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# Seasonal and diurnal variations of particulate nitrate and organic matter in the Central European atmospheric aerosol

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## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Abstract

Nitrate and several organic compounds such as dicarboxylic acids (e.g. succinic acid, glutaric acid), Polycyclic Aromatic Hydrocarbons (PAHs) or *n*-alkanes form the group of the most volatile compounds in atmospheric aerosol particles. The transition of these compounds between gas and particulate phase may significantly change the aerosol particles radiative properties, the heterogeneous chemical properties, and, naturally, the total particulate mass concentration. To better assess these time-dependent effects, three intensive field experiments were conducted in 2008–2009 at the Central European EMEP research station Melpitz (Germany) using an Aerodyne Aerosol Mass Spectrometer (AMS). Data coverage from all seasons highlighted organic matter as being the most important particulate fraction during summertime, while the nitrate fraction was more prevalent in winter. The variation in particulate nitrate was inherently linked to the gas-to-particle-phase equilibrium of ammonium nitrate, which depends on ambient temperature and relative humidity. During short episodes immediately after dawn, the particulate nitrate seems to disobey this dependency so that additional local nitrate formation, such as from HONO photolysis is needed as an explanation. During the summer 2008's experiment, a remarkable diurnal evolution in the oxidation state of the organic matter became evident, which could be correlated to hydroxyl radical (OH) and ozone concentrations indicating photochemical transformation process. In summer, the organic particulate matter seems to be heavily influenced by regional secondary formation and transformation processes, facilitated by photochemical production processes as well as a diurnal cycling of the substances between the gas and particulate phase. In winter, these processes were obviously much weaker, so that organic matter apparently originated mainly from aged particles and long range transport.

## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## 1 Introduction

Due to their influence on cloud formation, visibility, light scattering, and light absorption (IPCC, 2007), atmospheric aerosol particles are known to have important direct and indirect effects on earth climate. Moreover, aerosol particles can also affect ecosystems (e.g. Bohlmann et al., 2005; Jickells et al., 2005) and – upon interaction with the respiratory and cardiovascular systems, human mortality and morbidity (e.g. Pope, 2000; Ostro et al., 2007; Gurjar et al., 2010). In urban areas, the main sources of atmospheric aerosol particles are motor traffic, domestic heating, power generation, industrial processes (e.g. Allan et al., 2010; Aiken et al., 2009), while on a local scale additional sources such as cooking can come into play. In rural environments, particles are more significantly affected by local biogenic sources (e.g. Sjostedt et al., 2010; Slowik et al., 2010) but also long-range transports of polluted air masses (e.g. Dall’Osto et al., 2010; Dunlea et al., 2009; Healy et al., 2010; Singh et al., 2009; Hildebrandt et al., 2010).

It is well established that particles chemical composition is strongly depending on the gas-to-particle equilibrium. This is particularly true for ammonium nitrate (AN) which is known to be a semi-volatile compound. Moreover, organic aerosol concentrations are also depending on their gas-to-particle equilibrium. For example, Bao et al. (2009) demonstrated that the gas-to-particle equilibrium of low-molecular-weight dicarboxylic acids is not only depending on the gas and particulate concentrations but it can also be linked to the temperature and relative humidity. Consequently, heterogeneous reactivity has to be considered and might represent a source of secondary organic aerosols (SOA) as previously reported for chamber experiment (Volkamer et al., 2009). The organic compounds within the particles are mainly made of semi-volatile compounds for freshly generated SOA and become less volatile through oxidative so-called “aging” processes (Jimenez et al., 2009; Ng et al., 2010). Consequently a change in the gas-to-particle partitioning may be expected with time. Morgan et al. (2010) observed an important increase in nitrate and organics concentrations with altitude during airborne measurements over Europe which was correlated to variations in temperature

### Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



and relative humidity. This underlines the fact that particle mass concentration is linked to both semi-volatile precursor's concentrations and meteorological conditions. Moreover, the ammonium nitrate formation is not solely depending on its gas-to-particle equilibrium, it is also directly depending on the available ammonia which competes with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  to lead to the formation of AN and ammonium sulphate respectively. Thus, as a consequence of the decrease in sulphur dioxide emissions observed since the last decades, a resulting increase in available ammonia would lead to an enhancement of AN concentration in the particles (Pye et al., 2009; Bauer et al., 2007). Such process should become more important in agricultural areas where ammonia sources are more abundant by the use of soil fertilizers.

The presence of semi-volatile compounds in the particle phase also has a direct influence on the aerosol light scattering and radiative forcing (e.g. Morgan et al., 2010; Li et al., 2009), this might greatly affect the climate by increasing the total particle mass due to the condensation of semi-volatile compounds (Bauer et al., 2007). Regarding the legal regulation of the European Union for the  $\text{PM}_{10}$  mass concentration (European Directive 2008/50/EG), the question whether nitrate and semi-volatile organics are present in the particle phase or in the gas phase can be critical with respect to excess of the daily average legal limit value of  $50 \mu\text{g m}^{-3}$  (Putaud et al., 2004).

The aim of this work was to describe the organics and nitrate diurnal variations over a year and the influence of the meteorological conditions as well as the regional photochemistry. For this we employed an Aerodyne Aerosol Mass Spectrometer (AMS) during three intensive measurement campaigns in Melpitz, which were correlated to the intensive measurements periods of the EU-Project EUCAARI (European Integrated Project on Aerosol Cloud Climate Air Quality Interactions, Kulmala et al., 2009), the programme EMEP (Co-operative programme for monitoring and evaluation of the long-range transmissions of air pollutants in Europe) and the UBA (Umweltbundesamt, the German federal environment agency) providing for the first time, at Melpitz, high time resolved aerosol chemical composition. These measurements covered different seasons: summer (May–June 2008), autumn (September–November 2008) and winter

## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

(February–March 2009).

## 2 Experimental

### 2.1 The research station Melpitz (Germany)

All measurements were made at the research station Melpitz (12.93° E, 51.54° N), 50 km east of Leipzig, Germany. The station has been used since 1992 to examine the effect of atmospheric long range transport on local air quality. Since 2004, the station is part of the EMEP-level 3 network under reference DE44. The site itself is mainly surrounded by agricultural pastures and forests. The atmospheric aerosol observed at Melpitz can be regarded as representative of Central European background conditions, as confirmed by multiple site comparisons within EUSAAR (European Supersites for Atmospheric Aerosol Research) and the German Ultrafine Aerosol Network (Birmili et al., 2009 and Asmi et al., 2011). For a basic overview of the physical and chemical aerosol characterization methods, see e.g. Birmili et al. (2008), Spindler et al. (2010) and Spindler et al. (2004). Atmospheric aerosols observed at Melpitz range between two extremes: Atlantic (westerly) air masses with low particulate mass concentrations and continental (easterly) air masses with high particle mass concentrations (Birmili et al., 2001; Spindler et al., 2010). Differences between these air mass extremes are also manifested in their particulate chemical composition. The measurements were conducted during three field experiments, which covered different parts of the seasonal cycle. Table 1 provides an overview of these three campaigns.

Aerosol measurements were performed using both on-line and off-line instruments. All on-line instruments were set up in the same container laboratory and utilized to the same air inlet. This inlet line consisted of a PM<sub>10</sub> Anderson impactor located approximately 6 m above ground level. It was followed directly by an automatic aerosol diffusion dryer that maintained the relative humidity (RH) in the sampling line below 30% all the time (Tuch et al., 2009). After entering the container laboratory, the sampling

## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



flow was divided among the various on-line instruments. The off-line measurements are based on filter samples that are described in Sect. 2.3.

## 2.2 AMS measurements

An Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, here simply referred to as AMS, DeCarlo et al., 2006) was deployed at the research station Melpitz. The AMS was typically operated at 5 min time resolution. Briefly, the AMS allows two alternative detection modes to measure the particle size distribution (PTOF-mode) and the chemical composition of the particle (MS-mode). First of all, the particles enter into the instrument by crossing aerodynamic lenses, which allow to focus particles into a narrow beam and to remove the gas phase. Then, the particle beam is controlled by a chopper, a rotating wheel equipped with two slits. The chopper can have three different positions. In the first one (PTOF mode), the chopper cuts/chops the particle beam. Therefore, the AMS is able to measure the chemical size-dependent composition of the particle. In the second one, the chopper completely blocks the particle beam; in this position, only the remaining gas phase will be detected (MS-Closed). Finally, the chopper can be set up completely outside of the particle beam; in this last position, both particles and remaining gas phase are detected (MS-Open). The resulting particle mass spectrum (MS-Diff) corresponds to the difference between the total mass spectra (MS-Open) and the remaining gas phase mass spectra (MS-Closed). Before being detected by the Time-of-Flight mass spectrometer, the aerosol components are flash-vaporized by impaction on a heated surface (600 °C). The vapors are immediately ionized by an electron impact ionization source at 70 eV located close to the vaporizer. Due to the 600 °C surface temperature, the AMS can only measure the non-refractory (NR) part of the particles. Soot, crustal material and sea-salt cannot be detected. Therefore, based on the aerodynamic lenses transmission efficiency and the detected compounds, AMS results are commonly considered to correspond to the non-refractory PM<sub>1</sub> aerosol (NR-PM<sub>1</sub>) (Canagaratna et al., 2007).

### Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

---

**Seasonal and diurnal variations of particulate nitrate and organic matter**L. Poulain et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

The calculation of the particles mass concentration from AMS data requires knowledge of the collection efficiency (CE) of the instrument. The CE value is known to depend on several parameters such as the nitrate content, particle acidity and relative humidity (RH) in the sampling line (Huffman et al., 2005; Matthew et al., 2008). It is considered that in most cases, a CE of 0.5 represents a good assumption (e.g. Canagaratna et al., 2007). The contribution of relative humidity (RH) to the CE was removed using a dried aerosol with a  $RH < 30\%$  as previously mentioned. The CE was estimated by comparing the daily mean AMS sulphate concentrations against the daily  $PM_{10}$  filter concentrations (see Fig. S1 in the Supplement). This evaluation yielded a CE of 0.38 and 0.5 were obtained for the autumn and winter campaigns, respectively. As no  $PM_{10}$  filter samples were performed during the summer campaign, a CE value of 0.5 was assumed, in line with the dried inlet, neutralized particles (see below) and the low nitrate content, during this measurement period.

### 2.3 Filter samples

Parallel to the AMS,  $PM_{10}$  particles were sampled using a Digitel DHA-80 high volume sampler (Digitel Elektronik AG, Hegnau, Switzerland). Sampling was performed every day during 24 h from midnight to midnight. Each  $PM_{10}$  sample was collected on pre-backed quartz fibre filters (24 h at  $105^{\circ}\text{C}$ ) (Munktell Filter AB, Falun, Sweden). After sampling, the filters were conditioned for 48 h at  $20 \pm 2^{\circ}\text{C}$  and 50% RH before being weighed by a microbalance Mettler-Toledo (AT 261). According to the analytical method of Brüggemann and Rolle (1998), the filters were then analyzed using Ion Chromatography (Metrohm System 690, Switzerland) for the main water soluble ions ( $\text{Cl}^{-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^{-}$ ,  $\text{NH}_4^{+}$ ,  $\text{Na}^{+}$ ,  $\text{K}^{+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ).

### 2.4 Other measurements

The soot mass concentration was measured by a Multi-Angle Absorption Photometer (MAAP, Model 5012, Thermo-scientific, Petzold and Schonlinner, 2004). To use MAAP

data in conjunction with the AMS, which has an upper size cut-off around 1  $\mu\text{m}$ , soot concentration for  $\text{PM}_1$  are required. Temporary but concurrent measurements using two MAAPs in parallel, one connected to the  $\text{PM}_{10}$  inlet, and a second one to a  $\text{PM}_1$  inlet demonstrated that the soot concentration in  $\text{PM}_1$  is around 90% of that in  $\text{PM}_{10}$ , with this ratio being only weakly time-dependent. For our study here, we consequently estimated soot in  $\text{PM}_1$  by multiplying the soot concentration on  $\text{PM}_{10}$  by a constant factor of 0.90. By combining the MAAP measurements and the AMS NR- $\text{PM}_1$  chemical composition, a relatively comprehensive picture of chemical particle composition could be provided.

Standard meteorological parameters (temperature, RH, atmospheric pressure, solar radiation, precipitation, wind direction and wind velocity) were also continuously measured. During the summer campaign, gas phase measurements of  $\text{SO}_2$ ,  $\text{NO}_x$  and  $\text{O}_3$  were complemented by measurements of sulphuric acid concentration, OH radical concentration and photolysis rates of  $\text{NO}_2$  and  $\text{O}(^1\text{D})$ . Gaseous sulphuric acid and OH-radicals were measured by CIMS as previously described by Berresheim et al. (2000), Rohrer and Berresheim (2006) and Schlosser et al. (2009). The instrument was set up in a container located closed to the container laboratory previously described and sampled air from a height of 3 m above ground, 0.5 m above the container. From a continuous inlet air flow, a sample gas flow is split off in which OH is chemically titrated by addition of  $\text{SO}_2$  to yield  $\text{H}_2\text{SO}_4$ .  $\text{H}_2\text{SO}_4$  is then selectively ionized by  $\text{NO}_3^-$  ions at atmospheric pressure, and the resulting ions are transferred into a vacuum chamber through a counter flow of pure nitrogen gas by electrical fields. Here, ion-molecule clusters are broken up and the  $\text{HSO}_4^-$  ions are analysed by mass spectrometry.

The OH concentration is obtained after correction for background  $\text{H}_2\text{SO}_4$  and inlet chemistry, the latter considers the recycling of OH from  $\text{NO}+\text{HO}_2$ , and OH-losses by CO, NMHC, and  $\text{NO}_2$ . As clean rural to moderately polluted conditions were encountered in Melpitz, the correction factors to compensate for chemically induced changes of OH in the intake were typically 10% with a variability of  $\pm 6\%$ . The system has a sensitivity of  $2 \times 10^5$  molecules  $\text{cm}^{-3}$  and an estimated uncertainty of 30%.

**Seasonal and diurnal variations of particulate nitrate and organic matter**

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





The photolysis frequencies of  $\text{NO}_2$  and ozone to yield  $J(\text{O}^1\text{D})$  were measured by sets of up- and downward looking actinic filter radiometers (MetCon), thus providing  $4 \pi$  sr photolysis rates. They were characterized and calibrated versus a reference spectral radiometer at FZ-Jülich (Bohn et al., 2008).

### 3 Weather conditions overview

The measurements presented here cover most of the seasonal weather conditions that are typical for Melpitz (Table 1). The first campaign, performed in summertime (from end-May to mid-June 2008), was representative for the summer conditions. It was characterized by a stable high pressure system, sunny days and almost without precipitation. Ozone concentration presented a clear diurnal profile with higher concentration during the day and lower concentration during the night. A large variation in temperature was observed between day and night times with amplitudes close to  $20^\circ\text{C}$ . Similar diurnal changes were observed for the relative humidity. Most of the time, the wind-velocity was low and came from the eastern sector.

The second measurement period was performed in autumn (from mid-September to the beginning of November). This period covered the transition from summer to winter time. The temperature slowly decreased from a mean value of about  $10.4^\circ\text{C}$  at the beginning to a mean value of about  $6.6^\circ\text{C}$  at the end. Similarly, solar radiation also decreased from a maximum slightly below  $700 \text{ W m}^{-2}$  during the first week to  $400 \text{ W m}^{-2}$  during clear sky days and only  $100 \text{ W m}^{-2}$  during cloudy days at the end of the campaign. In parallel, RH increased and reached values close to saturation during the last week. Atmospheric pressure was less stable and alternate periods of low and higher pressure were observed. The ozone concentration was half of that during the summer campaign. On some days, ozone presented however a similar diurnal variation as in the summer campaign, especially during the first part of the campaign when photochemistry activities were still high and during most of the time we observed a relatively stable ozone concentration rather corresponding to the background ozone

## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



concentration. Additionally, many precipitation events were observed during the whole campaign. According to the air mass influence discrimination made by Spindler et al. (2010), the sampling station was mainly influenced by eastern air masses (until beginning of October) and by western air masses (from October on).

The last campaign performed in wintertime (from mid-February to mid-March 2009) was characterized by low temperatures, very low solar radiation and high RH close to saturation during the first half of the measurements period. The mean ozone concentration was higher than observed during the autumn with a marginal diurnal profile. Due to the low solar radiation, we conclude that the ozone concentration corresponded mainly to the background value. The winter period was also characterized by a slightly higher wind velocity, mainly coming from western directions.

## 4 Results

### 4.1 Seasonal changes of particle chemical composition

The mean particle mass concentration (NR-PM<sub>1</sub> from AMS plus black carbon from MAAP) for the three measurement periods was relatively constant, ranging from 9.65  $\mu\text{g m}^{-3}$  to 11.63  $\mu\text{g m}^{-3}$  (details values can be found in Table 2). This is in agreement with the mean PM<sub>1</sub> filter samples mass concentration measured simultaneously during the autumn (11.91 $\pm$ 4.67  $\mu\text{g m}^{-3}$ ) and winter (11.39 $\pm$ 5.57  $\mu\text{g m}^{-3}$ ) campaigns as well as the annual mean concentration of 12  $\mu\text{g m}^{-3}$  reported by Spindler et al. (2010) for the period from 2004 to 2006. The summer period was characterized by a large fraction of organic matter (OM) and sulphate. Throughout the year, the mass fraction of OM decreased and reached a minimum mass fraction in winter time. The mass fraction of sulphate to total PM<sub>1</sub> appeared to be relatively stable during autumn and winter (around 17 %), while the mass fraction of nitrate strongly increased from a minimum value in summer and reached a maximum in winter. In a lower proportion an increased of the mass fraction of ammonium and chloride was also observed from summer to

## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



winter. The observed seasonal changes are in good agreement with long-term measurements of particle chemical composition made at Melpitz using high volume PM<sub>1</sub> Digital filter samples by Spindler et al. (2010).

The neutralization state of the particles for each season was estimated using the same approach that previously described by Sun et al. (2010), Zhang et al. (2007b) and Zhang et al. (2005) and based on the following equation:

$$\text{NH}_{4\_pred} = 18 \times \left( \left( 2 \times \frac{\text{SO}_4}{96} \right) + \frac{\text{NO}_3}{62} + \frac{\text{Cl}}{35.5} \right) \quad (1)$$

Where  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$  represent the mass concentration (in  $\mu\text{g m}^{-3}$ ) of the species divided by their molecular weight. The number 18 is the ammonium molecular weight. It is important to note that this equation considered by default, a fully neutralization of the anions by ammonium and consequently that the inorganic species are present in the form of ammonium nitrate, ammonium sulphate and ammonium chloride. Moreover, the Eq. (1) also considered as negligible the contribution of metal ions, organic acids and bases (Zhang et al., 2007b). Results of PM<sub>1</sub> filter samples demonstrated (for autumn and winter campaigns) that the contribution of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  was negligible due to their low concentrations compare to  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . Using the Eq. (1), the particles are considered as fully neutralized if the estimated ammonium concentration predicts is similar to the measured ammonium concentration and more acidic if the estimated ammonium concentration is significantly lower than predicted ammonium (slope below 0.75 according to Zhang et al., 2007b). Results presented in Fig. 1, shows that particles can be considered as neutralized during the different seasons. This also indicated that there is enough ammonia in the gas phase to fully neutralized nitrate and sulphate. Origin of the ammonia in the gas phase could be partially explained by the location of the sampling station which is surrounding by agriculture field. Evaporation of the  $\text{NH}_3$ -based fertilizer present on the fields especially during warm day time might be expected.

## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

In complementary to the long-term filter samples measurements; the AMS with its high time resolution gave us the opportunity to investigate the diurnal variations of the particles' chemical composition. In the following, we will focus on the seasonal changes of aerosol organic matter and nitrate.

## 4.2 Changes in organic particulate composition

Changes in organic oxidation levels were followed using two different approaches: i) organic fragments  $m/z$  44 ( $\text{CO}_2^+$ ) which is mostly corresponding to the fragment  $\text{CO}_2^+$  coming from multifunctional organic acids (Takegawa et al., 2007) and  $m/z$  43 (mostly  $\text{C}_2\text{H}_3\text{O}^+$ ) and ii) the ratio OM/OC calculated using the elemental analysis method developed by Aiken et al. (2007) and Aiken et al. (2008). Their diurnal variations for each campaign are presented in Fig. 2. Generally, a more or less pronounced decrease of the organic fragments ( $m/z$  44 and  $m/z$  43) was observed during day time compared to night time. Such diurnal variations can be attributed to both dynamics effects, correlated with the increase of the mixed layer height, and thermodynamic properties of the organic compounds (typically their volatility). For this reason,  $m/z$  44 and  $m/z$  43 were normalized to the total OM concentration according to the respective notation  $f_{44}$  and  $f_{43}$ . Moreover, it is known that  $f_{44} > f_{43}$  characterized a highly oxygenated and low volatile OA, while  $f_{44} < f_{43}$  characterized a less oxygenated and semi-volatile OA (Ng et al., 2010). A comparison of the resulting diurnal profiles of  $f_{44}$  and  $f_{43}$  revealed a similar trend for all measurement periods with anti-correlated profiles. The seasonal variations of the diurnal patterns are discussed below.

Mean OM/OC ratios of  $1.73 \pm 0.06$ ,  $1.74 \pm 0.09$  and  $1.64 \pm 0.14$  were obtained for the summer, autumn and winter campaigns, respectively. These values are lower than the value of 2.1, which has been recommended for non-urban regimes by Turpin and Lim (2001). However, our values of OM/OC ratios are still within the range of the values previously reported for similar sampling locations by Bae et al. (2006), Chan et al. (2010) and references therein. In addition, a small seasonal variation was observed, OM/OC being higher in summer than in winter, which could be explained by a higher

## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



5 efficiency of particle photooxidation and SOA formation in summer than in winter. This is in agreement with conclusions drawn by Chan et al. (2010). As for  $f_{44}$  and  $f_{43}$ , the diurnal profiles of the OM/OC ratio are represented in Fig. 2 (right panel). Typically, OM/OC ratio showed the highest value during day time and a lower value during the night. Similar diurnal variation with a lower OM/OC ratio during night compared to day time has also been reported by Yu et al. (2005) at the rural station of Great Smoky Mountains National Park (Tennessee, USA).

10 The diurnal variations of  $m/z$  44 and  $m/z$  43 for the summer period show a strong decrease during day time, while  $f_{44}$ , OM/OC and O/C increase at the same time. These differences can be directly linked to the dynamics of the atmosphere, e.g. the increase of the mixed layer, which contributes to a dilution process by mixing the lower layer of the atmosphere with cleaner air from aloft. However, the increase of  $f_{44}$  and OM/OC reveals an important change of the oxidation level of OA. In parallel to these changes in the OA oxidation state, an increase of OH radical concentration was measured during day time with a maximum around  $8 \times 10^6$  molecules  $\text{cm}^{-3}$  in agreement with OH concentrations observed by Hock et al. (2008) and Holland et al. (2003) at different rural places in Germany during similar periods of the year. The time series of the OH concentration were compared to the time series of  $f_{44}$  and OM/OC (Fig. 3). With the exception of 27 May 2008, the increase of OH concentration is correlated to an increase of  $f_{44}$  and OM/OC, which confirms that a change in OA oxidation state can be linked to photochemical aging. This is illustrated in Fig. 2, which presents similar profiles of organic tracers ( $f_{44}$ , OM/OC) and ozone concentrations while  $f_{43}$  profiles anti-correlates with ozone concentration (correlation plots are available in Fig. S2 in the Supplement;  $f_{44}$  vs.  $\text{O}_3$   $r^2 = 0.96$ ,  $f_{43}$  vs.  $\text{O}_3$   $r^2 = 0.96$  and OM/OC vs.  $\text{O}_3$   $r^2 = 0.98$ ) indicating that photochemical aging of particles during day time leads to the formation of more oxidized OA. This was also shown in previous studies (e.g. Hildebrandt et al., 2010; Sjostedt et al., 2010). Furthermore, the condensation of low volatile compounds produced during VOCs ozonolysis on pre-existing particles cannot be excluded and should therefore be taken into consideration, additionally to the pure OA aging

## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Seasonal and diurnal variations of particulate nitrate and organic matter**

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



process. When  $f_{44}$  increased,  $f_{43}$  decreased, which may be explained by the presence of more low-volatile compounds in the OA (Ng et al., 2010). However, during the night,  $f_{43}$  strongly increased and consequently  $f_{44}$  decreased, indicating the presence of more semi-volatile compounds. Due to the previously mentioned large difference of temperature between day and night time (up to 20 °C), evaporation of the more volatile organic fraction during day time and its condensation in the evening have to be taken into account. The semi-volatile OA has a lower OM/OC ratio than a low volatile OA (Aiken et al., 2008; Jimenez et al., 2009). This could then explain the observed diurnal variation of the OM/OC ratio.

During the autumn campaign, the decrease of the organic compounds during day time was less pronounced, probably indicating a lower contribution of the dynamics of the atmosphere to the total particle concentration. Similarly, the changes of  $f_{43}$  during the day were less pronounced, which might be explained by a lower impact of the temperature variation between day and night times compared to summertime. However, as already observed during summertime, an increase of  $f_{44}$  and OM/OC ratio during day time was observed, which again – based on the similarity with the ozone pattern (Fig. S2 in the Supplement; OM/OC vs.  $O_3$ :  $r^2 = 0.96$  and  $f_{44}$  vs.  $O_3$ :  $r^2 = 0.96$ ) – could be related to photooxidation processes.

During the winter campaign, contrary to the other seasons (summer and autumn) organic fragments ( $m/z$  44 and  $m/z$  43) did not show any diurnal variations. This might be explained by the limited impact of the dynamic of the atmosphere as well as by the thermodynamic properties of the OA, because of the lowest temperature at this period. As described in Sect. 2, ozone had a small diurnal profile in winter and only  $f_{44}$  seemed to be slightly correlated to the ozone variation (Fig. S2 in the Supplement,  $f_{44}$  vs.  $O_3$ :  $r^2 = 0.94$ ). It is known that during winter time, photolysis rates are lower, which limits consequently the ozone formation and photo-aging process. Therefore, these factors should only have a small impact on the diurnal variation of OM/OC. Moreover, due to low biogenic emissions during winter time, local sources of OA and new particles should also be limited. Thus, particles measured during winter time could – when

compared with other seasons – mainly have been subject to long-range transport.

### 4.3 Changes in particulate nitrate concentrations

As discussed previously, the seasons strongly influence the nitrate concentration in particle phase. As expected, the lowest concentrations were measured during summertime and the highest during wintertime. The diurnal variation of the nitrate aerosol mass concentration is presented in Fig. 4. A relatively similar pattern can be observed in all three campaigns: a decrease of nitrate concentration during the day, reaching a minimum at the end of the afternoon, with an increase during the night. Ammonium nitrate (AN) is a volatile compound that evaporates as the temperature increases, leading to the formation of ammonia and nitric acid in the gas phase (Reactions R1 and R2) (Seinfeld and Pandis, 1998). Therefore, in order to obtain a better understanding of its seasonal variations, it is essential to consider the contribution of changes of meteorological conditions and AN thermodynamic properties (deliquescence formation and/or evaporation), to the measured aerosol nitrate concentrations. Moreover, the equilibrium between particle and gas phases is not only depending on temperature, but also on the local RH compared to the deliquescence relative humidity (DRH) of ammonium nitrate. As already described in Sect. 2, large variations of temperature and RH were observed during the different measurements. Hence, it is important to estimate how these two parameters could influence the nitrate's diurnal variation. Therefore, two conditions have to be considered: (i) when the ambient  $RH < DRH$ , ammonium nitrate will be in equilibrium with the solid phase (Reaction R1); and (ii) when  $RH > DRH$ , ammonium nitrate will be in equilibrium with the aqueous phase and deliquescent particles (Reaction R2).



The DRH was then calculated (Eq. 2) for all sampling points and compared to the ambient RH in order to distinguish periods in which AN is formed in the solid phase

## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



and periods in which AN is formed in the deliquescence phase (Seinfeld and Pandis, 1998).

$$\ln(\text{DRH}) = \frac{723.7}{T} + 1.6954 \quad (2)$$

For the period of  $\text{RH} < \text{DRH}$ , the dissociation constant ( $k_p$ ) of Reaction (R1) was calculated according to:

$$\ln k_p = 84.6 - \frac{24220}{T} - 6.1 \ln \left( \frac{T}{298} \right) \quad (3)$$

For the period of  $\text{RH} > \text{DRH}$ , the deliquescence constant ( $k_{\text{deliq}}$ ) was calculated according to:

$$k_{\text{deliq}} = 4.10^{17} \exp \left[ 64.7 \left( \frac{298}{T} - 1 \right) + 11.51 \left[ 1 + \ln \left( \frac{298}{T} \right) - \frac{298}{T} \right] \right] \quad (4)$$

Measurements of gas phase  $\text{NH}_3$  and  $\text{HNO}_3$  were not available for the different campaigns and hence it was not possible to directly estimate the equilibrium between AN and the couple  $\text{NH}_3$ -  $\text{HNO}_3$ . However, it is reasonable to consider that the particles were in equilibrium with the gas phase at a time  $t$ , and that changes of the AN should directly depend on changes of  $k_p$  or  $k_{\text{deliq}}$  at the time  $t + i$ , whereby  $i$  represents the next AMS measurement point. Consequently, if the nitrate mass concentration only depends on  $k_p$  or  $k_{\text{deliq}}$ , it should follow the variations of the corresponding equilibrium constant (Fig. 5).

Diurnal profiles of nitrate,  $k_p$ ,  $k_{\text{deliq}}$  and solar radiation over each entire measurement period are presented in Fig. 4. For all measurement periods, the nitrate mass concentration was anti-correlated to  $k_p$  during daytime, while it was correlated to  $k_{\text{deliq}}$  during the night. The duality of nitrate dependence to  $k_p$  and  $k_{\text{deliq}}$  was well pronounced during the summer period, which corresponds to the strongest diurnal variation of temperature and RH. This is in agreement with results reported by Rupakheti et al. (2005), who

**Seasonal and diurnal variations of particulate nitrate and organic matter**

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





**Seasonal and diurnal variations of particulate nitrate and organic matter**

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

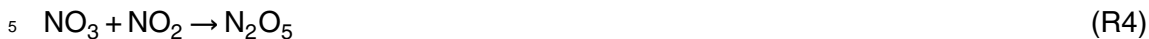
Interactive Discussion

also correlated the nitrate diurnal profile to temperature and RH variations. Although  $k_{\text{deliq}}$  was the only factor controlling the AN equilibrium during night time,  $k_{\text{deliq}}$  and  $k_p$  could both influence the nitrate concentration during day time, especially  $k_p$  during the warm and dry season and  $k_{\text{deliq}}$  during the cold and humid seasons (Fig. 5). Due to the increase of RH and to lower temperature, the contribution of  $k_p$  to the nitrate equilibrium became less important during the first period of the autumn campaign (Fig. 5). In parallel, the  $k_{\text{deliq}}$  value increased to completely drive the AN equilibrium at the end of the autumn campaign (Fig. 5). The reverse observation was made during the last campaign, due to drier and warmer conditions in the end of the winter period (Fig. 5). Finally, the less pronounced diurnal variation of particulate nitrate in winter time, associated with higher concentrations of AN, can be explained by the lower value of  $k_p$  in winter compared to summertime (approximately 220 times lower), while  $k_{\text{deliq}}$  changed only by a factor of 10 between these two campaigns. These results clearly illustrate the impact of regional meteorological conditions on the particulate nitrate mass concentration.

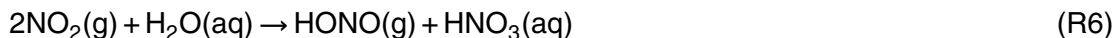
Figure 4 also shows the diurnal profiles of the solar radiation and organics concentrations. During the summer period, organics showed a decrease of concentration during day time, even if an intensive photochemistry occurred during this period (see Sect. 3.1). This was attributed to both the evaporation of the more volatile organic compounds and the contribution of the increasing level of the mixed layer. Therefore, the impact of the dynamics of the atmosphere might also directly contribute to the daily diminution of AN concentration, in addition to the dissociation process discussed here. Based on the organic signal, the impact of the mixed layer height could also be observed during the autumn campaign, but seemed to be quite limited during the winter campaign because of the relatively stable organics concentration.

Even if the increase of AN concentration during the night has to be linked directly to  $k_{\text{deliq}}$ , night chemistry has also to be considered. While during daytime, nitrate radical coming from Reaction (R3) was directly photolysed, during the night, it might have led to the formation of dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ), according to Reaction (R4). Because

of the high RH during the night, heterogeneous hydrolysis of  $\text{N}_2\text{O}_5$  has to be expected to lead to the formation of  $\text{HNO}_3$  (Reaction R5), which might be converted in AN due to the high value of  $k_{\text{deliq}}$  (Allen et al., 1989).



An interesting point is the systematic delay between the decrease of the  $k_{\text{deliq}}$ 's influence and the effective decrease of the AN concentration on the diurnal plot early in the morning (Fig. 4). During this time, the nitrate concentration appeared to be correlated neither to  $k_p$  nor to  $k_{\text{deliq}}$  and the duration of this phenomenon seems to be more important during winter (around 2 h) than during summer (1 h). There are two possible explanations for this phenomenon. First, the increase of nitrate mass concentration might be linked to changes in local air quality, corresponding to local emissions. However, due to the location of the sampling place, local sources of nitrate are relatively low. The second explanation is related to local photochemistry of HONO. Indeed, high concentration of HONO had previously been reported early in the morning at Melpitz (Acker et al., 2004; Spindler et al., 2003). The formation of HONO can, to some extent, be attributed to the reaction of  $\text{NO}_2$  with water on wet surface (Reaction R6), then also leading to the formation of  $\text{HNO}_3$  which represents another possible source of AN formation during the night.



Other sources of HONO are possible and the morning peak of HONO can also be linked to its photochemical formation by the reaction of  $\text{NO}_2$  with humic acid particles or soil (Stemmler et al., 2006, 2007).

During the summer period, measurements of OH radical concentrations and photolysis frequencies of  $\text{NO}_2$  ( $j_{\text{NO}_2}$ ) and O1D ( $j_{\text{O}(^1\text{D})}$ ) were performed in parallel to the

## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

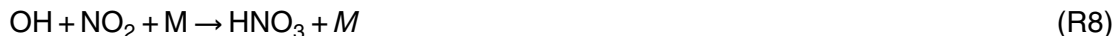
Interactive Discussion



AMS measurements. The resulting diurnal profiles of NO, OH,  $j\text{NO}_2$  and  $j\text{O}(^1\text{D})$  are presented in Fig. 6. An important peak of NO was observed in the morning, simultaneously with the dawn. The concentration of OH and  $j\text{O}(^1\text{D})$  increased at this time, indicating the presence of photochemistry processes. However, the ozone concentration as well as  $j\text{NO}_2$  increased slowly compared to the OH concentration and  $j\text{O}(^1\text{D})$ , confirming that the photolysis of HONO can be at the origin of the morning increases of HO and NO. This is in agreement with the fact that HONO photolysis Reaction (R7) is considered to be the major source of OH radical in the morning (Alicke et al., 2002).



Based on the low ozone concentration and the low photolysis rate of  $\text{NO}_2$ , the formation of  $\text{HNO}_3$  according to Reaction (R8) should be expected. It might then represent a possible local source of AN and a possible explanation for the increase of AN at this time. Later, the ozone concentration and  $j\text{NO}_2$  increase; NO will interact with ozone, and consequently, the formation of  $\text{HNO}_3$  should be limited. Less  $\text{HNO}_3$  formation in conjunction with higher contribution of  $k_p$  could contribute to the decrease of AN concentration.



Therefore, the longer time delay between the decrease of nitrate concentration and the change in the nitrate equilibrium observed during winter time can be linked to the lower ozone reactivity and the influences of temperature.

## 5 Conclusion

The comparison of the different AMS measurements at the Central European research station Melpitz (Germany) throughout a year showed a large contribution of organics and sulphate to total particle mass concentration during the summer period, whereas

### Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Seasonal and diurnal variations of particulate nitrate and organic matter**

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

the winter period was characterized by a large contribution of nitrate. In addition, the OM/OC ratio was slightly influenced by the season with higher values during summer than winter time. Even if at first glance, diurnal variations of organic and nitrate show similarities over the year, some important changes and influences of local meteorology and chemical reactivity could be observed.

The diminution of the total OA concentration during day time, which was mainly observed during the warm seasons, can be linked to the dilution effect of increasing mixed layer height. The influence of the mixed layer height at a regional site place was also reported by Sjostedt et al. (2010) and should be considered in future campaigns, especially during summer time. Significant photochemical aging and/or a condensation of low volatile compounds resulting from VOC ozonolysis were observed during day time in the summer period corresponding to increase of OM/OC and  $f_{44}$ . Consequently, the OM/OC as well as the more low-volatile OA increased during the day. Due to the large diurnal variation of temperature between day and night, semi-volatile OA increased during the night. The presence of a larger fraction of semi-volatile OA during the night can be linked to the decrease of the OM/OC ratio, which is in agreement with their lower OM/OC ratio compared to low volatile OA. The impact of photochemistry and temperature became less important during the cold seasons and thereby only a small increase of OM/OC and  $f_{44}$  was observed in winter. It is therefore possible to conclude that the winter OA mainly corresponded to long range transport of particles whereas summer OA was clearly influenced by the regional photochemistry. These results confirm the importance of the factor “season” in order to compare the OA compositions in meta-analyses of the worldwide particle composition (e.g. Ng et al., 2010; Zhang et al., 2007a) and the contribution of local chemistry to particle chemical composition.

The nitrate seasonality emphasizes the relation between the meteorological conditions and its thermodynamic properties, which directly controls its particle phase mass concentration. Then, the equilibrium between nitrate gas and particle phase only depends on  $k_{\text{deliq}}$  during night time, but both  $k_p$  or  $k_{\text{deliq}}$  might control the particulate nitrate mass concentration during day time, depending on temperature and RH.

Consequently, nitrate mass concentrations increase during the night and decrease during day. Additionally to AN thermodynamic properties, gas phase night chemistry and heterogeneous reactivity of  $\text{N}_2\text{O}_5$  during night time as well as HONO photolysis during the first hours of the dawn might also directly influence the AN concentration. Finally, consequently to the decrease of  $\text{SO}_2$  emissions, and therefore particles sulphate mass concentration (Spindler et al., 2004), ammonium nitrate represents an important compound for local air quality (Silva et al., 2007 ; Yin and Harrison, 2008). Our results confirm this point and underline the need for more systematic measurements of particulate AN and gas phase HONO, ammonia and nitric acid, in order to improve the knowledge of the nitrate chemistry and evaluate its atmospheric impact.

**Supplement related to this article is available online at:**

**<http://www.atmos-chem-phys-discuss.net/11/11611/2011/acpd-11-11611-2011-supplement.pdf>**

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## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Seasonal and diurnal variations of particulate nitrate and organic matter**

L. Poulain et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**Seasonal and diurnal variations of particulate nitrate and organic matter**

L. Poulain et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**Seasonal and diurnal variations of particulate nitrate and organic matter**

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q., Onasch, T. B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. R., Trimborn, A. M., Northway, M. J., Decarlo, P. F., Kolb, C. E., Davidovits, P., and Worsnop, D. R.: Chemical and microphysical characterization of ambient aerosols with the Aerodyne aerosol mass spectrometer, *Mass Spectrom. Rev.*, 26, 185–222, doi:10.1002/mas.20115, 2007.
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## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Carlo, P. F., Prevot, A. S. H., Baltensperger, U., Mihalopoulos, N., Donahue, N. M., and Pandis, S. N.: Aged organic aerosol in the Eastern Mediterranean: the Finokalia Aerosol Measurement Experiment-2008, *Atmos. Chem. Phys.*, 10, 4167–4186, doi:10.5194/acp-10-4167-2010, 2010.

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L. Poulain et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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L. Poulain et al.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)




[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


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**Seasonal and diurnal variations of particulate nitrate and organic matter**

L. Poulain et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**Seasonal and diurnal variations of particulate nitrate and organic matter**

L. Poulain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.

**Table 1.** Summary of the different meteorological conditions for the three measurements periods.

	Summer	Autumn	Winter
Measurements period	23.05.2008–09.06.2008	16.09.2008–03.11.2008	24.02.2009–27.03.2009
Temperature (°C) mean (min.–max.)	19.5 (5.2–31.7)	10 (–2.0–22.5)	5.3 (–3.3–14.2)
Atmospheric pressure (hPa)	1007.7±2.4	1010.4±9.6	1004.3±11.6
Relative Humidity (%) mean (min.–max.)	69.7 (29.8–100)	88.6 (44.4–100)	87.1 (38.7–100)
Wind speed (m.s <sup>-1</sup> )	2.2±1.4	2.2±1.7	3.2±1.7
Precipitation (mm)	0.013	0.028	0.024
Ozone (µg m <sup>-3</sup> ) Mean (min.–max.)	85 (5.1–164)	39.8 (4.9–108.4)	60.5 (6.1–103.2)
Solar radiation (W m <sup>-2</sup> ) (min.–max.)	264.1 (0–914)	81.4 (0–688)	76.8 (0–687)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.

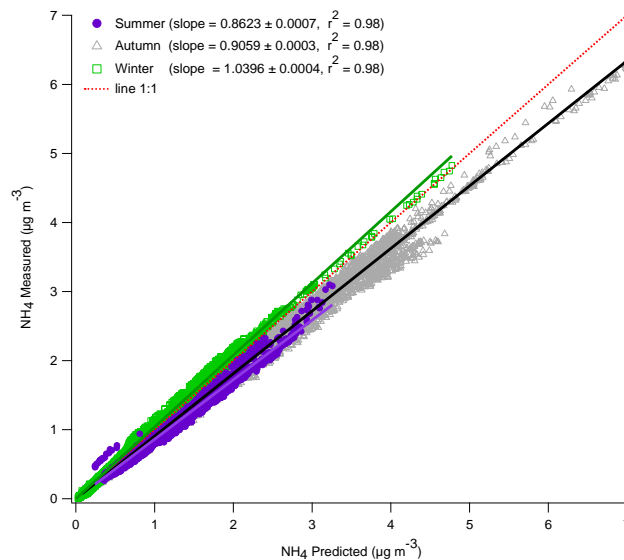
**Table 2.** Summary of the particle mass composition for the three measurements periods. The reported mass concentrations correspond to the mean value and the errors to the standard deviation calculated over each entire measurement period.

	Mass concentration ( $\mu\text{g m}^{-3}$ )			Mass fraction (%)		
	Summer	Autumn	Winter	Summer	Autumn	Winter
Organics	6.89±3.02	3.87±2.62	2.08±1.61	59.0±9.1	36.6±10.9	22.6±9.8
Nitrate	0.66±0.57	2.97±2.92	3.62±3.27	5.4±3.3	23.2±11.9	34.4±12.5
Sulphate	2.44±1.17	1.67±1.01	1.46±1.00	21.5±6.9	17.5±6.8	17.6±8.3
Ammonium	0.94±0.45	1.37±1.01	1.69±1.21	8.2±2.3	12.3±2.9	17.2±3.4
Chloride	0.02±0.01	0.09±0.14	0.13±0.11	0.2±0.1	0.7±0.7	1.6±1.1
Soot	0.62±0.26	0.99±0.73	0.59±0.48	5.6±1.9	9.6±3.8	6.5±3.3
Total	11.58±4.45	11.03±7.2	9.59±6.5			

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.



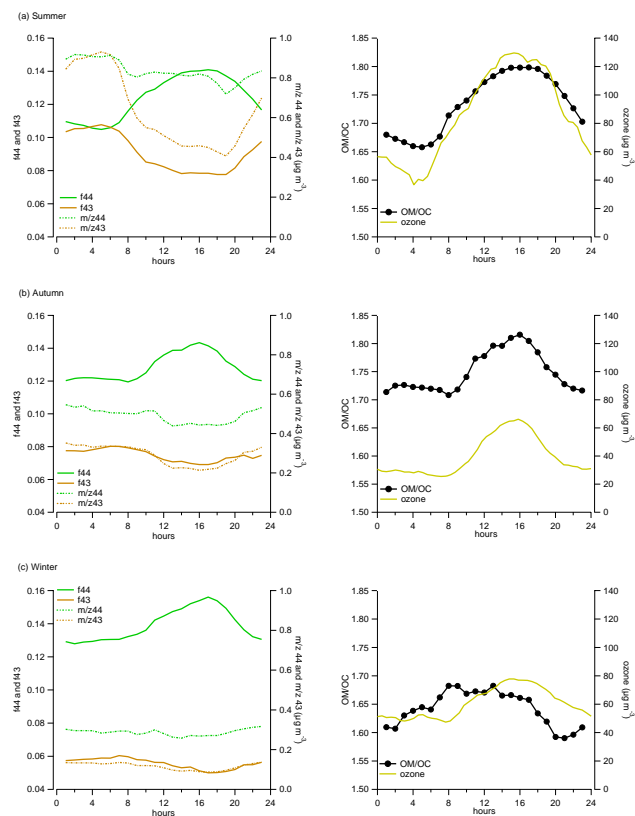
**Fig. 1.** Comparison of the measured ammonium with the predicted ammonium concentration assuming a fully neutralization by nitrate, sulphate and chloride for the three different campaigns.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.



**Fig. 2.** Diurnal variations of the organic aerosol tracers ( $m/z$  44,  $m/z$  43,  $f_{44}$ ,  $f_{43}$ ), OM/OC ratio and ozone concentration for **(a)** summer, **(b)** autumn and **(c)** winter.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

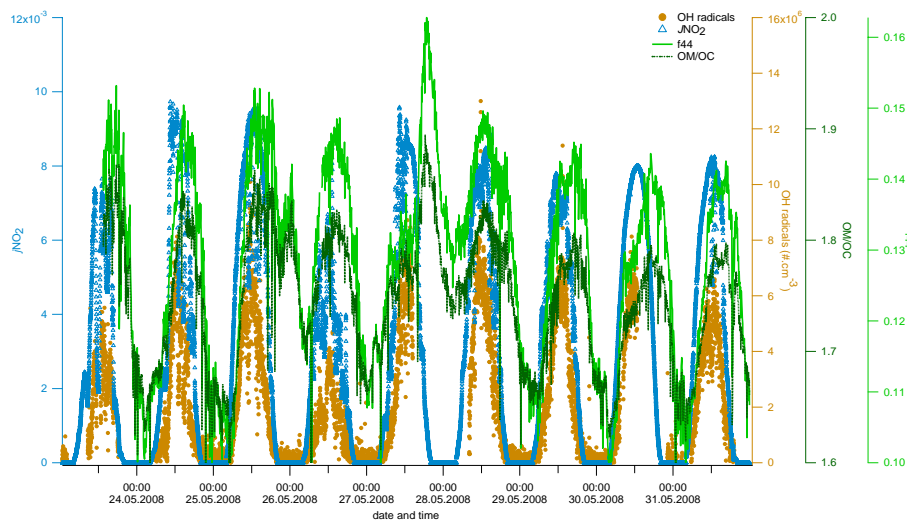
Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.



**Fig. 3.** Comparison of the  $f_{44}$  and OM/OC time series with the OH radical concentration and  $\text{NO}_2$  photolysis rate for the summer campaign.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

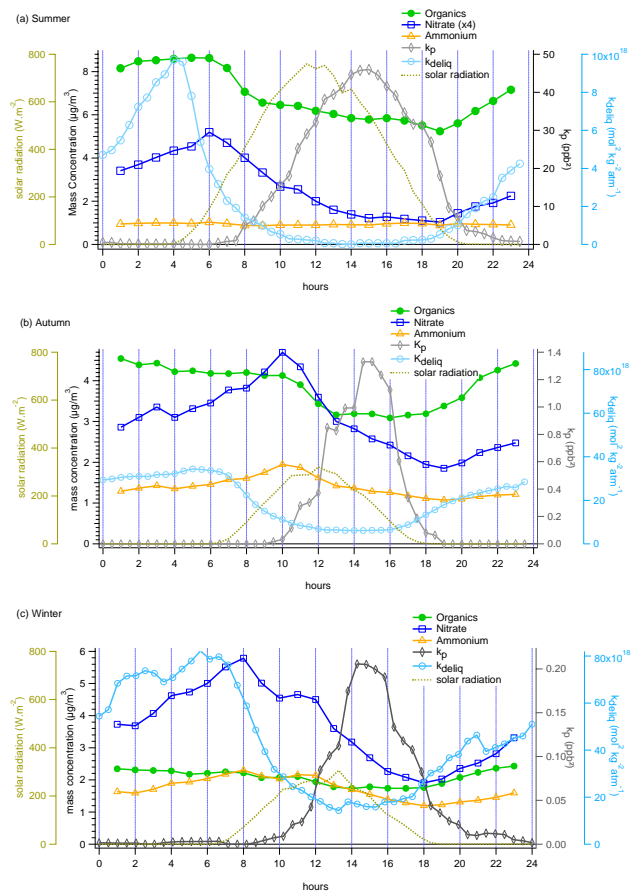
Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.



**Fig. 4.** Diurnal variations of the nitrate concentration and its thermodynamic constants for **(a)** summer, **(b)** autumn and **(c)** winter.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

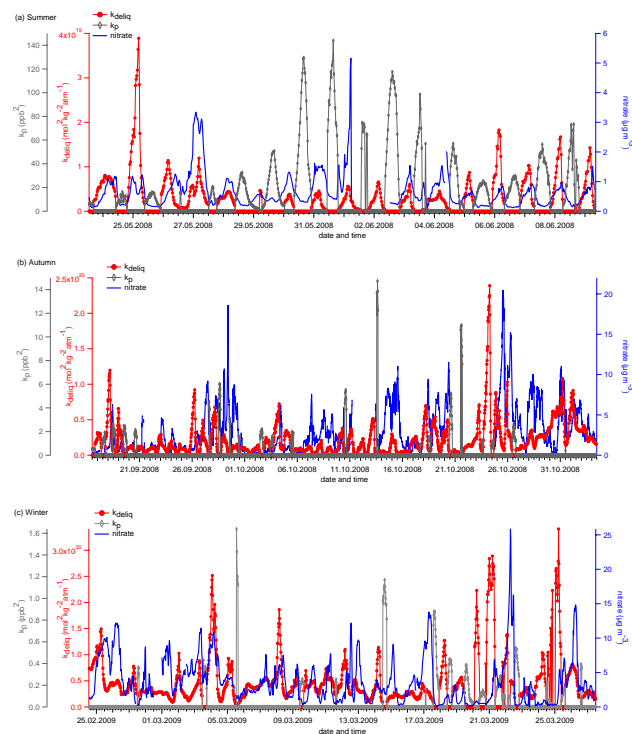
Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.



**Fig. 5.** Time series of the nitrate concentration during the three measurements periods ((a) summer, (b) autumn and (c) Winter). The time series of calculated equilibrium constants ( $k_p$  and  $k_{\text{deliq}}$ ) are also included.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

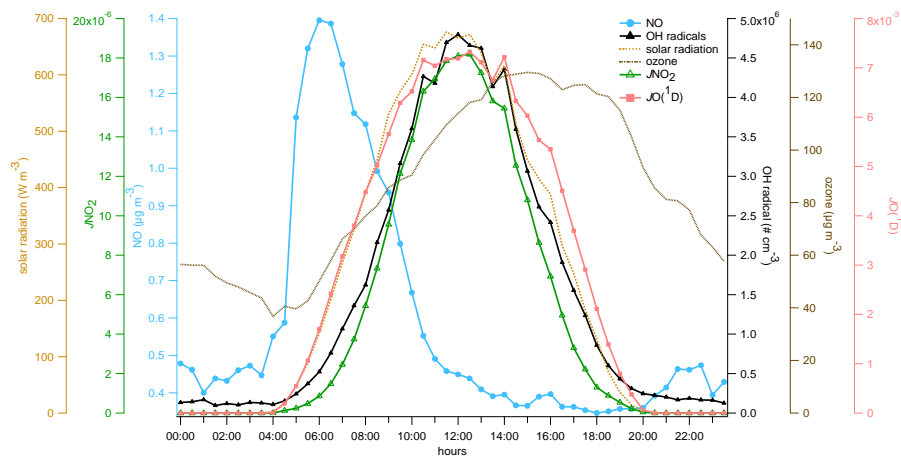
Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Seasonal and diurnal variations of particulate nitrate and organic matter

L. Poulain et al.



**Fig. 6.** Diurnal profile of NO concentration during summer and tracers of photochemistry activity (solar radiation, OH,  $jO(^1D)$ ,  $jNO_2$  and ozone).

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[⏪](#)
[⏩](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)