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Key Points:
- Particulate organic nitrate is ubiquitous in Europe
- The 34 to 44 percent of fine particulate nitrate is organic
- Nighttime chemistry is a dominant source of particulate organic nitrates

Supporting Information:
- Supporting Information S1
- Supporting Information S2

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Ubiquity of organic nitrates from nighttime chemistry in the European submicron aerosol

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Abstract In the atmosphere nighttime removal of volatile organic compounds is initiated to a large extent by reaction with the nitrate radical (NO_3) forming organic nitrates which partition between gas and particulate phase. Here we show based on particle phase measurements performed at a suburban site in the Netherlands that organic nitrates contribute substantially to particulate nitrate and organic mass. Comparisons with a chemistry transport model indicate that most of the measured particulate organic nitrates are formed by NO_3 oxidation. Using aerosol composition data from three intensive observation periods at numerous measurement sites across Europe, we conclude that organic nitrates are a considerable fraction of fine particulate matter (PM_1) at the continental scale. Organic nitrates represent 34% to 44% of measured submicron aerosol nitrate and are found at all urban and rural sites, implying a substantial potential of PM reduction by NO_x emission control.

1. Introduction

Atmospheric self-cleansing, i.e., removal of species through oxidation, is initiated by the radical species OH, O_3, and NO_3. While OH plays a key role during the day and is overall the dominant oxidant in the troposphere, NO_3 is one of the main oxidants during the night in addition to O_3. Due to its formation from the reaction of NO_2 with O_3 the main source of NO_3 is anthropogenic. Already in 1984 it was suggested that the reaction with NO_3 radicals is a dominant loss process for monoterpenes [*Winer et al.*, 1984]. Especially emissions that remain in the atmosphere at sunset or enter in the night undergo oxidation by NO_3 radicals [*Pye et al.*, 2010]. Model estimates conclude that 6–20% of the total isoprene emissions are oxidized by NO_3 [*Brown et al.*, 2009]. Oxidation of VOCs leads to either functionalization or fragmentation of precursor molecules, where fragmentation likely leads to products with higher vapor pressure than the precursors' vapor pressure. By contrast, functionalization results in a decrease of the vapor pressure [*Pankow and Asher*, 2008], which in the case of NO_3 radical reactions is dominated by addition reactions forming multifunctional nitrates ($RONO_2$). Products with low enough vapor pressures will partition to the particulate phase, forming secondary organic aerosol (SOA) and thereby contribute to air quality and climate impacts of particles.

While the formation of SOA through VOC oxidation by OH and O_3 has been studied in numerous simulation chamber and laboratory experiments [*Hallquist et al.*, 2009], only few experiments report the SOA yields from the oxidation with NO_3 [e.g., *Boyd et al.*, 2015; *Brown and Stutz*, 2012; *Fry et al.*, 2014]. For the biogenic VOCs investigated, SOA yields vary between 1 and 89% and $RONO_2$ yields between 19 and 66%. These reactions have also been shown to result in a substantial fraction (12 to 16%) of the oxidized nitrogen consumed by biogenic VOC oxidation in some continental regions [*Brown et al.*, 2009].

Observations of ambient atmospheric particles have shown that organic species are ubiquitous and represent a large fraction of observed mass loadings regardless of location of the measurement [*Zhang et al.*, 2007]. Recent attempts to model the organic aerosol (OA) mass have substantially improved the ability of models to reproduce measured organic mass loadings, yet large uncertainties remain with respect to OA sources [*Hallquist et al.*, 2009]. For instance, it has been shown using radiocarbon measurements that a major part of the OA mass is of modern origin in many areas, meaning that sources such as biogenic VOC and biomass burning are often dominant sources of OA [e.g., *Szidat et al.*, 2006]. Nevertheless, SOA is often observed to correlate well with gas-phase tracers for anthropogenic activity such as carbon monoxide (CO) [*Weber et al.*, 2007], and recent model results suggest that interactions of anthropogenic pollution and biogenic VOCs (BVOCs) may be important on a global scale [*Spracklen et al.*, 2011]. A prominent candidate for production of aerosol from modern carbon that would correlate with anthropogenic tracers is the reaction of NO_3 with BVOCs, which has been shown to serve as source of particulate organic nitrates in recent studies in the U.S. [*Fry et al.*, 2013; *Rollins et al.*, 2012; *Setyan et al.*, 2012; *Xu et al.*, 2015a, 2015b].

Here we present evidence from aerosol mass spectrometric (AMS) measurements with high time resolution that, in urban and rural sites in Europe, the reaction of VOCs with nitrate radicals represents an important source of OA.

2. Materials and Methods

Intensive AMS measurements were taken across Europe through three campaigns within the European Integrated Project on Aerosol Cloud Climate and Air Quality Interactions (EUCAARI)/European Monitoring and Evaluation Programme (EMEP) intensives in May 2008, October 2008, and March 2009 [*Crippa et al.*, 2013; *Kulmala et al.*, 2011]. Observations were compared with results from the EURopean Air pollution and Dispersion-Inverse Model (EURAD-IM) chemistry transport model [*Elbern et al.*, 2007] in order to evaluate the regional extent of our findings. Here we discuss the data analysis principles applied to derive organic nitrate mass concentration from AMS data and the setup of the EURAD-IM used for comparing to the measurement episodes.

2.1. AMS Data Analysis for Organic Nitrate

The working principles and modes of operation of the aerosol mass spectrometer (AMS) are described in detail elsewhere [*Canagaratna et al.*, 2007]. Here we report on the method used to quantify the organic nitrate in the measured total nitrate. In AMS measurements nitrate is primarily quantified by the determination of the total signal of NO_2^+ and NO^+ (high-resolution time-of-flight version, HR-TOF-AMS [*DeCarlo et al.*, 2006]) or the signal at *m/z* 30 and *m/z* 46 that is attributed to nitrate via the so-called fragmentation table (quadrupole aerosol mass spectrometer, Q-AMS [*Jayne et al.*, 2000]). Ambiguity remains for the Q-AMS data sets due to the correction of the interference of the CH_2O^+ ion at *m/z* 30, whereas *m/z* 46 is traditionally interpreted as being dominated by NO_2^+ [*Allan et al.*, 2004]. By contrast, the HR-TOF-AMS can unambiguously distinguish between the NO^+ and CH_2O^+ ions (see Table S1 in the supporting information for an overview of stations and AMS type applied).

The measured ratio of NO_2^+/NO^+ was taken from all AMS data sets to determine the fractional contribution of ammonium nitrate (NH_4NO_3, hereafter pInNO$_3$) and organic nitrate (pOrgNO$_3$) to the total observed signal at these two ions. This requires knowledge of the expected ratio of NO_2^+/NO^+ for pure ammonium nitrate and pure organic nitrate. As calibrations of the ionization efficiency of the AMS are typically performed with NH_4NO_3 particles, the measured ratio of NO_2^+/NO^+ for pure NH_4NO_3 particles is known for all instruments. Table S1 in the supporting information summarizes the measured calibration ratio R_{calib} of NO_2^+/NO^+ for the instruments deployed during the EUCAARI/EMEP intensive observation periods [*Crippa et al.*, 2013; *Kulmala et al.*, 2011]. Note that although there is some variability between instruments, the majority of the instruments report calibration ratios between 0.29 and 0.49 (22 out of 25 instruments). For the remaining

three data sets R_{calib} between 0.7 and 0.85 were reported. For organic nitrates literature data suggest a range of possible ratios (0.2 to 0.08) from experiments forming organic nitrates by oxidation of volatile organic compounds (VOCs) with NO_3 [*Boyd et al.*, 2015; *Bruns et al.*, 2010; *Fry et al.*, 2009, 2011; *Rollins et al.*, 2009]. Here we use a fixed value of NO_2^+/NO^+ (i.e., 0.1) for organic nitrates (see also Figures S1 and S2 in the supporting information). This number was chosen as it represents the minimum ratio of NO_2^+/NO^+ observed in the field data sets. Note that such low ratios of NO_2^+/NO^+ were also detected in some data sets where R_{calib} was reported high. Therefore, contrary to other studies, no systematic change in R_{OrgNO3} depending on R_{calib} was assumed [*Fry et al.*, 2013]. Our overall approach here is designed such that lower limits of $pOrgNO_3$ [*Xu et al.*, 2015a] are derived, with an estimated uncertainty of ± 20%.

Similar to previous attempts to determine the organic nitrate in AMS data sets [*Farmer et al.*, 2010], we apply the following formula to determine the fraction of particulate organic nitrate ($pOrgNO_{3frac}$) in the measured total nitrate from measured NO_2^+/NO^+ ratio:

$$pOrgNO3_{frac} = \frac{(1 + R_{OrgNO3}) \times (R_{measured} - R_{calib})}{(1 + R_{measured}) \times (R_{OrgNO3} - R_{calib})} \quad (1)$$

$$pOrgNO3_{mass} = pOrgNO3_{frac} \times NO3_{total} \quad (2)$$

where $R_{measured}$ is the measured intensity ratio of NO_2^+ and NO^+ ions as function of time in the individual data sets, R_{calib} is the ratio observed in NH_4NO_3 calibrations, and R_{OrgNO3} is set to 0.1 for all data sets. The mass concentration of $pOrgNO_3$ ($pOrgNO_{3mass}$) is then calculated by multiplying the measured total nitrate (NO_{3total}) with the fraction of $pOrgNO_3$ (2). Note that since NO_2^+ is always the ion with less signal intensity, through the use of measured NO_2^+/NO^+ ratio rather than NO^+/NO_2^+ ratio, we are using a formulation that approaches zero in the case of very low or nonexistant signal, whereas the use of NO^+/NO_2^+ ratio gives infinite numbers as the limit of detection is approached.

Note that the $pOrgNO_3$ calculated this way accounts for the nitrate functional group of organic nitrates only. This method was previously considered to reliably derive the $pOrgNO_3$ fraction when $pOrgNO_{3frac}$ is >0.15 [*Bruns et al.*, 2010]. Therefore, organic nitrate concentration data reported here were filtered for values >0.15. Also, in a conservative approach [*Bruns et al.*, 2010] we consider 0.1 μg m^{-3} $pOrgNO_3$ as detection limit and report data accordingly.

2.2. EURAD-IM Model Description

The EURAD-IM [*Elbern et al.*, 2007], is a Eulerian model running from local to continental scale. EURAD-IM is primarily used for chemical weather forecast and advanced data assimilation studies over Europe, using the RACM chemistry mechanism [*Stockwell et al.*, 1997]. Previous studies on a high-ozone episode [*Monteiro et al.*, 2012] and a dust storm [*Chervenkov and Jakobs*, 2011] indicated good performances of EURAD-IM. Within EURAD-IM, the aerosol dynamics such as nucleation, condensation, coagulation, diffusion, sedimentation, and aerosol-cloud interaction are simulated by the Modal Aerosol Dynamics Model for Europe (MADE [*Ackermann et al.*, 1998]). However, the initial MADE aerosol chemistry module only treated inorganic ions and water. To consider the formation of secondary organic aerosols, the Secondary ORGanic Aerosol Model (SORGAM) was developed and implemented into MADE [*Schell et al.*, 2001]. In SORGAM, both anthropogenic and biogenic hydrocarbons are first oxidized by oxidants like OH, NO_3, and O_3. The mass transfer from gas to particle phase is then driven by the gas/particle partitioning of the low-volatility oxidation products formed in gas phase. Aerosol dry deposition velocities are calculated according to *Zhang et al.* [2003]. Recently, it was shown that including SOA formation from NO_3 oxidation significantly improved the ability to model OOA at Cabauw, the Netherlands [*Li et al.*, 2013]. EURAD-IM is part of the MACC II (Monitoring Atmospheric Composition and Climate - Interim Implementation) consortium and, together with six other CTMs, operated and evaluated on a daily basis (http://www.gmes-atmosphere.eu/documents/maccii/deliverables/eva, 2013, 2013). It was found that especially NO_2 analyses performed very well.

In this study EURAD-IM was used with a spatial resolution of 15 km with improvements in the SOA scheme as described in *Li et al.* [2013]. Recently, Model of Emissions of Gases and Aerosols from Nature (MEGAN) 2.1 [*Guenther et al.*, 2012] has been implemented into EURAD-IM and was used for the calculation of biogenic emissions in this study. Anthropogenic emissions have been derived from the MACC-II TNO (Netherlands Organisation for Applied Scientific Research) emission inventory for the year 2009 [*Pouliot et al.*, 2012]. The

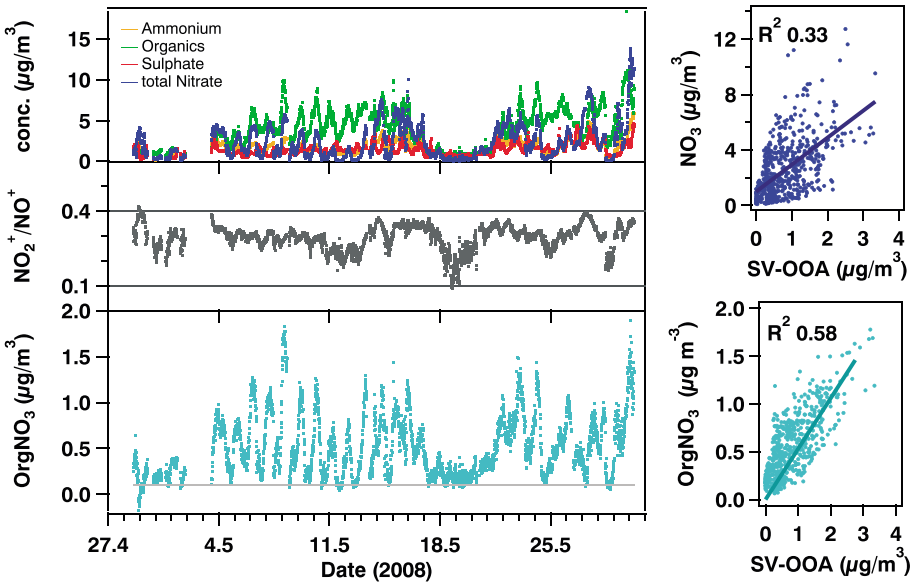

Figure 1. Measured mass concentrations of ammonium (orange), total nitrate (dark blue), sulphate (red), and organics (green) together with observed concentration ratio of NO_2^+/NO^+ ions (dark grey) and organic nitrate ($pOrgNO_3$, cyan) mass concentration at Cabauw, the Netherlands. Also shown are correlations of the SV-OOA factor with total nitrate (top right) and organic nitrate (bottom right).

Weather Research and Forcasting Model V3.5, driven by the Integrated Forcasting System operational analysis, has been used for the provision of meteorological fields needed by EURAD-IM. The comparison of model output with measurements presented in the following focuses on SOA formed through NO_3 oxidation.

3. Organic Nitrate Results From Cabauw Analysis

Figure 1 shows observed mass concentrations of the submicron nonrefractory aerosol species ammonium (orange), organics (green), sulphate (red), and total nitrate (blue) as measured with a HR-ToF-AMS at Cabauw, the Netherlands, in May 2008 [*Mensah et al.*, 2012]. Using the observed intensity ratio of the ions NO_2^+ and NO^+ (middle of Figure 1) to calculate the relative contribution of nitrate groups associated with either $pOrgNO_3$ or $pInNO_3$ to the measured total aerosol nitrate (pNO_3), we infer a pOrgNO3 mass concentration averaging 0.52 $\mu g\,m^{-3}$ and as high as 1.8 $\mu g\,m^{-3}$.

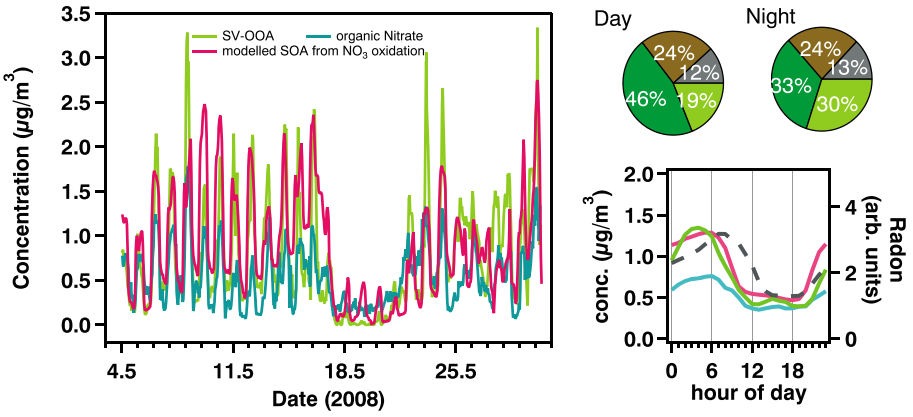

Figure 2. Time series of the mass concentrations of measured organic nitrate and SV-OOA and modeled SOA from NO_3 oxidation at Cabauw during May 2008. Inserts show the average diurnal including also Radon concentration (grey dashed line, right axis) as boundary layer dilution tracer and day and night pie charts of the relative contribution of individual organic PMF factors.

The time series of $pOrgNO_3$ is characterized by a distinct diurnal pattern with maxima during the night (see also Figure 2) and is correlated ($R^2 = 0.58$) with the less oxidized fraction of the oxidized OA (SV-OOA), as determined by positive matrix factorization (PMF [*Ulbrich et al.*, 2009]) and a unified multilinear engine (ME-2) analysis for all EUCAARI/EMEP data sets [*Crippa et al.*, 2013; *Paglione et al.*, 2014]. Note that this correlation between $pOrgNO_3$ and SV-OOA is more pronounced than the correlation of total pNO_3 with SV-OOA.

It has to be emphasized that $pOrgNO_3$ measures the nitrate functionality of organic nitrates only. To account for the total particulate organic nitrate mass ($RONO_2$), an estimate needs to be made regarding the molar mass of $RONO_2$ relative to molar mass of NO_3. As a lower limit we will assume a molar mass of 200 g mol^{-1} in calculations of the contribution of organic nitrates to total organics [*Xu et al.*, 2015a; *Lee et al.*, 2016].

Using the EURAD-IM model, the SOA formed from oxidation of VOCs by NO_3 was modeled for the measurement period of May 2008 at Cabauw [*Li et al.*, 2013]. As shown in Figure 2, the temporal behavior of the modeled SOA from NO_3 oxidation closely matches the observed SV-OOA and $pOrgNO_3$ time series. Maximum concentrations are observed for all three at 5:00 LT with a daytime minimum extending from 10:00 to 20:00 LT. For comparison, radon concentration, which can be considered as a tracer for boundary layer dilution, is observed to have a maximum between 7:00 and 8:00 LT, i.e., later than $pOrgNO_3$. This is in agreement with a modeled time lag of 2 h between the early morning decrease of SOA from NO_3 oxidation (due to NO_3 photolysis and thus halted production) and the decrease of a dilution tracer (due to breakup of the nocturnal boundary layer) in the EURAD-IM model. Together with a distinct daytime maximum of the photochemically formed sulphate (see Figure S3), we take this comparison as further support that the observed organic nitrate is primarily formed through nighttime NO_3 chemistry.

4. Organic Nitrate Across Europe

Extending the data analysis to the full EUCAARI/EMEP AMS data set [*Kulmala et al.*, 2011], we find that $pOrgNO_3$ is present throughout Europe (Figure 3) with observed concentrations likely a result of complex interplay of various sources and sinks. Maximum concentrations of $pOrgNO_3$ are observed for European sites with large anthropogenic influence, i.e., urban (two sites) and rural (nine sites) environments, whereas $pOrgNO_3$ is very low or below detection limit at the three remote and two high-altitude sites. Averaging over all stations, the fraction of aerosol nitrate that is observed to be $pOrgNO_3$ showed little variability with values of 34%, 38%, and 44% in March 2009, May 2008, and October 2008, respectively (see Table S1 and S2 in the supporting information for details [*Carbone et al.*, 2014; *Dall'Osto et al.*, 2010; *Freney et al.*, 2011; *Hildebrandt et al.*, 2011; *Lanz et al.*, 2010; *Mensah et al.*, 2012; *Minguillón et al.*, 2011; *Mohr et al.*, 2012; *Paglione et al.*, 2014; *Pikridas et al.*, 2010; *Poulain et al.*, 2011; *Saarikoski et al.*, 2012]). Assuming a molar mass of 200 g mol^{-1} for organic nitrates, the mean fractional contribution of organic nitrates to organics was 46% for stations fulfilling the threshold criterion of $pOrgNO_3 > 0.1\ \mu g\ m^{-3}$ (18 out of 25 data sets). Note that this is equivalent to a contribution of organic nitrates to nonrefractory PM1 of between 5.6 and 51% (average 22%).

Measurements of $RONO_2$ in ambient aerosol have so far mainly been performed from filter samples and therefore with low time resolution. Detection of $RONO_2$ is usually achieved via detection of the $-ONO_2$ group either optically or by mass spectrometry, with recent developments made toward high time resolution detection of RONO2 [*Ayres et al.*, 2015; *Hao et al.*, 2014; *Rollins et al.*, 2012; *Schlag et al.*, 2015; *Sun et al.*, 2012; *Xu et al.*, 2015a; *Xu et al.*, 2015b]. Comparing with literature data obtained mainly from offline and online aerosol analysis in individual case studies in the US and Europe [*Brown and Stutz*, 2012; *Fry et al.*, 2013; *Rollins et al.*, 2012; *Setyan et al.*, 2012; *Xu et al.*, 2015a; *Xu et al.*, 2015b], we find a high contribution of organic nitrates to total organic PM1. For example, recent analysis of data from the southeast U.S. find that organic nitrates contribute 5 to 12% to organic aerosol in summer [*Xu et al.*, 2015a; *Xu et al.*, 2015b], whereas the results here imply a contribution of organic nitrates to European PM1 organics of on average 46%. Exploiting the high time resolution of AMS measurements, for the first time it is shown in an extended data set (spanning a continent and multiple seasons) that the concentration of organic nitrate is maximum during the nighttime for 12 of the 19 data sets with $pOrgNO_3$ above detection limit (see Figures S4–S7). Recent modeling studies suggest that at the global scale, 13% of the biogenic SOA production originates from NO_3 oxidation [*Pye et al.*, 2010]. For summer time in the USA up to 3.35 $\mu g\ m^{-3}$ of SOA is formed from NO_3 oxidation of biogenic VOC, equivalent to a doubling of the terpene SOA in some regions,

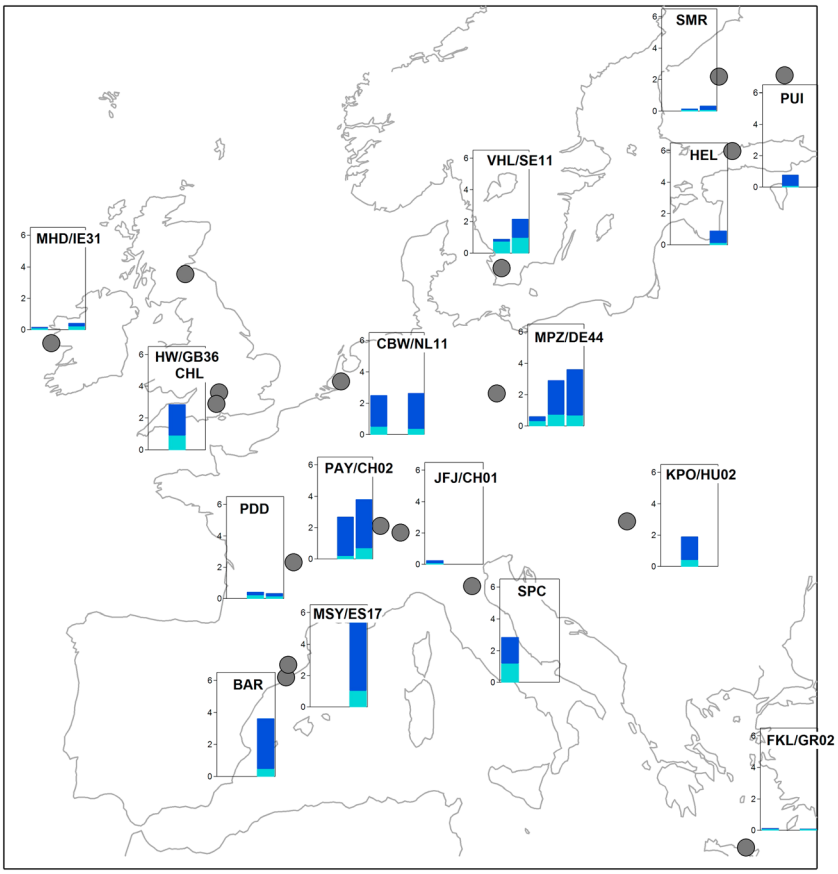

Figure 3. Map overview of particulate inorganic nitrate ($pInNO_3$, dark blue) and particulate organic nitrate ($pOrgNO_3$, cyan) mass concentrations ($\mu g\,m^{-3}$) as observed during the EUCAARI/EMEP intensive measurement periods in May 2008 (left bar), October 2008 (middle), and March 2009 (right). Organic nitrate mass concentrations are high in all urban and rural sites and reach maximum concentrations during the night (see supporting information for detailed time series plots, diurnals, and station abbreviations).

when considering the formation by NO_3 oxidation [*Pye et al.*, 2010]. Similarly, our simulations for Europe (details see supporting information) show an increase of SOA by 50 to 70% when considering SOA formation by NO_3 oxidation with maximum ground level concentrations of SOA from NO_3 oxidation in the range of 2 to 4 $\mu g\,m^{-3}$ in May 2008 (Figure 4).

As shown in Figure S8 and summarized in Table S3, EURAD-IM performed well in predicting organic PM_1 concentrations with an overall normalized mean error (NME) of 53% and a normalized mean bias (NMB) of −45%. It reproduces observed daily mean organic aerosol concentration within a factor of 10 for 98% of all data points and within a factor of 2 for 57% of all data points. On the other hand, EURAD underestimates SOA from NO_3 when compared with observed $pOrgNO_3$ with a normalized mean bias (NMB) of −50% and an overall

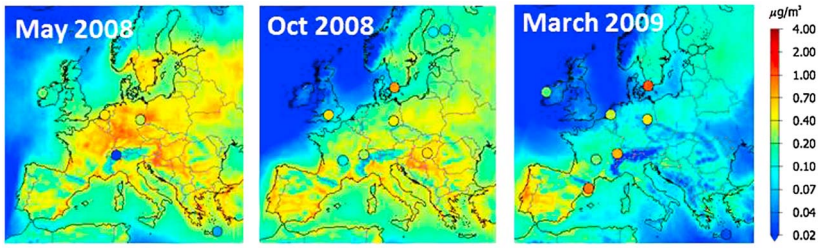

Figure 4. EURAD monthly mean concentration fields for SOA from NO_3 oxidation together with observed concentrations of $pOrgNO_3$ (colored circles) for May 2008 (left), October 2008 (middle), and March 2009 (right), respectively.

normalized mean error (NME) of 85%. This is worth mentioning specifically since $pOrgNO_3$ as measured here represents only a small fraction of SOA from NO_3 for two reasons. First, the $pOrgNO_3$ concentration reported is measure of the mass concentration of the nitrate functionality only of $RONO_2$. Second, the reaction of VOC with NO_3 also leads to the formation of products without NO_3 functionality, therefore not covered in the measurement assignment of $pOrgNO_3$ to SOA from NO_3 oxidation. This under estimation is likely due to overall uncertainties in the modeling of SOA. The model treats NO_3 oxidation of anthropogenic VOCs (Cresole and other hydroxy substituted aromatics, terminal, and internal alkenes) and biogenic VOCs (isoprene, α-pinene, and other cyclic terpenes with one double bond, d-limonene, and other cyclic diene-terpenes) according to the RACM [*Stockwell et al.*, 1997] chemistry mechanism. First and foremost, emission strengths of these VOCs are highly uncertain. Especially, the estimation of biogenic VOC emissions is critical due to a lack of detailed information about the type of plant cover. Further uncertainties may be introduced by the lumping applied to chemical species in the RACM chemistry mechanism and by the simplifying assumption that SOA formation from NO_3 oxidation for all biogenic VOC can be parameterized according to results obtained from α-pinene, limonene, and isoprene [*Li et al.*, 2013]. This assumption is a consequence of the limited number of experimental studies available. It should also be mentioned that the comparison shows a larger NMB for the March 2009 data set (−74%) potentially indicating the presence of additional sources of $pOrgNO_3$ beyond oxidation of VOC with NO_3. Due to the coarse model resolution (15 km) some of the measurement sites are not representative for the grid box used for comparison. Especially, a comparison of measurement data and model results is highly uncertain for the stations Jungfraujoch and Puy de Dome because of their exposed position. Also, in particular, the $pOrgNO_3$ measured at Vavihill, a continental background site with no local sources of pollution, situated in the southernmost part of Sweden, greatly exceeds modeled SOA from NO_3 (see also Figure 4). This potentially hints at additional sources for $pOrgNO_3$ at the Vavihill measurement site, potentially through influx of polluted air from continental Europe to the Nordic countries along a south-north transect. The inversion algorithm of EURAD-IM is currently designed as an inversion algorithm for gas phase [*Elbern et al.*, 2007]. Once the adjoint of SORGAM is available, it will be extended for SOA precursor emission estimation. Based on Moderate Resolution Imaging Spectroradiometer land use information, and higher horizontal resolution, the deficits can be addressed in a more systematic way. Furthermore, SORGAM improvements are expected taking recent experimental results on SOA formation due to reaction of α-pinene and β-pinene with NO_3 into account [*Boyd et al.*, 2015; *Nah et al.*, 2016; *Xu et al.*, 2015a, 2015b]. Disregarding the underestimation of daily mean $pOrgNO_3$ concentrations at some measurement sites, the ability of the EURAD-IM to demonstrate qualitatively the daily cycle of $pOrgNO_3$ and the dilution tracer radon supports the assumption that nighttime NO_3 chemistry contributes significantly to the $pOrgNO_3$ production.

The spatial distribution and diurnal pattern of $pOrgNO_3$ indicate a gradient of concentration with high concentration found in source regions, i.e., regions with high-NO_x emissions and during nighttime, and low concentrations in remote regions and during the day. Part of the diurnal pattern will be due to boundary layer dynamics, but the question remains to what extent the observed diurnal and regional variability is indicative of deposition losses, chemical reactions leading to fragmentation, or evaporative loss.

5. Implications and Conclusions

Across Europe a large fraction of the AMS measured nitrate is found to be organic, emphasizing the need to better understand sources and properties of particulate organic nitrates. The modeled continental distribution of SOA from NO_3 by the EURAD-IM supports the importance of NO_3 reactions during the night leading to SOA in regions with high-NO_x emissions. It also shows the need for more extensive investigations of the chemistry and emissions leading to $pOrgNO_3$.

Due to the lifetime of gas-phase $RONO_2$ with respect to photolysis (12–20 days), OH reactions (3–40 days), or thermal decomposition (up to months), some $RONO_2$ molecules may represent a temporary NO_x reservoir [*Aschmann et al.*, 2011; *Brown and Stutz*, 2012; *Nah et al.*, 2016]; whereas, other organic molecules may be lost rapidly due to gas-phase deposition [*Farmer et al.*, 2006; *Lee et al.*, 2016] or particle phase hydrolysis [*Boyd et al.*, 2015; *Liu et al.*, 2012]. Particulate $RONO_2$ could serve as source of NO_x in regions without major anthropogenic NO_x sources due to repartitioning of organic nitrates [*Fry et al.*, 2013] into the gas phase or release of NO_x following heterogeneous reactions [*Liu et al.*, 2012]. On the other hand, recent laboratory-based

observations indicate that $RONO_2$ might irreversibly condense on SOA [*Perraud et al.*, 2012]. This would imply that particulate $RONO_2$ can serve as an important NO_x sink.

Little is known about the properties of particulate organic nitrate with respect to both health risks and climate effects. Direct climate effects of organic nitrates may arise from their absorbing properties, which could be significantly higher than for SOA formed from OH or O_3 initiated oxidation [*Moise et al.*, 2015]. Similar to other organic semivolatile vapors, organic nitrates can be expected to cocondense with water when aerosol particles activate to cloud droplets [*Topping et al.*, 2013], impacting aerosol indirect effects on climate. At the median level, for all sites studied here organic nitrates suggest a comparable contribution to increasing kappa as nitric acid (see supporting information and Figure S9) [*Barley et al.*, 2011; *Topping and McFiggans*, 2012]. Such effects of organic nitrate condensation onto activating aerosol particles should be considered alongside those from nitric acid in increasing the number concentration of cloud droplets. Through its formation by NO_3 oxidation, and thereby its strong relation to anthropogenic NO_x emissions, particulate organic nitrates will be directly affected by NO_x emission controls [*Rollins et al.*, 2012] with the potential to decrease specifically nighttime PM_1 burdens in urban and rural sites in Europe.

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