

Annual evolution and generation mechanisms of particulate nitrate in Madrid

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Abstract

During the course of one year (March 2004–March 2005), PM_{2.5} particulate nitrate concentrations were semi-continuously measured every 10 min at a Madrid suburban site using the Rupprecht and Patashnick Series 8400N Ambient Particulate Nitrate Monitor (8400N). Gaseous pollutants (NO, NO₂, O₃, HCHO, HNO₂) were simultaneously measured with a DOAS spectrometer (OPSIS AR-500) and complementary meteorological information was obtained by a permanent tower. The particulate nitrate concentrations ranged from the instrumental detection limit of around 0.2 μg m⁻³, up to a maximum of about 25 μg m⁻³. The minimum monthly average was reached during August (0.32 μg m⁻³) and the maximum during November (3.0 μg m⁻³). Due to the semi-volatile nature of ammonium nitrate, peaks were hardly present during summer air pollution episodes. A typical pattern during days with low dispersive conditions was characterized by a steep rise of particulate nitrate in the morning, reaching maximum values between 9 and 14 UTC, followed by a decrease during the evening. On some occasions a light increase was observed at nighttime. During spring episodes, brief diurnal nitrate peaks were recorded, while during the autumn and winter episodes, later and broader nitrate peaks were registered. Analysis of particulate nitrate and related gaseous species indicated the photo-chemical origin of the morning maxima, delayed with respect to NO and closely associated with secondary NO₂ maximum values. The reverse evolution of nitrate and nitrous acid was observed after sunrise, suggesting a major contribution from HNO₂ photolysis to OH formation at this time of the day, which would rapidly produce nitrate in both gaseous and particulate phase. Some nocturnal nitrate maxima appeared under high humidity conditions, and a discussion about their origin involving different possible mechanisms is presented, i.e. the possibility that these nocturnal maximum values could be related to the heterogeneous formation of nitrous and nitric acid by the hydrolysis of NO₂ on wet aerosols.

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1. Introduction

Atmospheric aerosols can be primary or secondary in origin, directly emitted or formed from gas-

to-particle conversion processes. The particulate nitrates belong to this last group and are important because they are the final form for the removal of NO_x species by their conversion to HNO₃, N₂O₅ and organic nitrates. Some studies have shown that their contribution to the PM_{2.5} concentration is not negligible, obtaining heterogeneous data as a function of the sampling site and climatic conditions.

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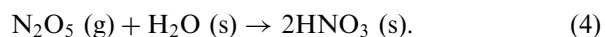
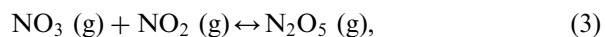
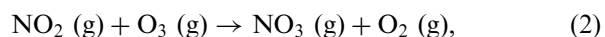
Tolocka et al. (2001) studied the PM_{2.5} composition in four US cities during January and February 1999, finding average particulate nitrate values of 39% for Rubidoux (CA), 20% for Philadelphia (PA), 15% for Phoenix (AZ) and 6% for Research Triangle Park (NC). Wittig et al. (2004a, b) found in Pittsburgh (PA) that the monthly particulate nitrate contribution to the total PM_{2.5} concentration could vary from 3% in July to 19% in January. In the case of the Baltimore (MD) Supersite (Park et al., 2005), the monthly nitrate contributions to PM_{2.5} ranged from 5% (July) to 16% (November) for the March–November period. In Europe, the situation is similar. Lonati et al. (2005) studied the PM_{2.5} chemical composition in Milan (Italy) and found that in winter the average nitrate was 32% of the total mass, whereas in summer it was 20%. Querol et al. (2004) studied the speciation of PM₁₀ and PM_{2.5} in several areas of Spain. The average annual PM_{2.5} nitrate values ranged from 2.2 to 3.3% in rural and urban background stations (Bemantes and Huelva) up to 8.3–11.6% in urban stations (Barcelona, Hospitalet). In the Madrid area, their measured concentrations were between 3.9% and 5.2%, but in some winter episodic situations, as demonstrated in this study, values of 20% have been reached.

Particulate nitrate is the final step of gaseous N-compounds after atmospheric oxidation and gaseous nitric acid is considered as its direct precursor. The main reactions which are usually considered for atmospheric nitric acid generation are (Seinfeld and Pandis, 1998):

Daytime reactions:

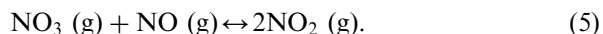


Nighttime reactions:



During daytime, most of the nitric acid production is generated by the first reaction and is limited by the OH radical concentration. The second reaction occurs only during nighttime, because the gaseous NO₃ radical is rapidly photolyzed during the daytime. N₂O₅ formation through reactions 2 and 3 is followed by reaction 4 to generate nitric acid. This takes place in hydrated aerosols rather than in the gas phase. The radical NO₃ also reacts

with NO, fast enough so that NO and NO₃ cannot coexist at NO concentrations above a few parts per trillion (Wayne et al., 1991).

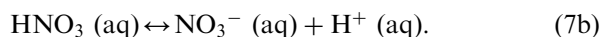
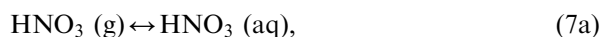


As a consequence of this, it is only possible to find the radical NO₃ during nighttime and not at ground level in urban scenarios (Brown et al., 2003).

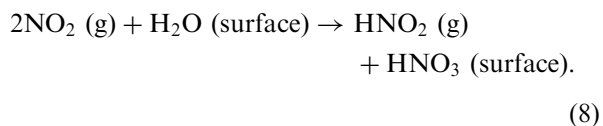
There are two possible pathways for the transfer of this gaseous nitric acid to the aerosol phase. The first possibility is through neutralization by a base, such as ambient ammonia released from vehicles equipped with catalytic converters (Perrino et al., 2002), which can react with nitric acid to form NH₄NO₃ (s):



This equilibrium is influenced by the ambient conditions (temperature, humidity, etc.; see Mozurkewich, 1993) and by the presence of other inorganic compounds, especially sulfate, because the ammonia preferentially reacts with it and only the remaining NH₃ can react with the nitric acid. This means that reductions in sulfate concentrations could cause an increase in the particulate nitrate concentration (West et al., 1999). The second pathway is absorption of the nitric acid by water droplets producing acid aerosols. Nitric acid is one of the most water-soluble atmospheric gases and, after dissolution, it dissociates to nitrate increasing its solubility and the droplet acidity (Seinfeld and Pandis, 1998):



Another rarely mentioned different route for generation of particulate nitrate is by the heterogeneous reaction:



This reaction has been considered for nitrous acid formation (Finlayson-Pitts et al., 2003; Acker et al., 2005) but very few studies take it into account for HNO₃ generation, because it is considered to remain at the surface (buildings, roads, soils, etc.; Kleffmann et al., 1998). When this surface is a water droplet or an aerosol particle covered by water layers, the nitric acid should remain in the aerosol

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