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THE ROLE OF NH3 ON PARTICULATE MATTER POLLUTION OVER PORTUGAL

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Abstract: Ammonia is widely present in the atmosphere due to a variety of anthropogenic sources, playing a vital role in aerosol nucleation events. Despite its negative impacts on human health, NH_3 is not regulated under the actual European Air Quality legislation. The analysis of the National Emission Inventory prepared annually by the Portuguese Environmental Agency indicates that total NH_3 emissions have decreased more than 20% since 1990. Agricultural activities are the major contributors (> 80%), followed by industrial activity over specific locations, waste treatment and road traffic. In order to examine the effects of NH_3 on air quality over Portugal, model simulations were performed using the WRF-CAMx modelling system. Two periods with distinct meteorological situations were selected in order to better quantify the importance of the dry and wet deposition phenomena on PM2.5 concentrations. A source apportionment analysis was performed in order to allow the estimation of the contribution and origin of each anthropogenic source to PM concentrations, with a focus on NH3 contribution to PM2.5 concentrations. According to the air quality modelling results, although industry is a relatively small source of NH_3 emissions compared to agriculture, its influence in urban areas, where it can have a major contribution to local ammonium nitrate formation, is higher. The air quality model was also able to demonstrate that wash-out of PM is the dominant mechanism for nitrogen deposition.

Key words: *ammonia emissions; air quality modelling; source apportionment; deposition; Portugal.*

INTRODUCTION

Ammonia (NH_3) is an important pollutant that plays a vital role in atmospheric chemistry as a precursor of fine inorganic secondary aerosol. When deposited to ecosystems, NH_3 may cause over-enrichment of nitrogen, decrease in biological diversity, damage to sensitive vegetation, and acidification of soils (Wu et al., 2008). Ammonia reacts with sulphuric and nitric acids to form ammonium sulphate and ammonium nitrate aerosol. Under favourable meteorological conditions, ammonium nitrate can contribute to PM2.5 concentration peaks (particulate matter with aerodynamic diameter smaller than 2.5 mm) (Hamaoui-Laguel et al., 2014), which have been linked to a range of adverse health effects such as increased rates of respiratory and cardiovascular illness (Pope et al., 2009). In addition, NH_3 will likely play an increased role in PM2.5 formation as the emissions of sulfur oxides and nitrogen oxides are reduced (Wu et al., 2008). Despite the above mentioned implications, NH_3 is not regulated under the actual European Air Quality legislation.

Agriculture is the main source of atmospheric ammonia. Generally, inventories describe animal husbandry and fertilizer application as the most significant sources (ECETOC, 1994; Bouwman et al., 1997). Other emission sources include human wastes, biomass burning, soil biogenic emissions, chemical industry, traffic and also electric utilities (Bouwman et al., 1997; Kean and Harley, 2000). The identification of pollution sources and their individual contributions to the atmospheric concentrations of pollutants is a very important step for the development of an effective air quality management. Source apportionment (SA) is one of the source-oriented methods commonly used to determine source-receptor relationships. A detailed and accurate source attribution requires the combined use of models and data from monitoring networks (Koo et al., 2009; Burr and Zhang, 2011; Li et al., 2013). Among the available modelling methods, receptor models have been widely used for SA during the past three decades (Fragkou et al., 2012) however they are limited by the frequency and spatial coverage of the monitoring network, but also by problems dealing with secondary pollutants (Seigneur et al 1999). More recent

studies have used 3-dimensional (3D) air quality models. In contrast to the receptor models that use atmospheric concentrations as inputs to calculate source contributions, these models use an emission inventory as the starting point, and are able to describe the chemical and physical atmospheric processes in order to predict pollutant concentrations at different spatial scales. Its disadvantages are related to the uncertainties inherent to the model, namely its formulation, and with the uncertainties in the input data (meteorology and emissions).

In this study, the WRF-CAMx modelling system has been applied over Portugal in order to examine the effects of NH_3 on air quality over Portugal, namely on PM2.5 concentrations. The Particulate Source Apportionment Technology (PSAT), implemented in CAMx, was performed in order to allow the estimation of the contribution and origin of each anthropogenic source to PM concentrations, with a focus on NH_3 contribution to PM2.5 concentrations. Two periods with distinct meteorological conditions were selected in order to better quantify the importance of the dry and wet deposition phenomena on PM2.5 concentrations.

AIR QUALITY MODELING AND SOURCE APPORTIONMENT

Modelling system and configuration

The Weather Research & Forecasting (WRF) (Skamarock et al., 2008) is a next generation mesoscale numerical weather prediction system designed to serve both operational forecasting and atmospheric research needs. CAMx (Morris et al., 2004) is a 3D chemistry-transport Eulerian photochemical model that allows for an integrated assessment of gaseous and particulate air pollution over many scales, ranging from continental to sub-urban.

The WRF-CAMx air quality modelling system has been applied to simulate gases and aerosols 3D concentration allowing the examination of the effects of NH_3 on particulate air quality over Portugal. The modelling setup included 2 nesting domains covering Europe (D1) and Portugal (D2) with 27 and 9 km horizontal resolution, respectively (Figure 1), both with about 15 km vertical column (non-regularly subdivided on 15 levels considering higher details near ground).

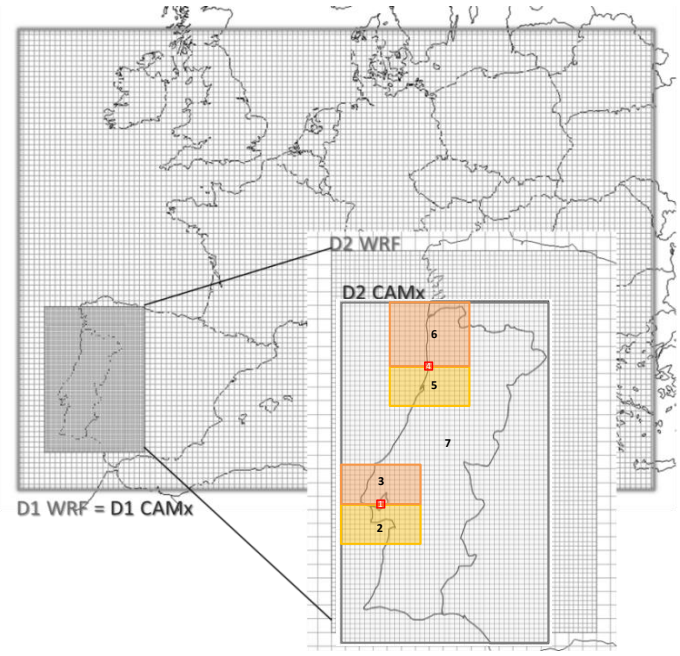

Figure 1. WRF and CAMx modelling domains. D2 CAMx includes the definition of the receptor regions (1-Lisbon and 4-Porto) and of the source regions (1-Lisbon, 2-South of Lisbon, 3-North of Lisbon, 4-Porto, 5-South of Porto, 6-North of Porto, 7-Continental Portugal) used for the SA study.

Emissions

The analysis of the National Emission Inventory prepared annually by the Portuguese Environmental Agency indicates that total NH_3 emissions have decreased 23% from 1990 to 2009 (similarly to what was found over Europe). Agricultural activities (namely animal husbandry and fertilizer application) are the major contributors (> 80%), followed by industrial activity over specific locations, waste treatment and road traffic.

Figure 2 shows the spatial distribution of NH_3 emissions in Continental Portugal for: combustion in manufacturing industries and production processes (SNAP 3 and 4), road transport (SNAP7), waste treatment and disposal (SNAP9) and agriculture (SNAP10). NH_3 emissions are distributed across the territory according to the level of intensity of livestock farming and agriculture. There are also some municipalities with relatively high emission values as a result of the presence of point source emissions associated with industrial activities.

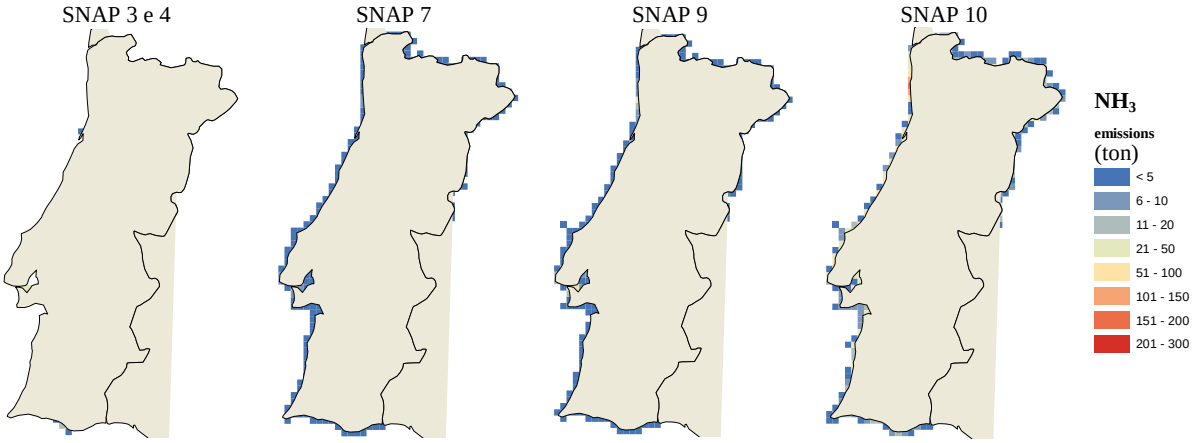

Figure 2. Spatial distribution of NH_3 emissions in Portugal for: combustion in manufacturing industries and production processes (SNAP 3 and 4), road transport (SNAP7), waste treatment and disposal (SNAP9) and agriculture (SNAP10).

Emission inputs were prepared for the two simulation domains. The most recent EMEP-EU27 gridded emissions by SNAP sector available (for the year 2009) for the pollutants CO, NH_3, NMVOC, SO_x, PM2.5 and PM10, were disaggregated by area for the European grid. For the domain over Portugal, the National Emission Inventory developed for regulation purposes was used. Emissions from anthropogenic sources are available by municipality for the whole territory of Portugal, and for the different SNAP emission categories, and were prepared for the 9x9 km^2 grid cell domain.

Particulate source apportionment

PSAT source apportionments are calculated using reactive tracers that operate in parallel to the main CAMx calculations for total species concentrations. For each class of PM, PSAT includes reactive tracers for the PM species and any related precursor species (Yarwood et al., 2005). PSAT results allow the conduction of culpability assessments to identify sources that contribute significantly to PM pollution and the design of the most effective and PM control strategies.

PSAT can apportion particulate concentrations from user defined geographic regions and emission categories plus initial concentrations and boundary conditions. For this study two receptor regions were defined: Lisbon and Porto (red squares in Figure 1); these urban areas were selected as they present significant NH_3 emissions (Figure 2) as well as some of the highest concentrations of PM. To identify the geographic origin of PM2.5 precursors, namely NH_3, 7 source regions were defined (Figure 1). To identify the activities with the greatest impact on PM2.5 concentrations, emissions for separate source groups were supplied as sets of separate emissions files; the following seven emission source groups were considered: biogenic, non-industrial combustion (corresponding to SNAP2), industry (SNAP3 and SNAP4), distribution of fossil fuels and solvent use (SNAP5 and SNAP6), transport (SNAP7 and SNAP8), waste treatment and disposal (SNAP9) and agriculture (SNAP10).

RESULTS

Simulation results show that, for both dry and the wet periods and for both urban areas, although road traffic is the main source of precursors of PM10, industrial activity is the main contributor to PM2.5 concentrations. Regarding the species composition of PM2.5, sulphate (SO_4^{2-}) is the dominant specie in Lisbon, while primary organic aerosols (POA) are the most important in Porto; ammonium (NH_4^+) represents around 10% of the total PM2.5 for both areas.

Figure 3 presents the relative contribution of each source category to NH_4^+ concentrations in Lisbon and Porto, for the average of the dry period (10th-19th October 2011) (results obtained for the wet period are very similar, therefore they are not presented). Although industrial activities are a relatively small source of NH_3 emissions compared to agriculture, their influence in these two urban areas is notorious with 48% and 43% of contribution to NH_4^+ concentrations. Agriculture is the second biggest contributor to NH_4^+ concentrations (31% in Lisbon and 40% in Porto), and waste treatment and disposal is the third (15% and 11%).

Figure 4 presents the relative contribution of each source region to NH_4^+ concentrations in Lisbon and Porto. As expected Lisbon and Porto receptor areas are mostly influenced by the emissions taking place in the equivalent source regions (with around 50% contribution to NH_4^+ concentrations). Both are also highly influenced by adjacent source regions, with predominance for the northern ones, reflecting the dominant wind flow (NW) in coastal Portugal.

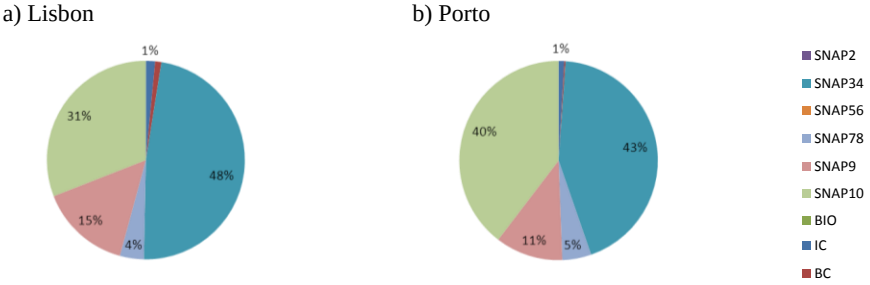

Figure 3. Relative contributions of each source category to the concentrations of NH_4^+ in a) Lisbon and b) Porto, for the average of the dry period (10th-19th October 2011).

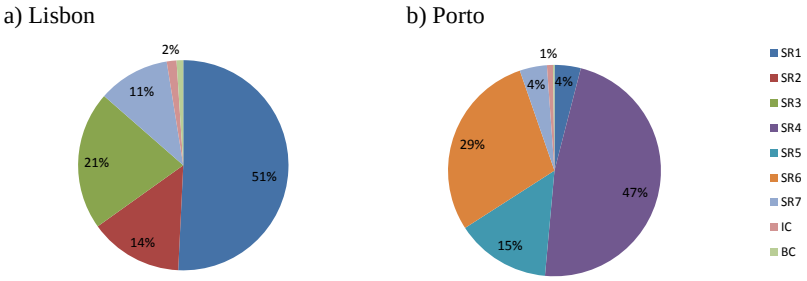

Figure 4. Relative contributions of each source region to the concentrations of NH_4^+ in a) Lisbon and b) Porto, for the average of the dry period (10th-19th October 2011).

Figure 5 shows the relative contribution of emission categories to NH_4^+ concentrations in Lisbon and Porto for selected source regions: for Lisbon SR1 (Lisbon) and SR3 (North of Lisbon), for Porto SR4 (Porto) and SR6 (North of Porto). In Lisbon SR1 and SR3 have similar compositions with industrial activity dominating the contribution to NH_4^+ concentrations, however SR3 presents a significant contribution of agriculture (37%). In Porto, SR4 already presents an important contribution from agriculture sources (22%) and SR6 is dominated by agriculture (58%) reflecting the more rural environmeny of Porto metropolitan area when compared to Lisbon. The contribution of SR7 (Continental Portugal) for both Lisbon and Porto (not shown) is almost exclusively due to agriculture activities (more than 80%).

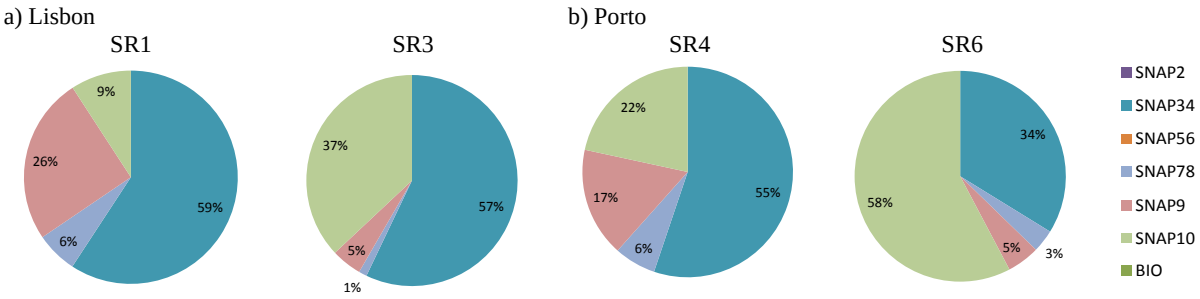

Figure 5. Relative contribution of emission categories to NH_4^+ concentrations in Lisbon and Porto for selected source regions: for Lisbon SR1 (Lisbon) and SR3 (North of Lisbon), for Porto SR4 (Porto) and SR6 (North of Porto), for the average of the dry period (10th-19th October 2011).

Wet deposition is the predominant removal process for particles, while particle size is the dominant variable controlling dry deposition processes (diffusion, impaction, and/or gravitational settling). As expected, simulated deposition fluxes of NH_4^+ (Figure 6) are much higher for the wet period over the Portuguese territory, with average wet deposition values reaching 1g.ha^{-1}, while dry deposition is around 0.1 g.ha^{-1} (ten times smaller).

FINAL REMARKS

The conducted air quality modelling exercise shows that although industry is a relatively small source of NH_3 emissions compared to agriculture, its influence in urban areas, where it can have a major contribution to local ammonium nitrate formation, is higher. The air quality model was also able to demonstrate that wash-out of PM is the dominant mechanism for nitrogen deposition

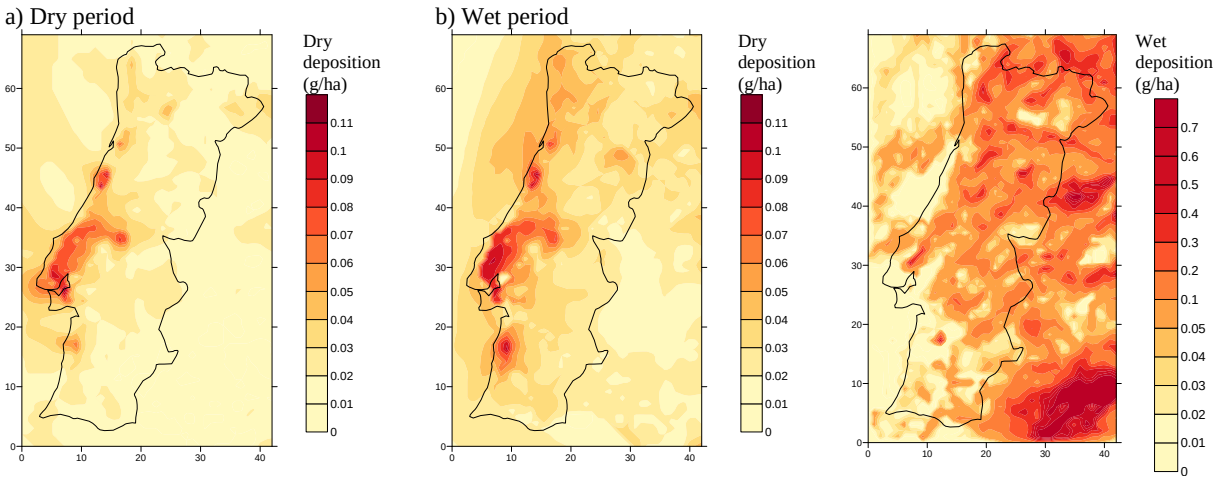

Figure 6. Simulated average deposition fluxes of NH_4^+ for a) the dry period and b) the wet period.

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