressure drop and filtration velocity (Liu et al., 2014; Hu et al. 2011; Cheng and Tsai, 1997). To better understand such processes, accurate methods in determining atmospheric aerosol composition are essential.

In coastal atmosphere, the nitric acid (HNO₃) regenerated from the dissociation process can react with coarse mode sea-salt aerosol to form coarse nitrate, causing a size-shift process of nitrate from fine to coarse mode. In addition, our data suggested strong evidence of major quantities of ammonium in PM_{2.5} than those in PM₁₀.

We summarize in this paper the results of many previous field studies carried out in a number of coastal and inland sites of the Mediterranean Basin (North and South Italy, Tunisia, Israel) aimed to determine the chemical composition, including ammonium salts, of PM₁₀ and PM_{2.5}. These data show that in all inland sites the concentrations of ammonium in the two size fractions were comparable, as expected for a species that is completely contained in the finer fraction of PM. In coastal sites, instead, ammonium in PM_{2.5} was unexpectedly higher than in PM₁₀:

$$[\text{NH}_4^+]_{\text{PM}_{2.5}} > [\text{NH}_4^+]_{\text{PM}_{10}}$$

In the marine boundary layer, nitric acid reacts with sodium chloride, according to the well-known reaction (1):



responsible for chloride losses in coarse sea-salt aerosol.

This reaction (1) could alter the equilibrium reaction (2):



subtracting nitric acid by conversion in sodium nitrate and resulting in an increase of evaporation.

Being the sea-salt aerosol in the coarse fraction, this reaction should be predominant on PM₁₀

To demonstrate this hypothesis we have carried out a new field study in a coastal area of Northern Italy. Atmospheric PM was daily sampled for two weeks on Teflon filters by using four different devices, operated side-by-side and simultaneously: - a sampler equipped with a PM₁₀ impactor operating at the flow rate of 2.3 m³/h; - a sampler equipped with a PM_{2.5} impactor operating at the flow rate of 2.3 m³/h; - a sampler equipped with a PM_{2.5} impactor operating at the flow rate of 0.6 m³/h; a sampler equipped with a PM_{2.5} cyclone operating at the flow rate of 0.6 m³/h. All the samples have been analysed for their ionic content and the obtained results have confirmed our previous observations.

We discuss in this paper the ionic composition of PM resulting from the four different sampling configurations. We also address the role played by the sampling flow rate and by the use of the impactor vs. cyclone for size-segregated sampling in enhancing the mechanism responsible for NH₃ depletion.

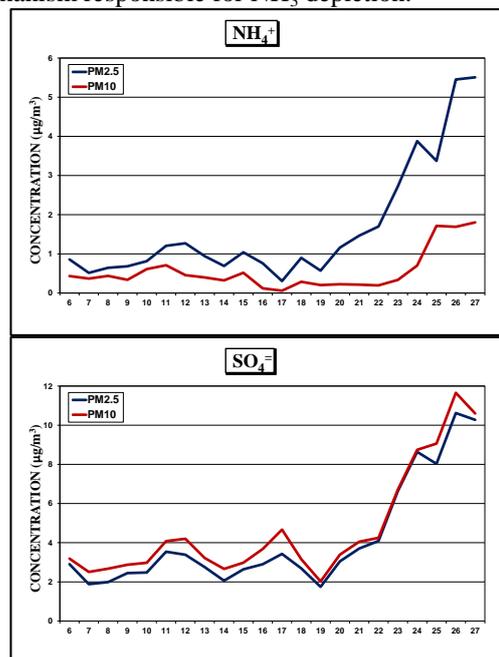


Figure 1: Time pattern of ammonium and sulfate concentration in PM₁₀ and PM_{2.5} at a coastal site.

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